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Accurate determination of α and Δ exponents in critical binary fluids by refractive-index measurements

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The critical behavior of the refractive index n of three critical mixtures, nitroethane-isooctane (N-I), isobutyric-acid–water (I-W), and triethylamine-water (T-W), has been investigated using a very sensitive and reliable interferometric method which enables gravity effects to be ignored. An accuracy $\delta n/n \simeq 4\times10^{-7}$ has been obtained in the range $T-T_c = 5\times10^{-4}$–20°C [$t = (T-T_c)/T_c = 1.7\times10^{-6}$–$7\times10^{-2}$]. All anomalies can be interpreted in terms of density or specific-heat anomalies. Thus, for the first time in binary fluids, the α exponent could be accurately determined, and was found very close to the renormalization-group (RG) value ($\alpha_{\mathrm{RG}} = 0.110\pm0.003$ for $n = 1$ and $d = 3$, to be compared with $\alpha_{\mathrm{N\text{-}I}} = 0.10\pm0.02$, $\alpha_{\mathrm{I\text{-}W}} = 0.12\pm0.05$, and $\alpha_{\mathrm{T\text{-}W}} = 0.113\pm0.005$). In the T-W system, the nonanalytical corrections are sufficiently high to allow, also for the first time, the critical exponent Δ to be determined accurately. The experimental value $\Delta_{\mathrm{T\text{-}W}} = 0.50\pm0.03$ is in good agreement with the value obtained by RG theory ($\Delta = 0.493\pm0.007$). The amplitude values of the diverging part are in agreement with the two-scale-factor universality and allow the universal constant $X = (R_\xi^+)^3$ to be determined, here also in agreement with the RG values [$X_{\mathrm{I\text{-}W}} = (2.0\pm0.2)\times10^{-2}$, $X_{\mathrm{RG}} \simeq 1.76\times10^{-2}$]. In the systems studied here, the regular variation was found to be close to ideal variation, suggesting that the mixing anomaly is due mainly to the critical behavior of the specific heat. In addition, we review the results for other systems which have been studied by density, volume, thermal diffusivity, and specific-heat measurements. Although the data are not generally very accurate or reliable, they all support the same general conclusions derived from the analysis of the present data.

Near the second-order phase transition of pure fluids[1] or binary mixtures,[2] the behavior of the specific heat at constant volume V (fluid) or at constant pressure p and composition x (mixt.) exhibits a power law divergence governed by the exponent $\alpha \simeq 0.1$. For a binary fluid at critical composition (x_c),

$$C_{p,x_c} = C_{p,x_c}^{\mathrm{reg}} + C_{p,x_c}^{0}\,|t|^{-\alpha},$$

with $t = T/T_c - 1$ and T_c the absolute critical temperature. The amplitude C_{p,x_c}^0 can be related to the amplitude of the correlation length $\xi = \xi_0|t|^{-\nu}$ by $C_{p,x_c}^0 = k_B X/\alpha\rho_c\xi_0^3$, where $X \simeq 10^{-2}$ is a universal constant, k_B is the Boltzmann constant, and ρ_c the critical density.

Direct measurements of C_{p,x_c} have not yet provided an unambiguous determination of the parameters α, C_{p,x_c}^{reg}, C_{p,x_c}^0 because of experimental difficulties associated with gravity effects and/or temperature instabilities.

An alternative method involves the measurement of the density variation ρ or the volume variation V near T_c, since both are connected to C_{p,x_c} through the well-known relationship

$$C_{p,x_c} - C_{V,x_c} = T_c V \alpha_{p,x_c}\left(\frac{\partial P}{\partial T_c}\right)_{V,x_c},$$

where

$$\alpha_{p,x_c} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,x_c} = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_{p,x_c}.$$

The anomaly in C_{p,x_c} is small, so the change in the behavior of ρ or V is weak, and until now the best determination gave rise to an uncertainty on α of ± 70%.[3] Moreover gravity effects are generally present since the measurement is integrated over all the sample height (V measurement) or over the buoy height (ρ measurements).

We have developed recently a new method[4] which reduces gravity effects to a level where they are no longer detected. The principle consists in measuring the refractive index variation at constant height near T_c by a high precision interferometer method. These variations are connected to the volume change and to local-field effects. This last phenomenon, sensitive only to the short-ranged part of the correlation function, has been shown to be negligibly small,[5] so the refractive index behavior exactly reflects the density anomaly.

Three critical mixtures have been investigated. The first was nitroethane-isooctane, chosen because $(\partial T_c/\partial p)_{V,x_c}$ is very low and ξ_0 not too small, so that the local-field effects alone should be evidenced. This first study has been reported.[5] The second mixture was isobutyric acid–water, which is interesting due to the matching in density of the two components and the high value of $(\partial T_c/\partial p)_{V,x_c}$. Moreover careful volume measurements[6] have already been performed on this mixture. The third is triethylamine water where the C_p anomaly is very high. Careful C_p measurements in this mixture have also been published.[7] This last mixture shows such a large anomaly that important nonanalytical corrections were evidenced. Thus, in addition to the determination of α, C^0_{p,x_c}, and X, we will analyze the influence of such corrections.

I. THEORETICAL BACKGROUND

As shown in Ref. 5, the variation of the refractive index n can be written in the following form

$$\Delta n = \left(\frac{\partial n}{\partial T}\right)^{\text{reg}}_{p,x_c}(T-T_c) + \Delta\rho_c + \Delta F_c \,.$$

The first term represents the regular thermal variation. The second term is connected to the density anomaly and the third to the effects of local field. We showed in Ref. 5 that this last effect was negligibly small in a system (N-I) where $\Delta\rho_c$ being very weak, it should have been the only observable anomaly. We will therefore neglect it in the following.

A simplifying hypothesis leads to the assumption that the whole deviation to the volume additivity is due to the anomaly of C_{p,x_c} itself, i.e., the regular value is assumed to be the ideal value. $(\partial n/\partial T)^{\text{id}}_{p,x_c}$ can be evaluated following the derivation of the generalized Lorentz-Lorentz (L-L) formula

$$(n^2-1)/(n^2+2) = \tfrac{4}{3}\pi(\alpha_1 N_1\phi_1 + \alpha_2 N_2\phi_2)[1/(1-F)]\,,$$

where α_i is the polarizability of molecule i considered alone. N_i is the number density of pure component i at the considered temperature and pressure. ϕ_i is the volume fraction of the component i.

$F \simeq 1\%$ is a correction due to local-fields effects independent of the critical behavior[5] and due to electronic overlaps, distortion of the molecular framework, and short-range part of the density correlations 1-1, 2-2, and 1-2.[8]

The derivative at constant pressure and composition can be expressed as

$$\left(\frac{\partial n}{\partial T}\right)^{\text{id}}_{p,\phi} = (n^2-1)\left(\frac{n^2+2}{6n}\right) \times \sum_{i=1}^{2} \frac{\phi_i}{(n_i^2-1)[(n_i^2+2)/6n_i]}\left(\frac{\partial n_i}{\partial T}\right)_{p,\phi} + \Theta(F_{12})\,.$$

$\Theta(F_{12})$ represents the influence of the cross-correlations 1-2 alone. In most cases, the total influence of F modifies the L-L derivatives $(\partial n/\partial T)^{\text{L-L}}_p$ of pure fluids by about 6%.[8] Neglecting $\Theta(F_{12})$ which is a part of F is certainly a much better approximation.

The critical part $\Delta\rho_c$ is proportional to α_{p,x_c} through the L-L relation, thus

$$\Delta\rho_c = -(n^2-1)[(n^2+2/6n)]\,\alpha^0_{p,x_c} \times [T_c^\alpha/(1-\alpha)](T-T_c)^{1-\alpha}\,,$$

where α^0_{p,x_c} is a function of C^0_{p,x_c}, and

$$\Delta\rho_c = -(n^2-1)\left(\frac{n^2+2}{6n}\right)\frac{T_c^{\alpha-1}}{1-\alpha}\left(\frac{\partial T_c}{\partial p}\right)_{V,x_c}\rho_c C^0_{p,x_c} \times (T-T_c)^{1-\alpha} = R(T-T_c)^{1-\alpha}\,.$$

This is the asymptotic behavior for $T-T_c \to 0$, but for larger values of $T-T_c$, nonanalytical corrections[9,10] can be relevant, and $\Delta\rho_c$ must be written

$$\Delta\rho_c = R(T-T_c)^{1-\alpha} \times [1 + b_1(T-T_c)^{\Delta} + b_2(T-T_c)^{2\Delta}\ldots]\,,$$

where the exponent Δ is expected[11] to be 0.50 and $b_1, b_2 \ldots$ depend on the system.

Finally the $(T-T_c)$ variation of n can be written as

$$\Delta n = \left(\frac{\partial n}{\partial T}\right)^{\text{reg}}_{p,\phi}(T-T_c) + R(T-T_c)^{1-\alpha}\left(1+\sum_j b_j (T-T_c)^{j\Delta}\right). \tag{1}$$

From the Δn variations versus $T-T_c$ four kinds of investigations can therefore be considered: (i) test of formula (1), i.e., of the Δn behavior versus $T-T_c$; (ii) determination of the exponent α; (iii) determination of the diverging part R and comparison with the value calculated from the amplitude relations; (iv) study of nonanalytical corrections and determination of the amplitudes b_j and the exponent Δ.

II. EXPERIMENTAL

All mixtures were prepared in cylindrical quartz cells of radius 1 cm and length $l = 5.000 \pm 0.002$ cm. The system nitroethane-isoctane (N-I) was prepared from distilled nitroethane whose purity was better than 99.5% as verified by chromatography and NMR measurements. The isooctane used had the quality "reference substance for gas chromatography." The isooctane mass fraction was $C_{\text{I}} = 0.5344 \pm 0.0008$, close to the critical value 0.5350 ± 0.0006.[12] The mixture was frozen in liquid nitrogen and sealed under vacuum. For the system isobutyric acid–water (I-W), isobutyric acid was of purity better than 99%. The quality of the water used corresponds to an Ohmic resistance of $18\times10^6\,\Omega$. The experimental mass fraction of the acid was $C_A=0.3889\pm0.0005$, close to the critical mass fraction 0.3885.[13] The mixture triethylamine-water (T-W) was prepared from triethylamine of purity better than 99.5% and water of $18\times10^6\,\Omega$ resistivity. The experimental mass fraction of triethylamine was $C_T=0.321\pm0.001$; the critical value is 0.321 following.[14] Since these two mixtures contain water, we sealed the corresponding cells at atmospheric pressure and at 0°C where the vapor pressures of the mixtures are very low.

The cell was placed into a thermally stabilized copper oven, itself enclosed inside an air regulated box, the whole giving a stability of $\pm5\times10^{-4}\,{}^\circ$C over more than one week and better on shorter periods as verified by a quartz thermometer.

The experimental setup (Fig. 1) is the same as in Ref. 4 and is essentially composed of an interferometer which is the cell itself illuminated by a laser beam ($\lambda=6328$ Å, 6 mW power). It is nearly insensitive to vibrations and temperature gradients outside the sample. For systems such as I-W or T-W where turbidity is important near T_c, we unbalanced the intensity of the interfering beams in order to maintain good contrast near the critical point. Data could thus be obtained as close as 5×10^{-4} to T_c.

The final uncertainty, due to the frequency drifts of the laser and the thermal stabilization accuracy is about 0.1 fringe, i.e., $\delta n\simeq7\times10^{-7}$. The thermal expansion of the quartz cell [linear thermal expansion coefficient $(1/l)(\partial l/\partial T)=4.0\times10^{-7}\,{}^\circ\mathrm{C}^{-1}$][15] corresponds to a correction of $\Delta n/\Delta T=+6.0\times10^{-7}\,{}^\circ\mathrm{C}^{-1}$.

Since the laser beam diameter is small (0.5 mm), the refractive index is measured at a given height, at a position nearly in the middle of the sample where the meniscus is situated in the inhomogeneous phase. Therefore the composition remains critical even if gravity induces a density gradient.[16] These composition gradients should deviate the beam in the sample and somewhat disturb the fringes, this however was never visible, possibly because the time necessary to form a density gradient is very long.

We always started from a thermal equilibrium state T_i to reach another thermal equilibrium state T_f. About one hour was sufficient to reach this equilibrium, since the thermal diffusivity of a binary mixture exhibits only a weak anomaly near T_c.[17] The fringes were recorded by a photodiode between the two temperature levels in order to estimate the integer number of the interference order, and the fractional part was directly measured on the photodiode plane. The refractive index variation Δn was inferred from the corresponding interference order number Δp by the relation $\Delta n=(\lambda_0/2l)\,\Delta p=6.328\times10^{-6}\Delta p$ (see Table I–III).

For systems I-W and T-W, the transition is well determined by the dissappearance of the transmitted beam. The critical temperature was determined for the system N-I (where the matching in refractive indices cancels the turbidity) by the sudden inversion of the fringes as reported in Ref. 12, due to the composition variation when the

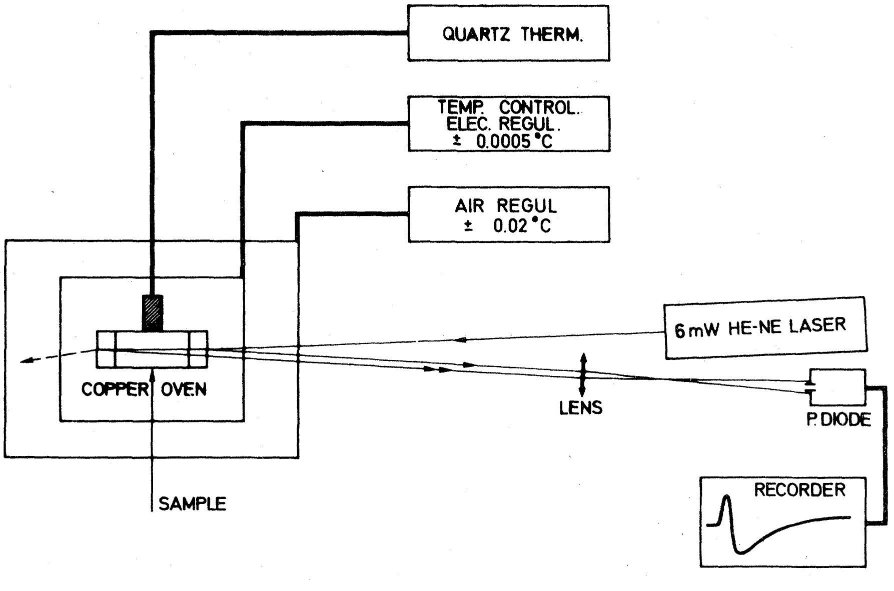

FIG. 1. Experimental setup.

TABLE I. Refractive index data ($n = 6.328 \times 10^{-6} P$) for nitroethane-isooctane ($T_c = 29.8480\,°\mathrm{C}$).

T(°C), P	T(°C), P
31.6087, 72.06	33.8073, 000.437
30.8750, 129.83	33.3432, 36.562
30.4155, 165.87	32.8810, 72.75
30.1864, 183.89	32.4188, 108.848
30.0489, 194.76	31.9553, 144.895
29.9717, 200.86	31.4912, 180.911
29.9260, 204.47	31.0295, 217.000
29.8980, 206.71	30.5665, 253.117
29.8880, 207.34	30.5645, 253.823
29.8688, 209.00	30.5636, 253.823
...	30.3795, 268.235
31.2502, 199.10	30.3787, 268.941
30.5159, 256.94	30.1948, 282.647
30.0531, 293.33	30.0100, 296.765
29.9021, 305.44	29.9646, 300.412
29.8663, 308.23	29.9180, 304.294
29.8605, 308.61	29.8978, 305.794
...	29.8898, 306.588
32.7686, 000.00	29.8835, 306.676
32.6774, 007.24	29.8815, 306.941
32.6322, 010.83	29.8794, 307.059
32.6189, 012.11	29.9264, 303.353
...	29.9253, 303.286
34.3307, 0	29.8802, 307.000
34.1435, 14.50	29.8770, 307.143
33.6800, 50.57	29.8751, 307.294
33.2155, 86.63	29.8730, 307.500
32.7520, 122.80	29.8721, 307.571
32.2895, 158.55	29.8714, 307.647
...	29.8681, 307.882
32.2877, 158.83	29.8667, 308.088
31.8253, 194.67	29.8641, 308.235
31.3612, 230.87	29.8633, 308.323
30.8976, 266.94	29.8621, 308.571
30.4344, 303.13	29.8580, 308.823
30.2488, 317.67	29.8564, 308.857
30.2488, 317.65	29.8552, 308.970
29.9625, 340.13	29.8540, 309.029
29.8587, 348.20	29.8530, 309.235
29.8555, 348.50	29.8541, 309.118
29.8516, 348.70	29.8510, 309.529
29.8491, 348.77	
...	
30.3162, 193.00	
29.9495, 222.28	
29.9028, 225.88	
29.8689, 228.55	
29.8630, 229.00	
29.8600, 229.14	
29.8574, 229.28	
29.8558, 229.39	
29.8537, 229.61	
29.8511, 229.78	
29.8485, 229.95	
...	

phase separation process takes place. The measured critical temperature was (weakly) related to the temperature T_a of the intermediate thermalized housing, showing a small temperature gradient between the sample and the thermometer. For the same T_a we detected no T_c drifts during the duration of each of the experiments (3 months each). In order to take into account a possible nonlinearity of the thermometer or other unknown sources of uncertainties, we also studied separately each component of these mixtures in an identical cell. The same temperature region as for the mixtures was investigated, in the same logarithmic scale, in order to detect possible systematic distortions.

In order to analyze the data, we use a program of statistical refining due to Tournarie.[18] To estimate the quality of the fit we considered the deviation between the calculated and measured values, and the distribution of errors measured by a quality coefficient Q. This parameters equals one if the errors are randomly distributed, but is drastically lowered if a systematical distortion occurs. Also the mean error $\sigma(n)$ can be determined.

III. RESULTS

A. Components (Table IV)

As shown in Table IV all components (except water) exhibit a simple linear relationship between Δn and T so that

$$\Delta n = \left(\frac{\partial n}{\partial T}\right)_p (T - T_c)\,.$$

Only for water must we add a polynomial development

$$\Delta n = \frac{\partial n}{\partial T}_p \left[1 + W_1(T - T_c) + W_2(T - T_c)^2\right](T - T_c)\,.$$

In the range 27°–38°C (I-W mixture), $W_2 = 0$, whereas in the range 2°–18°C (T-W mixture), W_2 is no longer negligible. These values are in agreement with previous published data.[19]

From these measurements, the value of the ideal (regular) contribution can be estimated and leads to

$$\text{N-I:}\quad \left(\frac{\partial n}{\partial T}\right)^{\mathrm{id}}_{p,\Phi} = -(4.779 \pm 0.010) \times 10^{-4}\,\mathrm{K}^{-1}$$

$$\text{I-W:}\quad \left(\frac{\partial n}{\partial T}\right)^{\mathrm{id}}_{p,\Phi} = \left[-2.270 - 8.80 \times 10^{-3}(T - T_c)\right] \times 10^{-4}\,\mathrm{K}^{-1}$$

$$\text{T-W:}\quad \left(\frac{\partial n}{\partial T}\right)^{\mathrm{id}}_{p,\Phi} = \left[-2.367 + 1.08 \times 10^{-2}(T - T_c) + 1.50 \times 10^{-4}(T - T_c)^2\right] \times 10^{-4}\,\mathrm{K}^{-1}\,.$$

TABLE II. Refractive index data ($n = 6.328\times10^{-6}P$) for isobutyric-acid–water ($T_c = 26.7930\,^\circ\mathrm{C}$).

T(°C), P	T(°C), P	T(°C), P	T(°C), P	T(°C), P	T(°C), P
37.7018, −00.470	33.1675, 180.941	28.2625, 367.437	27.0320, 411.151	38.5778, 001.437	26.8116, 456.187
37.6097, 002.389	33.0748, 184.529	28.1704, 370.823	27.0029, 412.121	38.1147, 020.437	26.8079, 456.250
37.5185, 006.176	32.9803, 188.059	28.0780, 374.176	26.9930, 412.468	37.6524, 039.375	26.8048, 456.353
37.5167, 006.118	32.8886, 191.647	27.9851, 377.500	26.9813, 412.765	37.1886, 058.125	26.8008, 456.412
37.4252, 009.882	32.7957, 195.294	27.8927, 380.848	26.9751, 413.000	36.7261, 076.937	26.7972, 456.529
37.3326, 013.706	32.7030, 198.882	27.8007, 384.176	26.9650, 413.303	36.2633, 095.625	26.7942, 456.500
37.2405, 017.470	32.6107, 202.470	27.7080, 387.470	26.9517, 413.765	35.8001, 114.235	...
37.1481, 021.235	32.5192, 206.059	27.6151, 390.765	26.9433, 414.061	35.3377, 132.812	
37.1465, 021.143	32.5191, 206.059	27.5234, 394.118	26.9380, 414.235	34.8753, 151.312	
37.0552, 024.882	32.4265, 209.706	27.4303, 397.424	26.9329, 414.424	34.4110, 169.882	
36.9630, 028.588	32.3338, 213.294	27.3373, 400.647	26.9266, 414.262	33.9487, 188.235	
36.8703, 032.389	32.2405, 216.944	27.2910, 402.273	26.9231, 414.706	33.4852, 206.437	
36.7784, 036.118	32.1483, 220.588	27.2456, 403.875	26.9193, 414.818	33.0225, 224.647	
36.7765, 036.147	32.0552, 224.059	27.1988, 405.485	26.9160, 414.941	32.5592, 242.706	
36.6841, 039.882	31.9621, 227.588	27.1522, 407.091	26.9130, 415.062	32.0967, 260.687	
36.5914, 043.647	31.8699, 231.176	27.1061, 408.647	26.9103, 415.187	31.6341, 278.529	
36.4996, 047.412	31.7767, 234.765	27.0601, 410.250	26.9072, 415.250	31.1714, 296.353	
36.4070, 051.176	31.6848, 238.294	27.0413, 410.875	26.9055, 415.218	31.1710, 296.294	
36.3128, 054.941	31.5915, 241.882	27.0116, 411.875	26.9018, 415.312	30.7085, 313.882	
36.2210, 058.706	31.4994, 245.412	26.9997, 412.242	26.8998, 415.375	30.2460, 331.437	
36.1275, 062.471	31.4078, 248.941	26.9890, 412.647	26.8965, 415.500	29.7836, 348.882	
36.0536, 066.235	31.3133, 252.529	26.9782, 413.059	26.8946, 415.625	29.3203, 366.176	
35.9432, 069.941	31.2207, 256.118	26.9692, 413.294	26.8911, 415.750	28.8581, 383.353	
35.8511, 073.706	31.1284, 259.647	26.9609, 413.562	26.8882, 415.812	28.3957, 400.333	
35.7582, 077.294	31.0367, 263.176	26.9558, 413.757	26.8844, 415.937	28.3937, 400.375	
35.6658, 081.000	30.9436, 266.465	26.9502, 414.000	26.8817, 416.062	27.9315, 417.187	
35.5740, 084.706	30.8526, 270.353	...	26.8783, 416.187	27.4686, 433.588	
35.4817, 088.470	30.7607, 273.941	29.1438, 335.000	26.8754, 416.250	27.2392, 441.647	
35.3889, 092.176	30.6679, 277.470	29.0513, 338.412	26.8721, 416.375	27.1457, 444.875	
35.2966, 095.882	30.5757, 281.059	28.9538, 341.765	26.8688, 416.500	27.1000, 446.437	
35.2037, 099.588	30.4833, 284.588	28.8630, 345.470	26.8661, 416.562	27.0539, 448.058	
35.2031, 099.588	30.3891, 288.117	28.7708, 348.706	26.8651, 416.562	27.0064, 449.647	
35.1110, 103.294	30.2975, 291.588	28.6777, 352.353	26.8616, 416.687	26.9821, 450.562	
35.0182, 107.000	30.2047, 295.118	28.5854, 355.765	26.8588, 416.812	26.9623, 451.187	
34.9268, 110.706	30.1119, 298.589	28.4927, 359.121	26.8553, 416.906	26.9420, 451.875	
34.8341, 114.412	30.0186, 302.118	28.4005, 362.470	26.8520, 417.062	26.9151, 452.750	
34.7412, 118.118	29.9266, 305.647	28.3075, 365.848	26.8461, 417.250	26.8993, 453.375	
34.7407, 118.235	29.8343, 309.176	28.2152 369.235	26.8430, 417.312	26.8929, 453.562	
34.6488, 121.941	29.7411, 312.588	28.1224, 372.588	26.8401, 417.500	26.8860, 453.750	
34.5565, 125.588	29.6488, 316.059	28.0300, 375.937	26.8370, 417.562	26.8786, 453.937	
34.4646, 129.235	29.5561, 319.529	27.9376, 379.242	26.8337, 417.625	26.8674, 454.375	
34.3719, 132.941	29.4635, 323.000	27.8454, 382.578	26.8306, 417.750	26.8625, 454.529	
34.2776, 136.882	29.3709, 326.437	27.7530, 385.848	26.8272, 417.875	26.8563, 454.687	
34.1854, 140.588	29.2800, 329.879	27.7511, 385.878	26.8240, 418.000	26.8513, 454.875	
34.0932, 144.235	29.1884, 333.242	27.6595, 389.235	26.8202, 418.125	26.8455, 455.117	
34.0010, 147.823	29.0951, 336.727	27.5670, 392.529	26.8169, 418.250	26.8412, 455.187	
33.9077, 151.529	29.0029, 340.176	27.4745, 395.765	26.8134, 418.375	26.8380, 455.312	
33.8150, 155.176	28.9115, 343.529	27.3830, 399.000	26.8103, 418.500	26.8369, 455.375	
33.7244, 158.823	28.8200, 346.941	27.2893, 402.242	26.8071, 418.750	26.8334, 455.470	
33.6315, 162.471	28.7267, 350.424	27.2240, 404.529	26.8481, 417.125	26.8296, 455.588	
33.5374, 166.147	28.6344, 353.848	27.1769, 406.151	26.8263, 417.875	26.8262, 455.647	
33.4452, 170.000	28.5416, 357.273	27.1316, 407.735	26.8215, 418.062	26.8226, 455.823	
32.3527, 173.647	28.4498, 360.688	27.0855, 409.250	26.8162, 418.250	26.8202, 455.879	
33.2603, 177.294	28.3568, 364.059	27.0529, 410.454	26.8102, 418.500	26.8153, 456.062	
			...		

TABLE III. Refractive index data ($n = 6.328 \times 10^{-6} P$) for triethylamine-water ($T_c = 18.3535\,°\mathrm{C}$).

T(°C), P	T(°C), P	T(°C), P	T(°C), P	T(°C), P
03.1230, 000.000	06.8125, 200.480	11.9745, 498.930	16.1015, 007.540	18.3525, 036.850
04.0455, 049.790	06.9055, 205.590	12.1595, 510.170	16.1925, 014.620	18.0700, 000.000
04.9695, 099.900	07.0895, 215.700	12.2510, 515.870	16.2845, 021.690	18.0820, 001.360
05.9825, 154.950	07.0915, 215.900	12.3435, 521.570	16.3775, 028.880	18.1182, 005.640
06.9975, 210.630	07.1845, 221.100	12.4355, 527.260	16.5605, 043.460	18.1384, 008.000
08.0025, 267.100	07.1365, 219.000	12.6215, 538.790	16.6525, 050.430	18.1587, 010.630
09.0215, 325.090	07.1815, 221.250	12.7135, 544.610	16.7455, 058.000	18.1787, 012.960
10.0325, 383.600	07.1735, 221.100	12.8055, 550.370	16.8375, 065.670	18.2188, 018.000
10.9595, 437.800	07.2655, 226.150	12.8980, 556.170	17.0225, 081.270	18.2386, 020.580
12.0670, 504.550	07.3585, 231.200	12.9905, 562.000	17.1145, 089.230	18.2702, 024.750
12.5285, 533.000	07.4495, 236.230	13.1755, 573.750	17.2065, 097.220	18.2778, 025.870
13.0825, 567.880	07.5425, 241.330	13.2685, 579.960	17.3915, 113.690	18.2908, 027.610
13.5455, 597.730	07.6345, 246.440	13.3605, 585.980	17.4835, 122.230	18.3077, 030.040
14.0075, 627.830	07.7265, 251.670	13.4525, 591.820	17.6680, 139.810	18.3236, 032.430
14.5005, 661.090	07.8180, 256.800	13.6380, 603.710	17.7135, 144.230	18.3285, 033.170
15.0565, 699.620	07.9105, 262.000	13.7305, 609.700	17.7605, 148.850	18.3343, 034.000
15.5145, 732.640	08.0955, 272.570	13.8230, 615.750	17.8525, 158.230	18.3353, 034.170
16.0685, 773.960	08.1865, 277.710	13.9145, 621.770	17.9445, 168.000	18.3363, 034.290
03.2155, 004.930	08.2795, 282.880	14.1025, 634.040	18.0375, 178.077	18.3385, 034.730
03.3080, 010.070	08.3725, 288.100	14.1735, 639.420	17.9905, 172.920	18.3395, 034.750
03.4005, 015.110	08.4655, 293.290	14.0820, 633.000	17.9857, 172.310	18.3405, 035.000
03.4925, 020.150	08.5565, 298.430	14.1315, 636.200	18.0021, 174.220	18.3412, 035.130
03.5855, 025.120	08.6485, 303.640	14.2235, 642.250	18.0233, 176.620	18.3441, 035.390
03.6755, 030.040	08.7415, 308.930	14.3165, 648.550	18.0695, 181.850	18.3442, 035.570
03.7690, 035.000	08.8335, 314.100	14.4085, 654.870	18.0897, 184.130	18.3450, 035.700
03.8615, 039.860	08.9275, 319.360	14.5930, 667.350	18.1103, 186.641	18.3462, 035.860
03.9535, 044.710	09.1125, 330.280	14.6865, 673.830	18.1318, 189.000	18.3472, 036.050
04.1375, 054.790	09.2045, 335.620	14.7795, 680.260	18.1508, 191.420	18.3482, 036.180
04.2305, 059.790	09.2975, 340.900	14.8715, 686.630	18.1699, 193.640	18.3501, 036.550
04.3225, 064.760	09.3905, 346.190	14.9635, 693.110	18.1892, 196.170	18.3516, 036.750
04.4145, 069.700	09.4820, 351.450	15.1485, 706.170	18.2082, 198.550	...
04.5125, 075.240	09.5745, 356.810	15.2405, 712.870	18.2275, 200.940	
04.6055, 080.200	09.6645, 362.140	15.3295, 719.090	18.2460, 203.430	
04.6935, 085.150	09.7565, 367.470	15.4225, 725.730	18.2646, 206.000	
04.7855, 090.000	09.8475, 372.880	15.6065, 739.270	18.2835, 208.670	
04.8775, 094.950	09.9395, 378.280	15.6995, 746.140	18.3019, 211.330	
05.0615, 104.850	10.1245, 388.950	15.7920, 753.000	18.3032, 211.670	
05.0625, 104.950	10.2185, 394.450	15.8840, 760.000	18.3205, 214.430	
05.1545, 109.900	10.3105, 399.820	15.9765, 766.910	18.3306, 215.960	
05.2475, 114.850	10.4035, 405.180	16.1605, 781.000	18.3382, 217.170	
05.3395, 119.900	10.4975, 410.550	16.2525, 788.090	18.3423, 218.000	
05.4315, 124.850	10.5905, 415.960	16.3445, 795.350	18.3447, 218.500	
05.5245, 129.850	10.6825, 421.320	16.4365, 802.610	18.3472, 218.840	
05.6155, 134.800	10.7745, 426.730	16.5295, 810.090	18.3498, 219.000	
05.7085, 139.770	10.8665, 432.270	16.6215, 817.550	...	
05.8005, 144.780	11.0515, 443.310	...	18.0996, 003.450	
05.8925, 149.800	11.1445, 448.860	16.0105, 000.620	18.1987, 015.450	
06.0745, 159.950	11.2365, 454.360	16.4690, 036.130	18.2553, 022.750	
06.1675, 165.000	11.3295, 459.820	16.9295, 073.420	18.2994, 028.870	
06.2595, 170.000	11.4205, 465.360	17.2985, 105.380	18.3155, 031.180	
06.3525, 175.200	11.5125, 470.840	17.5755, 130.920	18.3325, 033.690	
06.4445, 180.200	11.6065, 476.400	17.8055, 153.460	18.3374, 034.550	
06.5365, 185.260	11.6985, 482.040	17.8985, 163.000	18.3422, 035.330	
06.6295, 190.290	11.7895, 487.640	17.9905, 173.000	18.3488, 036.360	
06.7215, 195.390	11.8825, 493.360	18.0471, 179.270	18.3509, 036.700	

TABLE IV. Refractive index variation of components fitted to $\Delta n = (\partial n/\partial T)_p[1 + W_1(T - T_c) + W_2(T - T_c)^2](T - T_c)$.
For absolute values the correction due to the cell expansion is needed, i.e., add $+6.0\times10^{-7}$ to $(\partial n/\partial T)_p$.

Liquid	$(\partial n/\partial T)_p$ ($\times10^{-4}$)	W_1 ($\times10^{-2}$)	W_2 ($\times10^{-4}$)	Q	$\sigma(n)$ ($\times10^{-7}$)
Nitroethane (18 points)	-4.6606 ± 0.0017	...	...	0.673	14
Isooctane (25 points)	-4.8479 ± 0.0008	...	...	0.661	5.4
Isobutyric acid (138 points)	-4.3160 ± 0.0002	...	...	0.289	3.4
Water (32 points) (27 °C–38 °C)	-1.1131 ± 0.0002	$+1.22\pm0.01$	...	0.485	0.3
Triethylamine (46 points)	-5.2447 ± 0.0008	...	...	0.750	12
Water (75 points) (2 °C–18 °C)	-0.8157 ± 0.0009	-2.01 ± 0.20	-2.79 ± 0.08	0.598	3.5

We used the values of Table V. For reasons explained below, it is useful to calculate the uncertainty on the $(\partial n/\partial T)^{\mathrm{id}}_{p,\Phi}$ value in the N-I system.

B. The critical mixtures

We tried to fit the data to the following Δn variation (Fig. 2):

$$\Delta n = R|T - T_c|^{1-\alpha}[1 + b_1|T - T_c|^{\Delta} + b_2|T - T_c|^{2\Delta} + \dots] + A|T - T_c| + B|T - T_c|^2 + C|T - T_c|^3 .$$

The first term represents the α behavior modified at large $T - T_c$ by nonanalytical corrections, while the second term concerns the regular term. The principle of the fits is the following: (a) Table VI: all parameters $R, \alpha, b_1, b_2 \dots \Delta, A, B, C$ are considered as adjustable parameters. Of course they are not all relevant, and we progressively reduced the number of free parameters until the quality of the fit decreased, so determining the actually significant parameters. Practically, it is difficult to separate the behavior with exponents $2\Delta - \alpha$, $3\Delta - \alpha \dots$ from the regular behavior. So in any case only the single term b_1 will be determined, B and C integrating the effects of both the regular terms and the nonanalytical corrections of higher order. (b) Table VII: the correlation between R and A is very strong since α is small. So any extra information on A greatly increases the accuracy on R and α. The simplest way is to

TABLE V.

Fluid	n (6328 Å)	ρ ($g\times\mathrm{cm}^{-3}$)[b]	vol. fraction of
Nitroethane	1.3900 (30 °C)[a]	1.0404 (30 °C)	0.368 ± 0.001
Isooctane	1.3885 (30 °C)[a]	0.6937 (30 °C)	...
Isobutyric acid	1.3930 (20 °C)[b]	0.9490 (20 °C)	0.4013 ± 0.0005
Water	1.3330 (20 °C)[b]	0.9982 (20 °C)	...
Triethylamine	1.4000 (20 °C)[b]	0.7230 (20 °C)	0.3950 ± 0.001
N-I	1.3890 (30 °C)[c]	...	...
A-W	1.3568[c]	...	...
T-W	1.3591[c]	...	...

[a] References 8 and 12.
[b] Reference 15.
[c] From the L-L formula.

consider that the regular value is not far from the ideal value, i.e., evaluate A (B and C are connected to nonanalytical corrections as stressed in (a), which prevents them from being evaluated). Thus, for the N – I system where each component exhibits almost the same value of A, we could impose within ± 0.2% the regular term. For the T – W mixture, we imposed A within ± 13%, whereas for the I – W system we could not increase the accuracy, due perhaps to weak nonanalytical corrections, high enough to influence the regular behavior, but not sufficiently large to be accurately determined. (c) Table VIII: in order to test the amplitude relations, the best way is to impose both exponents Δ, α (and the regular term A for the N – I and T – W systems). (d) (Table IX): when nonanalytical corrections are necessary (T – W system), the accuracy on Δ is greatly increased when both α and A are imposed. In the same way, the determination of $b_1, b_2 \ldots$ is more accurate if α, Δ, A, B and C are imposed in the known limits.

Concerning the N-I mixture, the quality of the fit and the mean error enable no anomaly to be

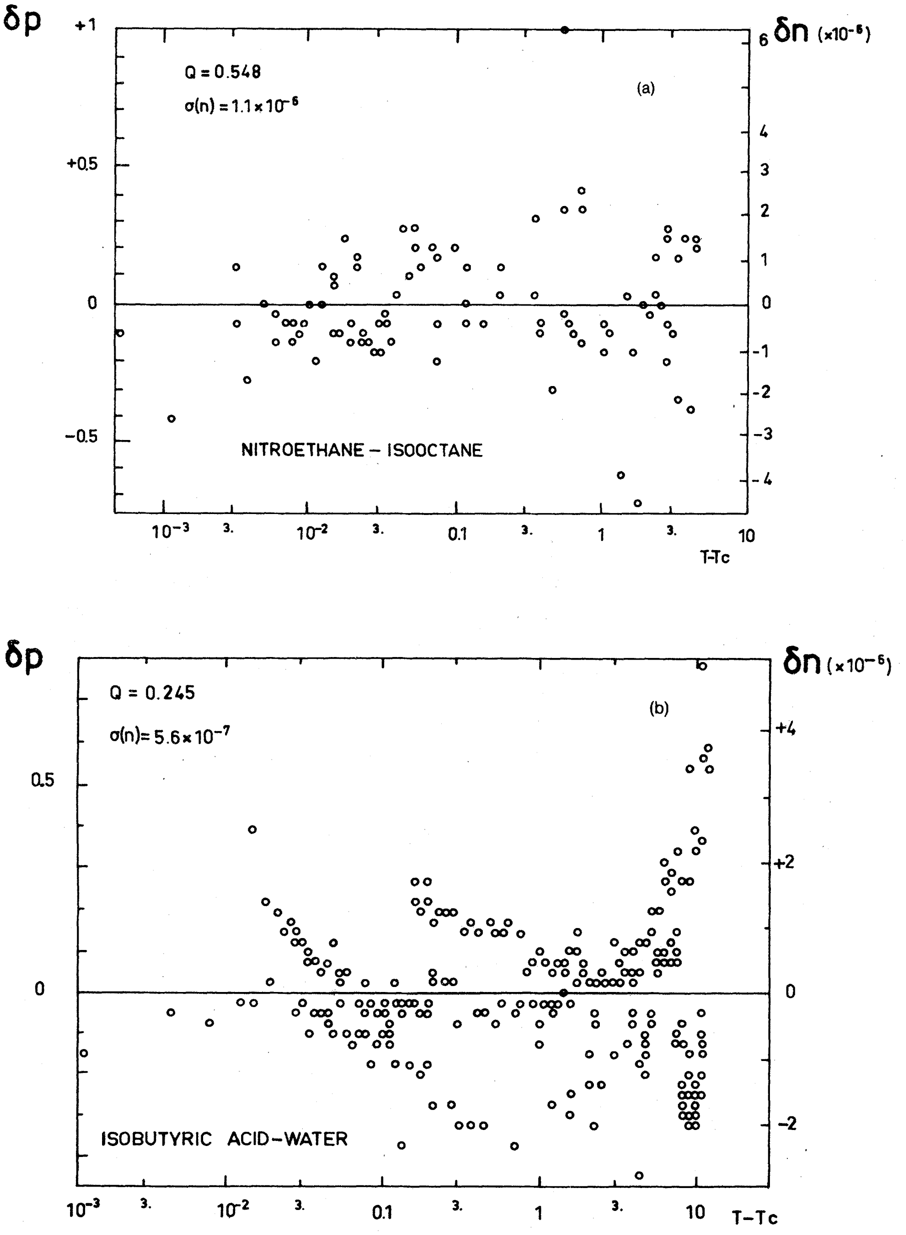

FIG. 2. Reduced deviation (semilog plot) of the experimental refractive index n, or the interference order p, with respect to $T - T_c$, when fitting to: (a) the Table VII formula and with the nitroethane-isooctane system; (b) the Table VI formula and with the isobutyric acid–water system; (c) the Table VII formula and with the triethylamine–water system.

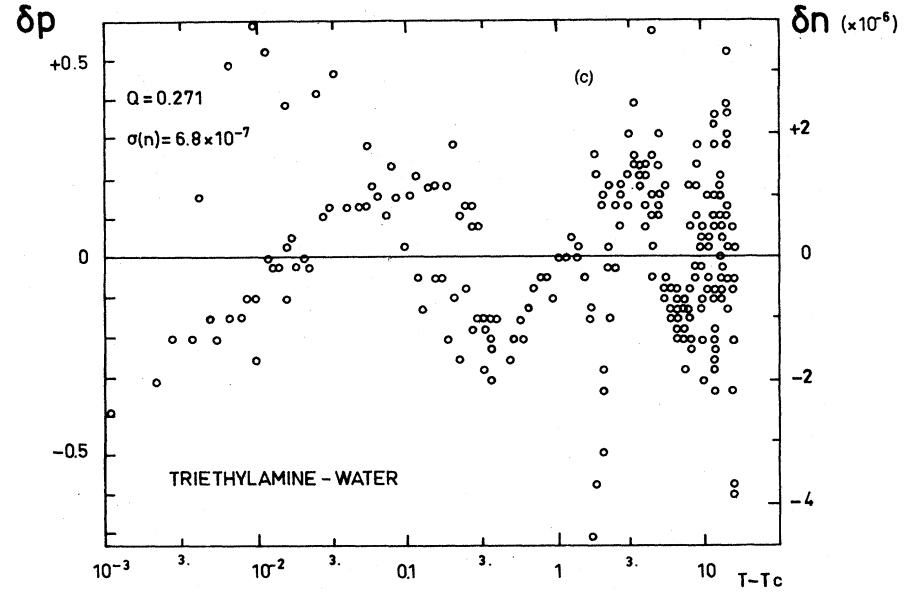

FIG. 2. (*Continued*)

observed, and only A can be determined. However, this regular term (when $R=0$ is assumed) is not in agreement with the ideal value whereas the volume additivity is verified within 1%[12] and that each components exhibits almost the same $(\partial n_i/\partial T)_p$ value. When this ideal value was imposed, the value $\alpha = 0.10 \pm 0.02$ was obtained. An amplitude $R \simeq 0.04$ times the regular parameter was found, whereas no corrections were necessary.

For the I-W mixture, it is not possible to accurately describe the results using only the regular terms. The exponent value $\alpha = 0.12 \pm 0.05$ was found. The amplitude $R \simeq 0.3A$.

Finally the T-W mixture allows both the α divergence and nonanalytical corrections to be determined. The value $\alpha = 0.11 \pm 0.02$ was obtained when only Δ was fixed. With A estimated within ±13%, we get $\alpha = 0.113 \pm 0.003$, with the corresponding amplitude $R \simeq 2.7$ times the regular term A. Concerning nonanalytical corrections, we found $\Delta = 0.50 \pm 0.03$, whereas nonanalytical corrections up to fourth order could be estimated when all the regular terms were fixed.

All these values are clearly much more accurate than those already reported. So we will compare our results as well as other data to the theoretical prediction of renormalization-group theory concerning the value of the exponent α and the exponent Δ, and the amplitude relation concerning R.

VI. DISCUSSION

The renormalization-group calculation, in the case of a scalar order parameter $n=1$ and dimensionality $d=3$ leads to a value $\alpha_{R\text{-}G} = 0.110 \pm 0.003$, in close agreement with our results (Table X), since for the T-W system a value of 0.113 ±0.005 was found. Thus, for the first time in binary fluids, an accurate experimental value of α has been found, which is in better agreement with the renormalization group than with the series expansion value [$\alpha = 0.125 \pm 0.020$ (Ref. 37)].

Another interesting feature concerns the Δ value, also found to be in close agreement with the renormalization-group result as can be seen in Table XI. Another Δ value is reported from the viscosity behavior of ethane near T_c, but it involves rather the dynamic exponents. Only few other experiments in fluid mixtures are concerned with nonanalytical corrections,[7,38,39] and both the magnitude of the correction and the accuracy of the experiment does not allow the Δ exponent to be obtained.

Concerning the universal amplitude relations between ξ_0 and the diverging part of C^0_{p,x_c}, we compared (Table XII), the experimental values using C^0_{p,x_c} data deduced from our R values and other data already published (unfortunately in this last case the uncertainty on C^0_{p,x_c} is often poor or unknown) with the dimensionless quantity $X = (\alpha \rho_c \xi_0^3/k_B) C^0_{p,x_c}$. The ξ_0 values enter to the third

TABLE VI. Δn variations of critical mixtures. Fit to:

$$\Delta n = R|T-T_c|^{1-\alpha}[1+b_1|T-T_c|^{\Delta}] + A|T-T_c| + B|T-T_c|^2 + C|T-T_c|^3 \; .$$

In the homogeneous region, $T-T_c>0$ for N-I and A-W, $T-T_c<0$ for T-W.

System	Parameters	$R(\times 10^{-4})$	α	b_1	Δ	$A(\times 10^{-4})$	$B(\times 10^{-6})$	$C(\times 10^{-7})$	Q	$\sigma(n)$ $(\times 10^{-7})$
Nitroethane + Isooctane	all free	-0.23 ± 0.9	0.075 ± 0.3	...	...	-4.727 ± 0.9	...	...	0.519	7.3
	regular law	...	...	...	...	-4.936 ± 0.002	...	...	0.507	9.7
Isobutyric Acid + water	all free [a] ($A \pm 50\%$)	0.77 ± 0.03	0.12 ± 0.05	...	...	-2.91 ± 0.3	-0.75 ± 0.06	...	0.245	5.6
	regular law	...	...	...	...	-2.256 ± 0.0025	-1.73 ± 0.025	...	0.093	10
Triethylamine + water [b]	all free [a] ($A \pm 50\%$)	-6.17 ± 1	0.11 ± 0.01	-0.275 ± 0.03	$\begin{pmatrix} 0.496 \\ \pm 7.10^{-3} \end{pmatrix}$	-2.265 ± 1	-16.8 ± 0.6	1.97 ± 0.08	0.269	7.1

[a] The regular term was assumed to be known ±50% and $\Delta = 0.493 \pm 7\times 10^{-3}$ was imposed.

[b] It was impossible to obtain a reasonable fit with the regular term alone.

TABLE VII. Determination of the α exponent alone. Fit to:

$$\Delta n = R|T-T_c|^{1-\alpha}[1+b_1|T-T_c|^{\Delta}] + A|T-T_c| + B|T-T_c|^2 + C|T-T_c|^3 \; .$$

Both Δ and the regular terms, A, B, C, were fixed within the known uncertainties.

System	Parameters	$R(\times 10^{-4})$	α	b_1	Δ	$A(\times 10^{-4})$	$B(\times 10^{-6})$	$C(\times 10^{-7})$	Q	$\sigma(n)$ $(\times 10^{-7})$
Nitroethane + isooctane	A imposed ±0.2%	-0.18 ± 0.01	0.10 ± 0.02	...	...	(-4.779 ± 0.010)	...	...	0.548	11
Triethylamine + water	Δ imposed A imposed ±13%	-6.14 ± 0.25	0.113 ± 0.005	-0.278 ± 0.01	$\begin{pmatrix} 0.491 \\ \pm 7\times 10^{-3} \end{pmatrix}$	(2.34 ± 0.3)	-16.2 ± 0.5	1.93 ± 0.07	0.271	6.8

TABLE VIII. Determination of the anomaly amplitude R. Fit to:

$$\Delta = R|T-T_c|^{1-\alpha}[1+b_1|T-T_c|^{\Delta}]$$
$$+A|T-T_c|+B|T-T_c|^2+C|T-T_c|^3 \ .$$

The α value 0.110 ± 0.03 was imposed as was also, when possible, the regular contribution A.

	Parameters	$R(\times 10^{-4})$	α	b_1	Δ	$A(\times 10^{-4})$	$B(\times 10^{-6})$	$C(\times 10^{-7})$	Q	$\sigma(n)$ $(\times 10^{-7})$
Nitroethane + isooctane	A imposed ±0.2 % α imposed	−0.18 ± 0.01	$\begin{pmatrix}0.110\\ \pm 0.03\end{pmatrix}$	...	...	(−4.779 ± 0.010)	...	...	0.495	7.7
Isobutyric Acid + water	α imposed	0.842 ± 0.018	$\begin{pmatrix}0.110\\ \pm 0.03\end{pmatrix}$	...	...	−3.00 ± 0.015	−0.74 ± 0.02	...	0.245	8.9
Triethylamine + water	A imposed ±13% Δ imposed α imposed	−6.16 ± 0.2	$\begin{pmatrix}0.115\\ \pm 2.5\times 10^{-3}\end{pmatrix}$	−0.273 ± 0.009	$\begin{pmatrix}0.492\\ \pm 6.8\times 10^{-3}\end{pmatrix}$	(−2.28 ± 0.2)	−16.0 ± 0.5	1.93 ± 0.07	0.278	6.9

TABLE IX. Nonanalytical corrections. Fit to:

$$\Delta n = R|T-T_c|^{1-\alpha}[1+b_1|T-T_c|^{\Delta}+b_2|T-T_c|^{2\Delta}+b_3|T-T_c|^{3\Delta}+b_4|T-T_c|^{4\Delta}]$$
$$+A|T-T_c|+B|T-T_c|^2+C|T-T_c|^3 \ .$$

The regular terms A, B, C, and α were fixed within the known limits. First Δ was set free in order to determine its value, and second Δ was fixed to the renormalization-group value $\Delta = 0.493 \pm 0.007$ to increase the accuracy on $b_1, b_2 \ldots$, while the regular terms were kept at their ideal values.

	Parameters	$R(\times 10^{-4})$	α	b_1	b_2 $(\times 10^{-3})$	b_3 $(\times 10^{-3})$	b_4 $(\times 10^{-3})$	Δ	$A(\times 10^{-4})$	$B(\times 10^{-6})$	$C(\times 10^{-7})$	Q	$\sigma(n)$ $(\times 10^{-7})$
Triethylamine + water	Reg = ideal ± 13% $\alpha = 0.110 \pm 0.003$	−6.14 ± 0.20	$\begin{pmatrix}0.114\\ \pm 3\times 10^{-3}\end{pmatrix}$	−0.274 ±0.024	...	...	...	0.499 ±0.029	$\begin{pmatrix}-2.29\\ \pm 0.3\end{pmatrix}$	−16.8 ±1.2	−2.0 ±0.1	0.296	7.3
	Reg = ideal ± 13% $\alpha = 0.110 \pm 0.003$ $\Delta = 0.493 \pm 0.007$	−6.18 ± 0.05	$\begin{pmatrix}0.1105\\ \pm 3\times 10^{-3}\end{pmatrix}$	−0.267 ±0.015	−5 ± 10	9.2 + 3	2.38 ± 0.35	$\begin{pmatrix}0.420\\ \pm 7\times 10^{-3}\end{pmatrix}$	(−2.34)	(1.08)	(0.15)	0.216	7.4

TABLE X. Measurements of the critical exponent α by different methods. The expected theoretical value by renormalization-group theory is (Ref. 11) $\alpha_{RG}=0.110\pm0.003$ and by series expansion (Ref. 37) $\alpha_{SE}=0.125\pm0.020$.

System	Measurements	Value of α
Nitroethane + isooctane	n	$0.10 \pm \begin{cases}0.02\text{ [a]}\\0.3\text{ [b]}\end{cases}$
Isobutyric acid + water	n	0.10 ± 0.05[b]
	V	0.12 ± 0.36[c]
	Cp	0.1 ± 0.1[d]
Triethylamine + water	n	$0.113 \pm \begin{cases}0.005\text{ [a]}\\0.01\text{ [b]}\end{cases}$
	Cp	0.240 ± 0.085[e]
Cyclohexane + methanol	V	0.11 ± 0.07[f]
	Cp	0.1 ± 0.1[g]
Nitroethane + trimethylpentane	Λ/Cp	0.059 ± 0.003[h]
Heptane + methanol	Cp	0.1 ± 0.1[i]
CS_2 + methanol	Cp	0.1 ± 0.1[j]
Perfluoromethyl cyclohexane + carbon tetrachloride	Cp	0.055 ± ?[k]

[a] Ideal value ≃ imposed (Table VII).
[b] Table VI.
[c] Reference 6.
[d] Reference 20.
[e] Reference 7.
[f] Reference 3.
[g] Reference 21.
[h] Reference 17.
[i] Reference 22.
[j] Reference 23.
[k] Reference 24.

power, so even a small uncertainty on this quantity gives rise to a large uncertainty on X. Nevertheless, for two systems, isobutyric acid–water and carbon tetrechloride-perfluromethyl cyclohexane a value of 2.0 is found, in reasonable agreement with the renormalization calculation $X=(R_\xi^+)^3\simeq1.76\times10^{-2}$ [Ref. 1(b)] and the series expansion result $X\simeq1.60\times10^{-2}$ [Ref. 1(a)].

Finally, one can note that for the three mixtures that we have studied here and which show weak, mean and high-amplitude anomalies, respectively, the regular part was always found to be close to the calculated ideal value. In Table XIII we report also others systems where the V, ρ and Λ/Cp variations have been studied. They all support the same conclusion, namely that the anomaly of volume mixing seems to be almost fully related to the critical behavior of the specific heat.

TABLE XI. Values of the nonanalytical correction exponent Δ in several systems. The value $\Delta_{RG}=0.493\pm0.007$ is inferred from the renormalization-group calculation (Ref. 11), and $\Delta_{SE}=0.6\pm0.1$ from the series expansion (Ref. 37).

System	Measurement	Δ
Triethylamine – water	Refractive index	0.50 ± 0.03[a]
Ethane	Viscosity[c]	0.5 ± 0.1[b] (dynamic exponent)

[a] From Table IX with α imposed.
[b] References 30 and 35.
[c] Reference 36.

V. CONCLUSION

Very accurate data of the critical refractive index variations of three mixtures, nitroethane-isooctane, isobutyric acid–water, triethylamine-water have been reported. All the observed anomalies could be explained in relation to the density behavior alone, which itself is related to the specific-heat anomaly.

For the first time accurate values of the exponent α have been obtained, with values 0.10 ± 0.02, 0.12 ± 0.05, 0.113 ± 0.005, respectively, which are very close to the predictions of renormalization-group theory ($\alpha_{RG}=0.110\pm0.003$ with $n=1$ and $d=3$). Moreover the amplitude of this anomaly can be used, together with the correlation length ξ_0, to check the two scale factor

TABLE XII. Relation between the amplitude of the diverging part of the specific heat C^0_{p,x_c} obtained by different measurement methods and the amplitude ξ_0 of the correlation length. X is expected to be 1.76×10^{-2} from renormalization-group calculation [Ref. 1(a)] and 1.60×10^{-2} from series expansion [Ref. 1(b)].

System	Measurement	$(\partial T_c/\partial p)_{v,x_c}$ $\left(\begin{matrix}\times10^{-8}\ \mathrm{cm}^2\\ \mathrm{dyn}^{-1}\,{}^\circ\mathrm{C}^{-1}\end{matrix}\right)$	$\frac{\alpha\rho_c C^0_{p,x_c}}{k_B}=X/\xi_0^3$ $(\times10^{21}\ \mathrm{cm}^{-3})$	ξ_0 $(\times10^{-8}\ \mathrm{cm})$	X $(\times10^{-2})$
Nitroethane-isooctane	n	0.26[t] ±0.05	1.8 ±0.5[a]	2.3 − 3.1[l]	3.8 ± 2.6
	Λ/Cp		0.8 ± ?[s]	3.25 ±0.06[r]	2.8 ± ?
Isobutyric acid +water	n	−5.20[b]	0.46 ± 0.03[a]	3.5 ±0.1[m]	2.0 ± 0.2
	V	±0.25	0.68 ± ?[b]	...	2.9 ± ?
	ρ		1.06 ± ?[c]	...	4.3 ± ?
	Cp		0.29 ± ?[d]	...	1.2 ± ?
Triethylamine +water	n	2.03[u] ±0.03	8.4 ±0.3[a]	1.0 − 2.0[n]	$3.8^{+4.6}_{-3.0}$
	ρ		18.7 ± ?[e]	...	8.4 ± ?
	Cp		17 ±4[f]	...	$7.6^{+6.6}_{-5.9}$
Cyclohexane + methanol	V	3.10[v]	1.8 ± ?[g]	3.4 ±0.1[o]	7.1 ± ?
	Cp		0.53 ± ?[h]	...	2.1 ± ?
Cyclohexane + aniline	n	0.67[v]	1.8 ± ?[s]	2.5 ±0.1[s]	2.8 ± ?
Nitroethane-trimethylpentane	Λ/Cp	0.37[t] ±0.05	2.4 ± ?[i]	2.26 ±0.07[p]	2.8 ± ?
	ρ		3.2 ±1[j]	...	3.7 ± 1.5
Carbon tetrachloride + perfluoromethyl cyclohexane	ρ	4.0[w] ±0.16	1.10 ± 0.15[c]	2.7 ±0.2[q]	2.1 ± 0.7
	Cp		1.10 ± 0.07[k]	...	2.1 ± 0.5

[a] From Table VIII.
[b] Reference 6.
[c] Reference 26.
[d] Reference 20.
[e] Reference 27.
[f] Reference 7.
[g] Reference 3.
[h] Reference 21.
[i] References 17 and 30.
[j] Reference 28.
[k] Reference 24.
[l] References 29-31.
[m] Intensity data of Ref. 32.
[n] Reference 7 and our turbidity data.
[o] Reference 33 with correction $\frac{6}{5}$ as stressed in Ref. 25.
[p] References 30 and 34.
[q] Reference 40 with correction $\frac{6}{5}$ as stressed in Ref. 25.
[r] Impure sample containing at least 5% water (Ref. 30).
[s] Reference 30.
[t] Reference 41.
[u] Reference 42.
[v] Reference 43.
[w] Reference 44.

universality. The general agreement is good but the errors remain large, due chiefly to the lack of accurate ξ_0 values. In the triethylamine-water mixture, a noticeable influence of nonanalytical corrections was found, allowing the corresponding exponent Δ to be measured. The value 0.50 ± 0.03 is nearly the same as that deduced from the renormalization-group calculation (0.493 ± 0.007). Finally, the ideal part of the density behavior near T_c was found to be close to the measured regular part, strongly suggesting that the volume anomaly of mixing is mainly due to the criticality.

These various points have been compared to other data found in the literature which concern volume, density, or specific-heat measurement, for the same mixtures and for other systems. Although the accuracy on most of these parameters is not as high as that obtained from refractive index measurements, they nevertheless support the same conclusions.

Note added in proof. From Ref. 45 it appears that a new analysis of the critical exponents of the Ising model by high-temperature series expansion, using a modified ratio method, gives $\alpha_{\mathrm{SE}}=0.110$.

TABLE XIII. Comparison between the experimental regular part of the coefficient of thermal expansion and the ideal value.

System	Measurement	Nonanalytical correction	Reg./ideal
Nitroethane + isooctane	n	No	1.0058 ± 0.0065 [a]
	Λ/Cp	No	1.0 ± ? [g]
Isobutyric + acid + water	n	No	1.322 ± 0.007 [b]
			0.84 ± 0.02 [c]
	V	No	0.95 ± ? [d]
Triethylamine + water	n	Yes	0.96 ± 0.17 [b]
Methanol + cyclohexane	V	?	0.77 ± ? [e]
Nitroethane + trimethylpentane	ρ	No	0.97 ± 0.01 [f]
	Λ/Cp	No	1 ± ? [g]

[a] Table VI. Ratio $A^{\mathrm{reg}}/A^{\mathrm{id}}$.
[b] Table VII. Ratio $A^{\mathrm{reg}}/A^{\mathrm{id}}$.
[c] Table VIII. Ratio $B^{\mathrm{reg}}/B^{\mathrm{id}}$.
[d] Reference 6.
[e] Reference 3.
[f] Reference 28.
[g] Reference 30.

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