

Static light scattering measurements along a critical decomposition line of a ternary liquid mixture

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In the present paper we publish results of static light scattering measurements in the ternary system *N,N*-dimethylformamide + *n*-heptane + toluene. We determined the critical decomposition line in a concentration range of 0 up to 25 mole-% toluene. In seven mixtures along this line we obtained the correlation length of fluctuations and the generalized osmotic susceptibility as a function of the temperature. We apply simple power laws to calculate the critical exponents of both properties. The determined exponents show a systematic growth if the fraction of the third component increases. This growth exceeds the values for critical exponents that were predicted by the critical exponent renormalization. [S1063-651X(99)09810-4]

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I. INTRODUCTION

Static and dynamic light scattering measurements have proved to be powerful techniques for studying critical phenomena in fluid phases. The angle dependent intensity and the spectrum of scattered light can be easily related to the magnitude and the dynamics of critical fluctuations [1,2]. Many papers published in the last decades concern the analysis of these long-range correlations in binary systems in the neighborhood of their plait points (system aniline+cyclohexane, e.g., [3–6]). It could be shown that theoretical concepts like renormalization group or mode-mode coupling theory are in impressive agreement with the results of measurements in binary fluid mixtures. In a three-component system one could expect that the plait point should behave analogous to the critical mixing point of a two-component system. But in fact there is an important difference in case of a ternary plait point: under constant pressure it is a part of a critical line on a coexistence surface. There are only a few papers that deal with the critical behavior in three component critical fluids. Bak and Goldburg [7] observed no change in the critical exponent of osmotic susceptibility when they add up to 6% phosphoric acid to a critical mixture of water and phenol. In contrast to this result a mixture of brombenzene, water, and acetone gave a critical exponent which was larger than the binary one [8]. Fisher and Scesney explained this trend by renormalization of critical exponents from analysis of the free electron Ising model [9,10], e.g.,

$$\nu_x = \frac{\nu}{1-\alpha}; \quad \gamma_x = \frac{\gamma}{1-\alpha}, \quad (1)$$

where ν is the critical exponent of the correlations length of concentration fluctuations ξ , γ denotes the exponent of the generalized osmotic susceptibility $C\chi_T$, and α is the heat

capacity exponent above the plait point. The subscript x denotes that this quantity is a renormalized exponent.

In an extended investigation of the ethanol-water-chloroform system Chu and Lin [11] found larger exponents for the correlation length and the osmotic susceptibility than expected by critical exponent renormalization. In [12] it was shown that the common power laws gave significantly higher values of critical exponents if the system contains 7% of a third component. Equation (1) could not completely explain this behavior. The analysis of correction to scaling at the same system gave no clear and satisfying results because of the self-compensation of scaling terms. This situation compelled us to investigate the critical behavior of ternary systems in more detail. Especially since there are no experimental data along a critical line of fluid multicomponent systems. This should be useful to improve perturbation concepts such as the free electron Ising lattice to become valid in real ternary or multicomponent systems. We start here with static investigations of a ternary system. In order to obtain the effect of increased fraction of the third component only, we choose a system that shows only a weak asymmetry of the critical line. The system *N,N*-dimethylformamide + *n*-heptane + toluene is a common model system for fluid-fluid extractions and meets this condition satisfying.

II. THEORY

Light scattering can be observed whenever there are local fluctuations in the dielectric constant ϵ of the medium. The intensity I_s of the scattered light is given by

$$I_s(q) = A \sin^2(\Phi) \langle |\delta\epsilon(q)|^2 \rangle \quad (2)$$

in the static point of view. In this equation A denotes a constant determined by the wavelength λ of incident beam. Φ is the phase shift between incident and scattered beam and q is the so-called wave vector. It is defined by

$$q = 4\pi \frac{n_D}{\lambda^4} \sin\left(\frac{\theta}{2}\right), \quad (3)$$

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with the scattering angle θ and the refractive index n_D . In a fluid mixture the local fluctuations of the dielectric constant are a function of fluctuations in pressure p , temperature T , and concentration c . Under the given conditions the concentration fluctuations are doubtless much more essential than the others. So we can formulate the scattered intensity as

$$I_s(q) = A \sin^2 \left(\frac{\partial \epsilon}{\partial c} \right)_{p,T}^2 \langle |\delta c(q)|^2 \rangle. \quad (4)$$

The quantity $\langle |\delta c(q)|^2 \rangle$, describing the concentration fluctuations in space, is the static structure factor $S(q)$. It is strongly connected to the space autocorrelation function of the concentration fluctuations $G(r)$

$$S(q) = V \int_V e^{iqr} G(r) q dr, \quad (5)$$

where V denotes the scattering volume. Within the Ornstein-Zernike-theory [13] the correlation function of concentration fluctuations is described by

$$G(r) \propto \frac{\exp(-r/\xi)}{r}. \quad (6)$$

A comparison to the static structure factor from the fluctuation theory of Einstein and Smoluchowski [14] leads to a description of the static structure factor,

$$S(q) = \langle |\delta c(q)|^2 \rangle = k_B T c^2 \frac{\chi T}{1 + q^2 \xi^2}, \quad (7)$$

where χ_T is the osmotic susceptibility, ξ denotes the correlation length of concentration fluctuations, and k_B is the Boltzmann constant. With respect to Eq. (4) the intensity of scattered light becomes

$$I_s(q) = \frac{C \chi_T T}{1 + q^2 \xi^2}, \quad (8)$$

where C is a temperature independent factor containing the macroscopic concentration, the concentration dependence of ϵ , and k_B . This equation leads to the method of Ornstein, Zernike, and Debye (the OZD method). Since this procedure does not enable us to evaluate the quantity C we cannot calculate the osmotic susceptibility χ_T itself. Instead, we obtain a generalized osmotic susceptibility $C \chi_T$.

Equation (6) is correct only for ranges of r that are not too small. Because of the divergence of the static structure factor in the neighborhood of the critical point, a small number η was introduced by Fisher describing a critical singularity of the correlation function Eq. (6). So we can write [15]

$$G(r) \propto \frac{\exp(-r/\xi)}{r^{1-\eta}}. \quad (9)$$

According to renormalization group analysis one must expect $\eta \approx 0.06$ for the 3D Ising model. Experimental investigations gave values between $\eta = 0.065$ [16] and $\eta = 0.086$ [17]. But for ternary mixtures it is not obvious whether this

exponent has to be renormalized the same way as Eq. (1). If we consider the static structure factor exponent, Eq. (8) must be modified to yield

$$I_s(q) = \frac{C \chi_T T}{(1 + q^2 \xi^2)^{1-\eta/2}}. \quad (10)$$

Because there is no theoretical limit defined for the range of criticality we cannot exclude that corrections to scaling become evident even in the vicinity of the critical point. These corrections modify the the power laws, which are determined by scaling hypothesis. However, approaching the critical point the amount of these corrections to scaling should decrease and finally disappear.

By application of the renormalization group theory Wegner proposed a description of the critical singularity within an extended range of temperature. For the correlation length he obtained

$$\xi(T) = \xi_0 \epsilon^{-\nu} (1 + \xi_1 \epsilon^{0.5} + \xi_2 \epsilon^{1.0} + \xi_3 \epsilon^{1.5}),$$

$$\epsilon = \frac{T - T_c}{T_c}. \quad (11)$$

If we disturb a binary critical mixture by adding a third component we could imagine that in this case the corrections to scaling are applicable even in the critical range. In a binary mixture, however, in the temperature range $T - T_c < 1.2$ K the contribution of the Wegner terms ξ_1, \dots, ξ_3 should be close to zero.

III. EXPERIMENT

A. Sample preparation

1. Glassware cleaning.

All light scattering cells, syringes, Erlenmeyer flasks, and viscosimeters were immersed in a mixture of water, sodium hydroxide, and hydrogen peroxide for several days, to remove any organic impurities. Then this glassware was rinsed with distilled water and subjected to ultrasonic vibrations for an hour. Hot water steam was used to remove all remaining dust particles from inside the flasks and cells. The cleaned glassware was carefully dried at a temperature of 120 °C under vacuum, and cooled to room temperature after 8 h under a nitrogen atmosphere. All glassware was sealed with Parafilm before storing.

2. Materials.

Certified ACS spectranalyzed *n*-heptane (99.9 mole %) and toluene (99.6 mole %) were used without further purification with the exception of removing traces of water. Both substances were refluxed with calcium hydride and distilled.

We used *N,N*-dimethylformamide (DMF) with a content of 99.5 mole %. Usually DMF contains traces of free alkali (NH_3) and acetic acid. Therefore we performed an azeotropic distillation with water to extract the ionic impurities under nitrogen atmosphere to avoid oxidation processes. The increased content of water was removed by dynamic drying with Zeosorb 4A. After repeated rectification the DMF fractions were multiply frozen in liquid nitrogen and evacuated.

TABLE I. Composition of the samples and their decomposition temperatures.

Sample	Mole fraction DMF x_d	Heptane x_h	Toluene x_t	Decomp. temp. T_c^{vis} in K
DH01	0.482	0.518	0.000	341.882
DHT06	0.402	0.354	0.233	290.387
DHT08	0.409	0.368	0.233	296.535
DHT09	0.440	0.446	0.114	320.879
DHT12	0.426	0.423	0.147	312.856
DHT17	0.410	0.383	0.207	301.351
DHT19	0.451	0.472	0.078	328.412

The substances were stored under an argon atmosphere. A water analysis by Karl-Fischer-titration gave less than 15 ppm water in the DMF fractions.

3. Sample preparation.

For determination of the critical compositions coexistence data by Nowotna, Paschke, and Winkelmann [18] and Beuterkamp [19] were used. For each plait point we prepared several mixtures with target compositions close to the proposed critical line. These mixtures have a constant toluene fraction but differ in the DMF-heptane ratio. To avoid the influence of dust the mixtures were filtered through teflon membranes (0.2 μm pore width) into the cylindrical sample cells (diameter:10 mm). To exclude oxygen and water from the air all operations were carried out under an argon atmosphere. The sample cells were flame-sealed for the determination of the visual decomposition temperature T_c^{vis} and the phase ratios R . We determined the decomposition temperature by using a 5 mW He-Ne laser beam that vanishes if the phase separation begins. We could reproduce the values of T_c^{vis} three months after the preparation with a precision of less than 5 mK. All samples were tested by the volume equivalence criterion. We obtained the ratio R between the upper and lower phase volumes for several temperatures below T_c^{vis} . A sample was defined to be critical if $R=1$ at 20 mK below the decomposition temperature. The measured compositions and temperatures of the seven critical samples are shown in Table I.

B. Light scattering apparatus

All described light scattering measurements are carried out in a commercial apparatus as shown in [12], which is mounted on a vibration-damped table. As a light source we used a water cooled neodymium-doped yttrium aluminum garnet (Nd:YAG) laser of about 150 mW at 532 nm wavelength. Because of very high scattered light intensity at near critical states the incident beam intensity has been reduced by a liquid crystal attenuator. In particular, we reduced the incident beam intensity to only 2% of the source intensity. After passing the attenuator the incident intensity and beam position were analyzed using a quadrant-diode coupled in with a beam divider plate. The sample cell was positioned in the center of the scattering cell that was filled with toluene. For analyzing the scattered light a photomultiplier tube was mounted on a goniometer, which allows one to scan a range

of angles from 13° up to 152° with an accuracy of better than 0.01°. A fast photon count correlator platine ALV-5000/Fast was connected directly to the photomultiplier and enabled us to obtain lag times down to 13 ns for dynamic analysis of scattered light.

To determine the quality of optical adjustment, test measurements were carried out with pure toluene as a scattering medium showing no angle dependence of the scattering intensity. During the whole measurement period the angle dependence of scattered light intensity was less than 3%.

In order to keep the temperature constant we used a single Julabo type FP40 thermostat with circulating water as a medium. For decomposition temperatures of less than 313 K we could retain ± 0.002 K temperature control over extended periods of time. The room temperature was 298 K during the measurements. At higher decomposition temperatures the difference to the room temperature led to larger fluctuations. Temperature measurements in the scattering cell were carried out with a Pt-100 resistor thermometer and a thermistor with a sensitivity of better than 0.2 mK.

C. Scattered light measurement

After centrifugation to remove dust particles from the scattering volume, the sample cell was positioned into the apparatus. It was allowed to come to thermal equilibrium by observing the scattered intensity over a time range of about 2–3 h. In all samples we measured intensities at 21 angles between 40° and 140° and 117 temperatures in a range from $T - T_c = 0.02 - 1.2$ K. The sampling time at each angle and temperature was 10 s. This procedure was repeated ten times to get 100 seconds of total measurement time interrupted by 5 s autoscaling procedure between each sampling time.

The measured scattering intensity I_s was corrected for scattering volume, intensity fluctuations, dark counts, etc. according to the methods proposed by Kao and Chu [20]. To extract the effect of criticality from our measurements we applied the following procedure for background correction. We used the same mixture and measured the intensity of scattered light at 35 K above the critical temperature. At this high temperature no critical effects are expected and thus I_B is taken for background correction. Because of the low boiling temperature of the toluene in the measurement cell we perform the background measurements for the sample DH01 at 12 K and for DHT19 at 25 K above T_c^{vis} . The corrected intensity is denoted by I_{sc} .

IV. DATA ANALYSIS

Since the temperature dependence of the observed properties in the critical range is strongly non-linear, the application of a special powerful least-squares fitting procedure became essential. Instead of a standard implementation of the Marquard-Levenberg algorithm we applied a special procedure of Golub, Pereyra [21], and Osborne [22]. They designed an algorithm to solve problems of a type of multiple nonlinear regression with a model function Y_{calc} that is separable. The program attempts to compute a weighted least-squares fit to a separable function

$$Y_{\text{calc}}(\alpha, \beta, x) = \sum_{j=1}^L \beta_j \Phi_j(\alpha, x) + \Phi_{L+1}(\alpha, x), \quad (12)$$

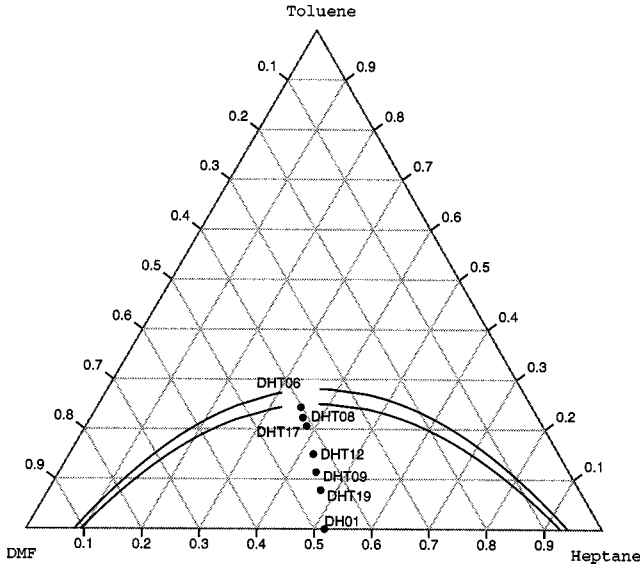


FIG. 1. Isotherm projection of the system *N,N*-dimethylformamide + *n*-heptane + toluene. The circles (●) denote the measured samples. The solid curves show the binodal decomposition at 298.15 and 303.15 K calculated with NRTL by Paschke.

which is a linear combination of nonlinear functions Φ_j . It determines L linear parameters β_j and the vector of nonlinear parameters α by minimizing the norm of residuals r ,

$$|r|^2 = \sum_{i=1}^N W_i [Y_i - Y_{\text{calc}}(\alpha, \beta, x_i)]^2, \quad (13)$$

where W_i denotes the weight of each point (Y_i, x_i) . This weight is given by the reciprocal of the square of the uncertainty for that measured point. The residual r is modified to incorporate, for any fixed α , the optimal linear parameters for that α . It is then possible to minimize only the nonlinear parameters. After the optimal values of the α have been determined, the linear parameters can be recovered by linear least-squares techniques [21]. This is achieved by a modification (see Osborne [22]) of the Marquard-Levenberg procedure using stable orthogonal Householder reflections on a modification of the Jacobian.

The main advantage of this procedure over other least squares programs is that no initial guesses are needed for the linear parameters. Not only does this make it easier to use, but it often leads to faster convergence. We used the program code VARPRO for the determination of the critical amplitudes, exponents, and critical temperatures, as well as for the calculation of the Wegner coefficients. Here we especially benefited from the fact that the objective function Y is separable.

V. RESULTS AND DISCUSSION

A. Phase diagram

The investigated system shows only a weak asymmetry of the projection into the isotherm plane of the critical line as shown in Fig. 1. Therefore, we could restrict our discussion to the changes caused by the increasing fraction of toluene. Because of the uncertainties resulting from a multiple weigh-

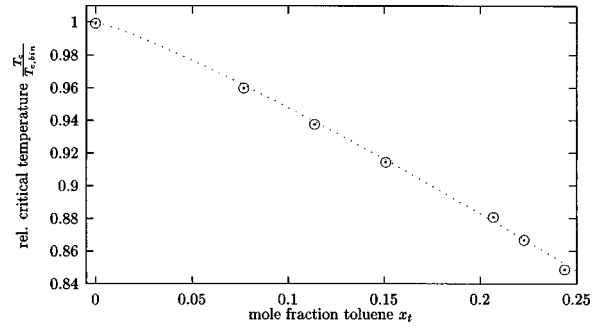


FIG. 2. Relative decomposition temperature vs mole fraction of the third component. The dotted line shows the power law according to Eq. (14).

ing process during sample preparation the mole fraction in Fig. 1 shows a slight scatter. However, the critical conditions are guaranteed by the coexistence volume criterion. The decomposition temperatures of our samples in dependence on the composition are shown in Fig. 2. Here the temperatures are normalized to the critical temperature of the binary mixture DH01. The critical line of the ternary system is restricted to yield a zero slope if x_t becomes zero. Therefore, we use a power law

$$\frac{T_c}{T_{c,\text{bin}}} = a - bx_t^{-c} \quad (14)$$

to describe the concentration dependence of the critical temperatures within a composition range of toluene from $x_t = 0$ to $x_t = 0.25$. The parameters of Eq. (14) are shown in Table IV.

B. Determination of correlation lengths and osmotic susceptibilities

According to Eq. (7) we applied the common procedure by Ornstein, Zernike, and Debye (OZD method)

$$\frac{I_B T}{I_{\text{sc}}(q)} = \frac{1}{C_{\chi T}} + \frac{\xi^2}{C_{\chi T}} q^2 \quad (15)$$

to determine the generalized osmotic susceptibility and the correlation length from the corrected scattering intensity at a given temperature. By this method we calculated the susceptibility $C_{\chi T}(T)$ from the scattered intensity at zero angle and the correlation length $\xi(T)$ from the slope. Especially measurements at temperatures near the critical point show slight nonlinearities in the angle dependence of the scattered light intensities. The origin of this behavior as well as the uncertainties of the determined properties are discussed in [12]. In the case of violated linearity conditions we restricted ourselves to the linear range of angles for the OZD method.

We were not able to give a single estimate for the uncertainties $\Delta\xi$ of $\xi(T)$ over the whole range of measured temperatures. But we can specify estimates for the following cases:

- (i) In the range $T - T_c \gg 1.5$ K, due to the low scattering intensity we found $\Delta\xi \approx 2$ nm.
- (ii) If $T - T_c = 1.5 - 0.2$ K the higher intensity leads to $\Delta\xi < 1$ nm.

TABLE II. Results of fitting the temperature dependence of correlation lengths $\xi(T)$ along a critical line to a simple power law Eq. (16).

Sample	x_t	ξ_0 in nm	T_c in K	ν_x	Variance
DH01	0.000	0.175 ± 0.025	341.887 ± 0.015	0.622 ± 0.016	1.976
DHT06	0.233	0.074 ± 0.015	290.394 ± 0.010	0.842 ± 0.015	1.838
DHT08	0.223	0.077 ± 0.007	296.530 ± 0.007	0.828 ± 0.009	2.073
DHT09	0.114	0.096 ± 0.028	320.871 ± 0.006	0.761 ± 0.015	1.994
DHT12	0.147	0.085 ± 0.010	312.851 ± 0.008	0.789 ± 0.010	2.115
DHT17	0.207	0.082 ± 0.011	301.357 ± 0.006	0.804 ± 0.012	2.217
DHT19	0.078	0.111 ± 0.015	328.401 ± 0.004	0.728 ± 0.011	1.939

(iii) At $T - T_c < 0.2$ K, the system became very sensitive to temperature fluctuations and the uncertainties grow up to $\Delta \xi \approx 10$ nm.

Similar ranges are obtained for the generalized osmotic susceptibility. But there the precision of the measurement is limited to a higher extent by the temperature constancy achieved. Therefore, the uncertainties in the susceptibilities are larger at higher decomposition temperatures. As shown in Eq. (8) the OZD does not consider the singularity of the static structure factor. But within the range of uncertainties we obtain very similar results when we apply the modified Eq. (10).

C. Calculation of critical exponents by simple power laws

Our data were measured very close to T_c . Therefore, we assume that power laws will describe the temperature dependence of correlation length

$$\xi(T) = \xi_0 \left(\frac{T - T_c}{T_c} \right)^{-\nu} \quad (16)$$

and generalized osmotic susceptibility

$$C\chi_T(T) = C\chi_{T,0} \left(\frac{T - T_c}{T_c} \right)^{-\gamma}. \quad (17)$$

To determine the parameters in Eqs. (16) and (17) we performed nonlinear least-squares fits applying the VARPRO code, described above. As input we used weighted $\xi(T)$ and $C\chi_T(T)$ data from the OZD method. The critical amplitude

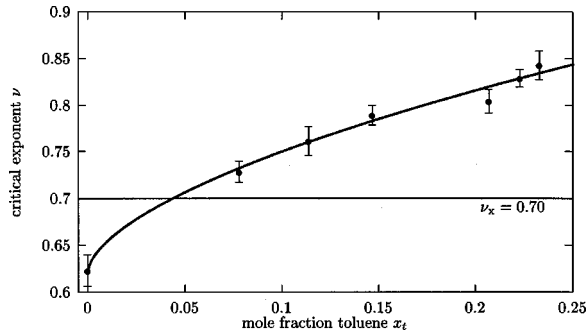


FIG. 3. Critical exponent ν of the correlation length of critical fluctuations $\xi(T)$. The measured exponents according to the power law (16) are shown as \bullet within their error bars. The solid curve denotes the model Eq. (18). The renormalized susceptibility exponent ν_x according to Eq. (1) is represented as a horizontal line.

was considered as a linear parameter, whereas T_c and the exponents were treated as nonlinear parameters in the fit.

Correlation length. In Table II the results of the fit procedures for the temperature dependence of the correlation length are shown. We achieve a satisfying fit quality for all seven samples. The calculated critical temperatures are in very good agreement with the experimentally measured decomposition temperatures shown in Table I. The determined critical exponent ν at $x_t = 0$ has a value that corresponds to the three-dimensional Ising model with respect to the measurement and fit uncertainties. But a mole fraction of toluene of $x \approx 0.08$ leads to a larger exponent which exhibits the limit of the renormalized exponent according Eq. (1) ($\nu_x = 0.70$). In Fig. 3 the critical exponent ν as a function of the mole fraction of the third component is shown. In our ternary mixtures the exponents of correlation lengths is apparently larger and increases with the growing mole fraction of the third component. In order to compare this result with the free electron Ising model we show the value of ν_x , too. This leads to a validity limit of the exponent renormalization at approximately 4% toluene. Again we used a power law

$$\nu = a - bx_t^c \quad \text{resp.} \quad \gamma = a - bx_t^c \quad (18)$$

to find a general description of the critical exponent over extended ranges of composition. The corresponding parameters are shown in Table III. The calculated critical amplitudes ξ_0 show a characteristic dependence from the sample composition, too. We obtained a downward shift as shown in Fig. 4.

Osmotic susceptibility: The behavior of the determined susceptibility exponents is similar to that of our correlation length exponents. Table IV shows the fitting results for the generalized osmotic susceptibility $C\chi_T(T)$ in our seven samples. The quality of these fit results is slightly less satisfying than those of the correlations lengths (see Figs. 5 and

TABLE III. Parameters of the power law model for the mole fraction dependence of the critical line [Eq. (14)] and the determined critical exponents along this line [Eq. (18)].

Parameter	$\frac{T_c}{T_{c,\text{bin}}}$	ν	γ	η
a	1.00 ± 0.00	0.62 ± 0.01	1.26 ± 0.04	-0.03 ± 0.06
b	-0.77 ± 0.04	0.51 ± 0.06	0.43 ± 0.07	0.83 ± 0.28
c	1.17 ± 0.04	0.60 ± 0.08	0.39 ± 0.12	0.90 ± 0.37

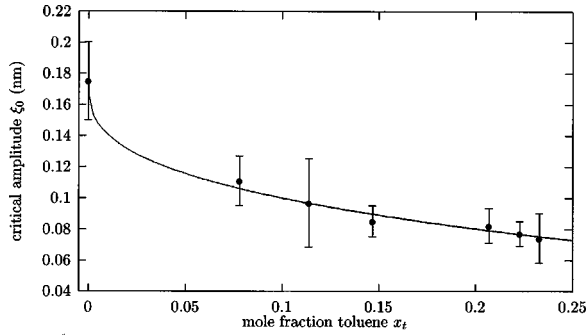


FIG. 4. Critical amplitude ξ_0 of the correlation length $\xi(T)$ of the critical fluctuations according to the power law (16).

6.) The calculated critical temperature shows a slightly larger uncertainty, too. However T_c is in agreement with experimental determined values T_c^{vis} . Again the calculated exponent γ of the binary mixture DH01 suggests Ising-like behavior. Figure 3 shows the susceptibility exponents of our samples as a function of the mole fraction of toluene as well as the limit from the exponent renormalization, Eq. (1). As one can see an amount of more than 10 mole-% of toluene leads to a significantly larger exponent γ . Similar to the case of correlation length above this limit the exponent seems to increase linearly with concentration. For concentrations $x_t \rightarrow 0$ we suppose that γ reaches the binary exponent. Thus, in an overall description we propose a functional form as in Eq. (18). If we assume that the critical exponent renormalization treats the third component as an impurity to a binary mixture, it should be valid as a limiting law in a small concentration range. For the ternary system considered here we expect that a concentration range $0 \leq x_t \leq 0.08$ should not be exceeded.

Scaling law: In all systems of the same universality class a set of scaling laws should be valid. One of these connects the correlation length exponent ν to the susceptibility exponent γ . Unfortunately, the hyper scaling relation

$$(2 - \eta)\nu = \gamma \quad (19)$$

contains the static structure factor exponent η which we cannot determine independently from the OZD method. Therefore, it was not possible to test the validity of this law. On the other hand, if Eq. (19) is valid for our system we can use it to obtain η . Its dependence from the toluene content is shown in Fig. 7. For the mixtures with $x_t < 0.1$ (DH01 and DHT19) Eq. (19) holds true for $\eta = 0$ with respect to the

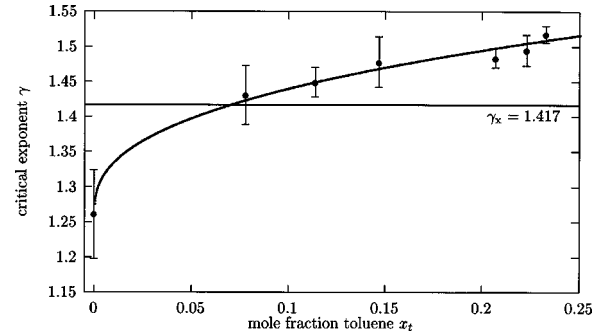


FIG. 5. Critical exponent γ of the generalized osmotic susceptibility $\chi_T(T)$. The measured exponents according to the power law (17) are shown as \bullet within their error bars. The solid curve denotes the model Eq. (18). The renormalized susceptibility exponent γ_x according to Eq. (1) is represented as a horizontal line.

measurement uncertainties. Within the range of measured mole fractions η becomes significant and increases linearly. However the uncertainties of the determined structure factor exponents are rather large. In addition the absolute values of η are in the same order as uncertainties of the other exponents. But the result compelled us to the assumption that η has to be renormalized in the case of ternary mixtures.

VI. SUMMARY

The purpose of our investigations was to study the critical singularities in a ternary fluid system along a critical line. We performed measurements at seven critical mixtures with increasing amount of the third component. Because of the weak asymmetry of the miscibility gap we can assume that the third component is the only origin for any effects in the critical singularities.

Assuming the validity of common power laws we determined critical exponents of the correlation length of critical fluctuations as well as their generalized osmotic susceptibilities. For both exponents we obtained a significant shift. This result agrees with our previous measurements at the system aniline+cyclohexane+p-xylene [12]. While the exponents of the binary system show the values well known from the three-dimensional Ising model the ternary exponents increase beyond exhibits the limit given by the free electron Ising model. Therefore, we conclude that in a relatively small composition range up to 8 mole-% toluene, the incomplete Fischer renormalization is a satisfying description for the graph of critical exponents. But for larger amounts of the

TABLE IV. Results of fitting the temperature dependence of generalized osmotic susceptibility $\chi_T(T)$ along a critical line to a simple power law Eq. (17).

Sample	x_t	$\chi_{T,0}$ in a.u.	T_c in K	γ_x	Variance
DH01	0.000	1.813 ± 0.205	341.888 ± 0.016	1.261 ± 0.063	3.864
DHT06	0.233	0.885 ± 0.067	290.391 ± 0.011	1.518 ± 0.012	3.757
DHT08	0.223	0.953 ± 0.084	296.532 ± 0.008	1.495 ± 0.022	3.994
DHT09	0.114	1.022 ± 0.113	320.869 ± 0.007	1.449 ± 0.021	4.143
DHT12	0.147	0.978 ± 0.104	312.851 ± 0.008	1.478 ± 0.036	4.052
DHT17	0.207	0.974 ± 0.091	301.355 ± 0.011	1.484 ± 0.014	3.998
DHT19	0.078	1.052 ± 0.071	328.403 ± 0.011	1.431 ± 0.042	4.213

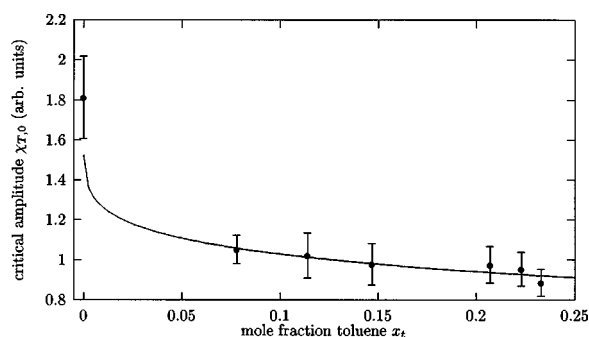


FIG. 6. Critical amplitude $\chi_{T,0}$ of the generalized osmotic susceptibility $\chi_T(T)$ according to the power law (17).

third component, this perturbation model seems not to be valid. Our six ternary mixtures give larger exponents and show a characteristic nonlinear mole fraction dependence. We found that power laws will describe this mole fraction dependence of the critical exponents along a critical line. It would be useful to investigate more in detail the composition dependence of the critical exponents in the range close to $x_t=0$. The asymmetry of the critical line may influence the critical behavior too.

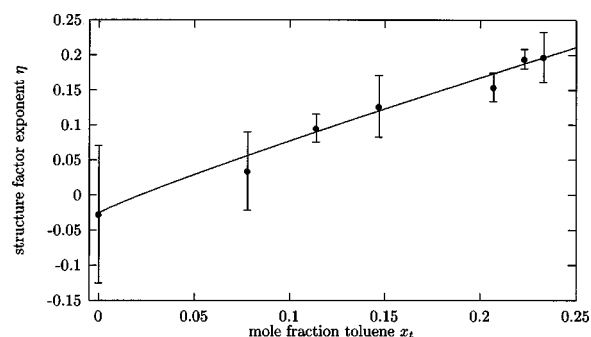


FIG. 7. Structure factor exponent η calculated by Eq. (19). The measured exponents according to the power law (17) are shown as ● within their error bars. The solid curve denotes a power law model analogous to Eq. (18).

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