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Evidence for an Intrinsic Refractive-Index Anomaly in a Critical Binary Liquid Mixture

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New experimental data for the refractive-index behavior in the homogeneous phase below the lower critical solution point in critical-composition liquid mixtures of triethylamine and water are presented. From a comparison with existing density data it is concluded that the critical anomaly in the refractive index includes an intrinsic effect opposite in sign to the density contribution.

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The large fluctuations which develop near the consolute point of binary liquid mixtures affect many physical properties like density, dielectric constant, and refractive index. The density ρ exhibits an anomaly which can be related to the singularity in the heat capacity at constant pressure and concentration $C_{p,x}$, which has a power-law divergence with the critical exponent α. An anomaly is also expected for the static dielectric constant ϵ and the refractive index n on the basis of thermodynamic[1,2] as well as microscopic[3,4] theories. The thermodynamic arguments of Sengers *et al.*[2] and Mistura[1] predict that in addition to an anomalous contribution arising from the density behavior, there should be an intrinsic anomaly in ϵ and n related to dT_c/dE^2, where T_c is the critical temperature and E the electric field. The intrinsic anomaly of the static dielectric constant has been established unambiguously for some binary systems.[5-7] The possible existence of an intrinsic refractive-index anomaly has so far, however, eluded experimental verification. An anomalous behavior for n different from the density anomaly, reported by Hartley *et al.*,[8] was apparently caused by an experimental artifact.[9] As a matter of fact, some authors[10,11] have analyzed their refractive-index data on the assumption that n reflects the behavior of the density alone.

In this paper we report new refractive-index data as a function of the temperature in the one-phase region near the lower critical solution point of triethylamine+water (TW). From a comparison with density[12] and heat-capacity[13] data we arrive for the first time at unambiguous evidence for an intrinsic refractive-index anomaly in a critical binary liquid mixture. A comparison with the previously published n results for this system by Beysens and Bourgou[10] is also made. The possible existence of an intrinsic critical anomaly in the refractive index of TW was suggested previously by Furrow and Green[12] on the basis of a comparison of their density data with the refractive-index results of Beysens and Bourgou.[10] However, no definite conclusion was possible because of substantial inconsistencies (see further) in the refractive-index data.

Seven different experimental runs have been carried out for two different samples with the critical composition of 32.1-wt.% triethylamine.[14] This is the same composition as used by Thoen and co-workers[13] for the heat capacity, by Furrow and Greer[12] for the density, and by Beysens and Bourgou[10] for refractive-index measurements. The Hewlett-Packard (type 5525A) laser interferometer was used to measure the change of the refractive index[15] over the temperature range between about 5 °C and the critical temperature $T_c = 18.3\,°\mathrm{C}$. The resolution obtained with our setup was about 3 ppm. The temperature of the sample cell was controlled by the circulation of a fluid mixture from a temperature-controlled bath. The temperature of the sample cell was measured with a quartz thermometer and the stability was better than 1 mK.[16]

For our first critical sample three different runs have been done. The first run was an exploratory run and not very detailed near T_c. Run 2 is our most detailed run for this sample and many data were obtained near the critical point. Run 3 was a faster control run. No systematic deviations could be found between the three runs. Subsequently we prepared a fresh critical sample and carried out four different runs for it. There is very good agreement between each of these runs (4 to 7) and with the results for the first sample. Figure 1 shows the refractive-index difference $\Delta n = n - n_c$ as a function of temperature for runs 2, 5, and 7. About fifty data points were measured for each of these runs, but for display reasons only a small fraction is given in the figure. Even on this large-scale plot, the anomalous decrease in the refractive index is clearly visible. The anomaly in TW is more pronounced than is usually observed in other systems.[11]

Modern theory of critical phenomena predicts that the mass density and the refractive index in the one-phase region near a liquid-liquid critical point can be represented by the following functions[2,17]:

$$\rho = R_1 + R_2 t + R_3 t^{1-\alpha} + R_4 t^{1-\alpha+\Delta} + R_5 t^{1-\alpha+2\Delta} + \cdots, \tag{1}$$

$$n = N_1 + N_2 t + N_3 t^{1-\alpha} + N_4 t^{1-\alpha+\Delta} + N_5 t^{1-\alpha+2\Delta} + \cdots, \tag{2}$$

where for a lower critical solution point t is the reduced temperature $(T_c - T)/T_c$, α is the critical exponent which characterizes also the divergence of the heat capacity $C_{p,x}$, and Δ is the first correction-to-scaling exponent. The most recent renormalization-group calculations[18] find $\alpha = 0.11$ and $\Delta = 0.50$. In Eqs. (1) and (2) one has $R_1 = \rho_c$ and $N_1 = n_c$, with ρ_c and n_c the values of the density and refractive index at the critical point. For the heat capacity $C_{p,x}$ one can write the following expression[13,17]:

$$C_{p,x} = C_1 C_2 t + C_3 t^{-\alpha} + C_4 t^{-\alpha+\Delta} + C_5 t^{-\alpha+2\Delta} + \cdots. \tag{3}$$

Using the experimentally verified geometric analysis of phase diagrams of multicomponent systems by Griffiths and Wheeler,[19] and rigorous thermodynamic relations, one arrives at the following relation between R_3 nand C_3 in Eqs. (1) and (3):

$$R_3 = \frac{\rho_c^2 C_3}{1-\alpha} \frac{dT_c}{dp}. \tag{4}$$

The quantity dT_c/dp is the slope of the critical line. For triethylamine+water Eq. (4) can be verified with the density data of Furrow and Greer,[12] and heat-capacity data of Thoen and co-workers,[13] and the dT_c/dp result of Timmermans[20] and of Myers *et al.*[21] Within an experimental uncertainty of about 5% it is very well satisfied.[12] This gives confidence for the reliability of all the experimental data involved.

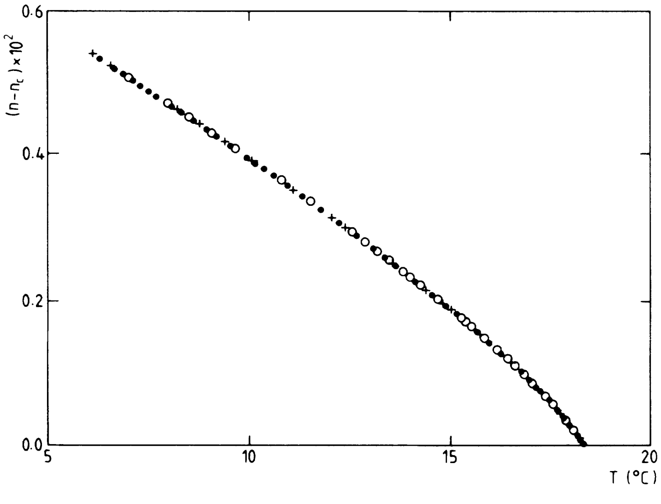

FIG. 1. The refractive-index difference $\Delta n = n - n_c$ as a function of temperature in the one-phase region below the lower critical solution point in samples of 32.1 wt.% of triethylamine in water. Data for three of the seven runs measured are given: run 2 (solid dots), run 5 (open circles), and run 7 (plusses).

According to theory,[2] the leading critical contributions to the refractive index arising from the density anomaly and from dT_c/dE^2 both have a $t^{1-\alpha}$ temperature dependence, and there will thus be two contributions to the amplitude N_3 in Eq. (2). If one makes the usual assumption[10,11] that only the density contribution is important, one can relate N_3 via R_3 to the heat-capacity amplitude C_3 in Eq. (3). From the definition $\alpha_{p,x} = -\rho^{-1} \times (\partial\rho/\partial T)_{p,x}$ for the thermal expansion and the exact relation

$$\left(\frac{\partial n}{\partial T}\right)_{p,x} = \left(\frac{\partial n}{\partial \rho}\right)_{p,x} \left(\frac{\partial \rho}{\partial T}\right)_{p,x} = -\rho \left(\frac{\partial n}{\partial \rho}\right)_{p,x} \alpha_{p,x}, \tag{5}$$

it follows that

$$\rho(T) - \rho(T_c) = \int_{T_c}^{T} \left(\frac{\partial \rho}{\partial n}\right)_{p,x} \left(\frac{\partial n}{\partial T}\right)_{p,x} dT \approx \left(\frac{\partial \rho}{\partial n}\right)_{p,x}^{\text{reg}} [n(T) - n(T_c)]. \tag{6}$$

In the last part of (6) the additional assumption[11] of a regular temperature-independent $(\partial\rho/\partial n)_{p,x}$ value is made. From this it then follows immediately that

$$R_3 = (\partial\rho/\partial n)_{p,x}^{\text{reg}} N_3. \tag{7}$$

A value for $\partial\rho/\partial n$ is usually estimated via the Lorentz-Lorenz (LL) formula analysis[11,12] away from T_c. The LL formula gives a simple analytic relationship between n and ρ, allowing one to calculate $\partial\rho/\partial n$ in noncritical systems with an accuracy of the order of a few percent.[22] Since $\partial\rho/\partial n$ values obtained in this way are nearly temperature independent,[23] the LL value for $\partial\rho/\partial n$ can be calculated away from T_c. If there is, however, an intrinsic critical effect, the above procedure will result in a violation of Eq. (7) and the R_3 value derived from it will not correspond with the experimental result from the density data. Conversely, this then also implies that the LL formula cannot be used for the proper calculation of $\partial\rho/\partial n$ near the critical point. Such a situation can be made very clear graphically by the transformation of the direct ρ and n data into the following quantities:

$$D_\rho \equiv \frac{\rho-\rho_c}{t} = R_2 + R_3 t^{-\alpha}\left[1+\frac{R_4}{R_3}t^{\Delta}+\frac{R_5}{R_3}t^{2\Delta}+\cdots\right], \tag{8}$$

$$D_n \equiv \left(\frac{\partial\rho}{\partial n}\right)_{p,x}^{\text{reg}} \frac{n-n_c}{t} = \left(\frac{\partial\rho}{\partial n}\right)_{p,x}^{\text{reg}} \left[N_2+N_3 t^{-\alpha}\left(1+\frac{N_4}{N_3}t^{\Delta}+\frac{N_5}{N_3}t^{2\Delta}+\cdots\right)\right]. \tag{9}$$

The right-hand sides of Eqs. (8) and (9) have been derived from Eqs. (1) and (2). In a plot of D_ρ as a function of $x \equiv t^{-\alpha}$, the limiting slope for $x \to \infty$ $(t \to 0)$ should be equal to R_3. For D_n the same limiting slope should be obtained provided Eq. (7) is satisfied. In fact, if there is no inherent critical anomaly in the refractive index, D_ρ and D_n should then fall on the same curve.

Using our refractive-index data and the density results of Furrow and Greer[12] we have calculated values for D_ρ and D_n. For $\partial\rho/\partial n$ in Eq. (9) we used the value 2.44 $\text{g}\cdot\text{cm}^{-3}$ which was obtained via Eq. (5) from the temperature dependence of ρ and n between about 7 and 12 °C. This result agrees with the value of 2.45 $\text{g}\cdot\text{cm}^{-3}$ estimated from the Lorentz-Lorenz analysis.[11,12,23] In Fig. 2 D_ρ data (open symbols) and D_n data (solid dots) are plotted as a function of temperature. Far away from T_c, D_ρ and D_n values are identical. On approaching the critical point the D_ρ results fall systematically above D_n, and the difference becomes larger and larger, which is less visible near T_c because of the linear T scale. In order to account for a small difference in T_c, the D_ρ data in this figure have been shifted by $+0.137$ °C. In Fig. 3 the D_ρ data (around curve a) and our D_n data (around curve b) have been plotted as functions of $x \equiv t^{-\alpha_{\text{I}}}$ (with $\alpha_{\text{I}} = 0.11$). The solid squares, plusses, and crosses are D_ρ from the three different density runs of Furrow and Greer.[12] Triangles are D_n data from four of our refractive-index runs. Curve a has been calculated from the best fit with Eq. (1) to the density data.[12] It has a limiting slope of 0.69 $\text{g}\cdot\text{cm}^{-3}$. Curve b is calculated from a fit with Eq. (2) to the data of our run 5 (with $\alpha = 0.11$, $\Delta = 0.50$, and $T_c = 18.3011$ °C imposed). The limiting slope here is 0.375 $\text{g}\cdot\text{cm}^{-3}$, corresponding to an N_3 value of 0.153. Similar fits[24] for all our runs resulted in an average value $N_3 = 0.148 \pm 0.008$. The data represented by the solid dots and the open circles are obtained from two refractive-index runs of Beysens and Bourgou[10] sufficiently close to T_c (their runs 2 and 3). The solid dots (run 2 of Ref. 10) are in good agreement with our results. The best fit by Furrow and Greer[12] to these data gave $N_3 = 0.158$. The open circles (run 3 of Ref. 10), however, show very large systematic deviations with the other data. This large discrepancy between these two

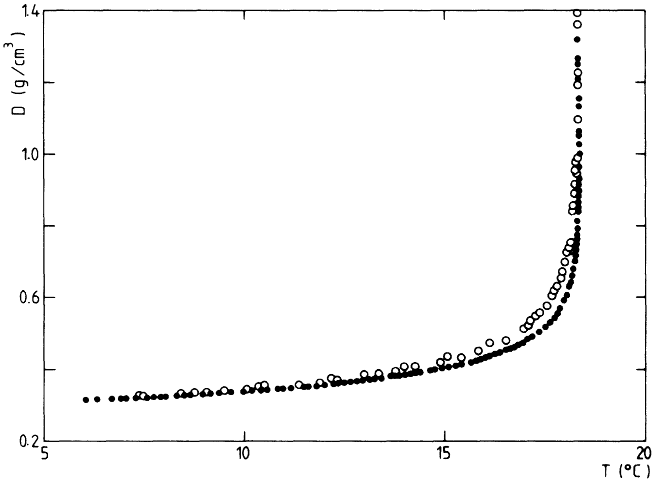

FIG. 2. Temperature dependence of the quantities D_ρ (open circles) and D_n (solid dots), defined in Eqs. (8) and (9), for the homogeneous phase below T_c in mixtures of triethylamine and water with critical composition.

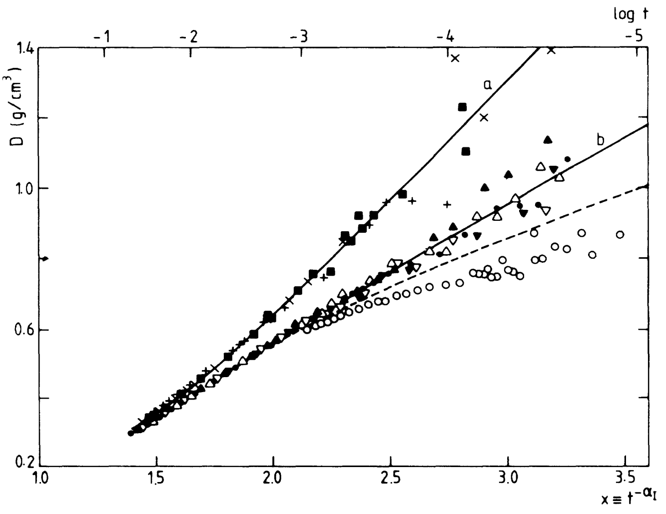

FIG. 3. The quantities D_ρ and D_n [Eqs. (8) and (9)] plotted as functions of the variable $x \equiv t^{-\alpha_{\text{I}}}$, with $t = (T_c - T)/T_c$ and $\alpha_{\text{I}} = 0.11$ the Ising value for the specific-heat exponent α. Data for D_ρ are calculated from the density data of Ref. 12: run 1, plusses; run 2, squares; and run 3, crosses. Curve a represents the best fit of Furrow and Greer (Ref. 12) to their runs 2 and 3. Our D_n data for different runs are given by the triangles and inverted triangles: run 2, solid triangles; run 4, solid inverted triangles; run 5, open triangles; and run 7, open inverted triangles. Curve b represents the best fit to the data for our run 5. D_n data for two runs of Beysens and Bourgou (Ref. 10) are given by solid dots (their run 2) and open circles (their run 3). The dashed line represents a simultaneous fit by Beysens and Bourgou to all their data.

Beysens and Bourgou runs was also noticed by Furrow and Greer.[12] The dashed line in Fig. 3 represents D_n data from a simultaneous fit by Beysens and Bourgou to all their data.[10] In view of the internal discrepancies such a fit must be considered as very unreliable.

From the above analysis we arrive at a difference of almost a factor 2 between the value $R_3 = 0.69 \pm 0.04$ $\mathrm{g \cdot cm^{-3}}$ from the density data[12] and our average value $N_3(\partial\rho/\partial n)_{p,x}^{\mathrm{reg}} = 0.36 \pm 0.02$ $\mathrm{g \cdot cm^{-3}}$. This clearly demonstrates the presence of an intrinsic $t^{1-\alpha}$ anomalous contribution in the refractive index which is opposite in sign to the density contribution. With the assumption of the validity of Eq. (7), the temperature independence of $(\partial\rho/\partial n)_{p,x}$ is not justified. That $(\partial\rho/\partial n)_{p,x}$ changes appreciably with temperature on approach to T_c can also be verified by the calculation of its value with Eq. (5) from the temperature derivatives of fitting results with Eqs. (1) and (2) for the direct ρ and n data. One finds that $(\partial\rho/\partial n)_{p,x}$ changes from about 2.45 $\mathrm{g \cdot cm^{-3}}$ far away from T_c to a value of about 3.5 $\mathrm{g \cdot cm^{3}}$ at $T_c - T = 1$ mK. Although the intrinsic contribution to the refractive index might be much smaller for other systems, the neglect[11] of it to arrive at the heat-capacity anomaly amplitude and to test universal amplitude ratios involving this quantity is questionable.

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

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

[3] G. Stell and J. Hoye, Phys. Rev. Lett. **33**, 1268 (1974).

[4] J. Goulon, J.-L. Greffe, and D. W. Oxtoby, J. Chem. Phys. **70**, 4742 (1979).

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

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

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

[8] C. L. Hartley, D. T. Jacobs, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. Lett. **33**, 1124 (1974).

[9] Reference 80 of Ref. 2.

[10] D. Beysens and A. Bourgou, Phys. Rev. A **19**, 2407 (1979).

[11] D. Beysens, A. Bourgou, and P. Calmettes, Phys. Rev. A **26**, 3589 (1982), and references therein.

[12] G. P. Furrow and S. C. Greer, J. Chem. Phys. **79**, 3474 (1983).

[13] J. Thoen, E. Bloemen, and W. Van Dael, J. Chem. Phys. **68**, 735 (1978); E. Bloemen, J. Thoen, and W. Van Dael, J. Chem. Phys. **73**, 4628 (1980).

[14] F. Kohler and O. K. Rice, J. Chem. Phys. **26**, 1614 (1957); J. F. Counsell, D. H. Everett, and R. J. Munn, Pure Appl. Chem. **2**, 335 (1962).

[15] J. M. St.-Arnaud and T. K. Bose, J. Chem. Phys. **65**, 4854 (1976), and **71**, 4951 (1979).

[16] Details of the experimental setup will be given in a future publication.

[17] S. C. Greer and M. R. Moldover, Ann. Rev. Phys. Chem. **32**, 233 (1981), and references therein.

[18] J. C. LeGuillou and J. Zinn-Justin, Phys. Rev. B **21**, 3976 (1980), and J. Phys. Lett. **46**, L137 (1985).

[19] R. B. Griffiths and J. C. Wheeler, Phys. Rev. A **2**, 1047 (1970).

[20] J. Timmermans, J. Chim. Phys. **20**, 491 (1923).

[21] D. B. Myers, R. A. Smith, J. Katz, and R. L. Scott, J. Phys. Chem. **70**, 3341 (1966).

[22] D. Beysens and P. Calmettes, J. Chem. Phys. **66**, 766 (1977).

[23] From the Lorentz-Lorenz relation one obtains $\partial\rho/\partial n = 6\rho n(n^2-1)^{-1}(n^2+2)^{-1}$. Using our Δn data and additional absolute values of n (measured with an Abbé refractometer), we have calculated $\partial\rho/\partial n$ with the above expression for the temperature interval between 5 °C and $T_c = 18.3\,^\circ\mathrm{C}$. It was found that these $\partial\rho/\partial n$ values changed less than 0.5% over this temperature range.

[24] Details of the analysis and the fitting procedure will be published later.