Critical Behavior near a Vanishing Miscibility Gap

Roger G. Johnston[(a)] and Noel A. Clark
Department of Physics, Condensed Matter Laboratory, University of Colorado, Boulder, Colorado 80309

and

Pierre Wiltzius and David S. Cannell
Department of Physics, University of California, Santa Barbara, California 93106

(Received 6 August 1984)

We report measurements of the osmotic susceptibility and correlation length for the pseudobinary mixture of guaiacol (*o*-methoxy phenol) plus glycerol-water as a function of temperature and water content x [$x \equiv$ weight of water/(weight of water plus weight of glycerol)]. This system exhibits a limited two-phase region which vanishes for $x < x_0 \simeq 0.0137$. We observed a smooth transition from nearly Ising-type behavior for $x \gtrsim 4x_0$ through a non-power-law regime to doubled exponents for $x \simeq x_0$ and saturating divergences with doubled exponents for $x < x_0$.

PACS numbers: 64.70.-i, 64.70.Ja

Many binary liquid mixtures have consolute critical points which exhibit three-dimensional Ising-type critical behavior and exponents ($\gamma = 1.24$, $\nu = 0.63$). In mixtures, where orientational entropy plays a role, one often finds "reentrant" miscibility; the two-phase region exists over a temperature range $T_l < T < T_u$. In this case the coexistence curve is a closed loop with critical points at two temperatures, T_l and T_u. For certain reentrant mixtures, by variation of the pressure or the concentration, x, of a third dilute component, the temperature difference $\Delta T = T_u - T_l$ can be reduced to zero at, say, $x = x_0$, i.e., the closed-loop coexistence curve can be shrunk to a point and caused to vanish.[1] In the case of guaiacol (*o*-methoxy phenol) plus glycerol-water, the dilute component is water which is almost insoluble in guaiacol. Consequently, this ternary system should be quasibinary with the water serving as an external field to modify the interactions.

Here we report on a light scattering study of the evolution of the critical behavior in a series of mixtures of varying water content x [$x =$ weight of water / (weight of water plus weight of glycerol)]. We find that (1) the osmotic susceptibility χ and correlation range ξ approach Ising behavior ($\gamma = 1.24$, $\nu = 0.63$) for $x \gtrsim 4x_0$, (2) non-power-law behavior occurs for $x \lesssim 2x_0$ crossing over to power-law behavior with doubled exponents as $x \to x_0$, and (3) saturating divergences with doubled exponents occur in the one-phase region $x < x_0$. We find that the data are quantitatively accounted for by a simple model of the Leung-Griffiths type[2] in which the observed behavior is attributed to approaching the line of critical points bounding the coexistence surface in a direction which becomes tangential to that line as $x \to x_0$. This picture is consistent with the microscopic model proposed by Walker and Vause[3,4] for hydrogen bonding mixtures which transforms under the renormalization group into an Ising model with an effective interaction parameter depending smoothly on temperature and other parameters in the initial model.[4] Similarly, a model involving parametrization of the critical temperature[5] has been found to account for the behavior of reentrant nematic–smectic-*A*–nematic transitions in liquid crystals as the smectic-*A* temperature region is reduced to zero.[6] The results presented here, however, are the first quantitative investigation of reentrant behavior involving a system whose critical properties are well understood.

In the guaiacol plus glycerol-water system, the two-phase region appears at $T = T_0 = 63.06 \pm 0.2\,^\circ\mathrm{C}$ for $x = x_0 = 0.0137 \pm 0.0002$ and is nearly symmetric about T_0, with $\Delta T/T_0 = 0.100(x - x_0)^{1/2}$, and $(T_u + T_l)/2T_0 = 1 - 2.23 \times 10^{-3}(x - x_0)$, as shown in Fig. 1. The critical concentration of guaiacol w_{cl}, corresponding to the lower critical solution temperature, $T_l(x)$, varied linearly with x and was nearly equal to that for the upper critical solution temperature for each x, being 51 wt.% at $x = 0.0137$ and 47 wt.% at $x = 0.053$. In our experiments the guaiacol concentration was adjusted to $w_{cl} \pm \sim 0.5$ wt.% for each value of x studied.

The intensity and angular distribution $I(\theta, x, T)$ ($18^\circ \leq \theta \leq 163^\circ$) of light scattered by eleven different samples with $x > x_0$ were measured as functions of temperature for $T < T_l(x)$, and two samples with $x < x_0$ were also studied. The apparatus has been described in detail previously.[7] The data for each value of x and T were accurately fitted by the Ornstein-Zernike form and gave $\xi(x,t)$ to ± 20 Å and $S(x,T) \equiv I(\theta = 0, x, T)$, which is proportional to $\chi(x,T)$, to $\pm 3\%$.

Figure 2 shows S and ξ vs $t = (T_l - T)/T_l$ for four samples with $x > x_0$, corresponding to ΔT values of 65.9, 26.3, 9.4, and 1.6 °C. The values of S have been normalized relative to toluene being unity. The solid lines are fits to the model discussed below. Since multiple scattering occurred for $S \gtrsim 2 \times 10^4$, such data were not considered.

Figure 3 shows data for two samples with $x < x_0$,

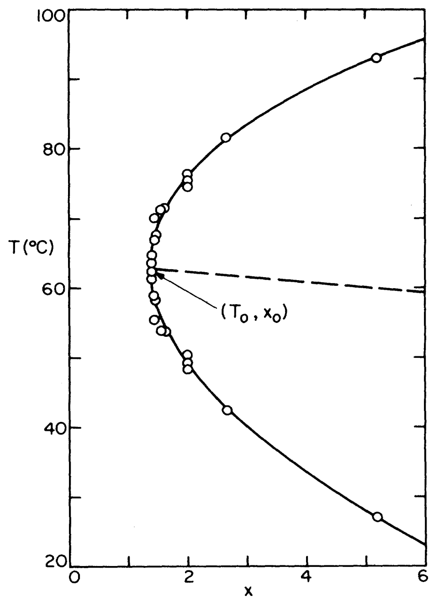

FIG. 1. Upper and lower critical solution temperatures for guaiacol-glycerol-water mixtures vs water content where $x \equiv$ weight of water / (weight of glycerol plus weight of water).

where phase separation did not occur. The maxima occurred in the temperature range from 63.04 to 63.08 °C and the average was taken as T_0. The peak values of S and ξ increased as $x \rightarrow x_0$, and for $|T - T_0|$ large, the behavior was a power law with doubled exponents as shown.

All our results may be understood in terms of the geometric picture of phase transitions developed by Griffiths and co-workers.[2,8,9] This picture includes exponent renormalization caused by the manner in which the experimental path approaches a line of critical points.[10,11] For a reentrant mixture, the coexistence surface in a space of thermodynamic fields, such as T and the chemical potential difference Δ between guaiacol and the pseudosubstance (glycerol-water), with pressure held constant, consists of a line segment ending in critical points. Here we assume that the addition of water allows us to control another field, X, which does not alter the nature of the phase transitions. Viewed in this three-dimensional space (Δ, T, X), the coexistence surface is bounded by a line of critical points, any one of which may be approached

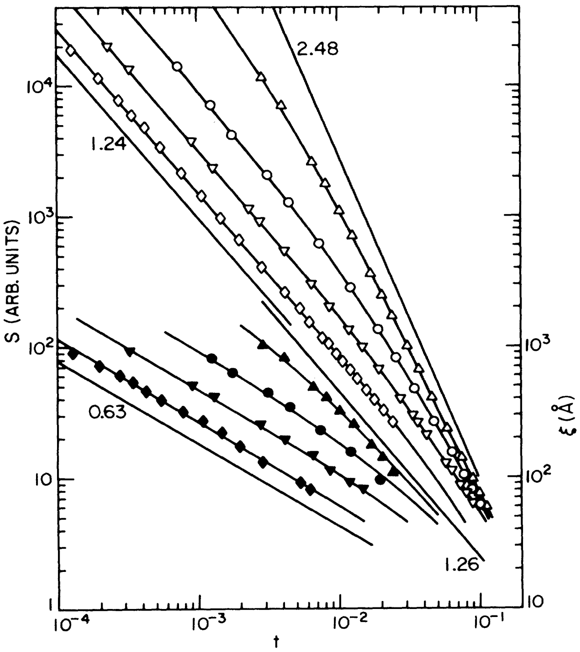

FIG. 2. Susceptibility S (open symbols) and correlation length ξ (filled symbols) vs the reduced temperature difference $t \equiv (T_l - T)/T_l$ from the lower critical solution temperature T_l, for samples having various temperature differences ΔT between the upper critical solution temperature T_u and T_l. The data correspond to $\Delta T = 65.9$ °C (diamonds), 26.3 °C (inverted triangles), 9.4 °C (circles), and 1.6 °C (triangles). The curves through the data are the result of a model discussed in the text, and the limits of Ising exponents are also shown.

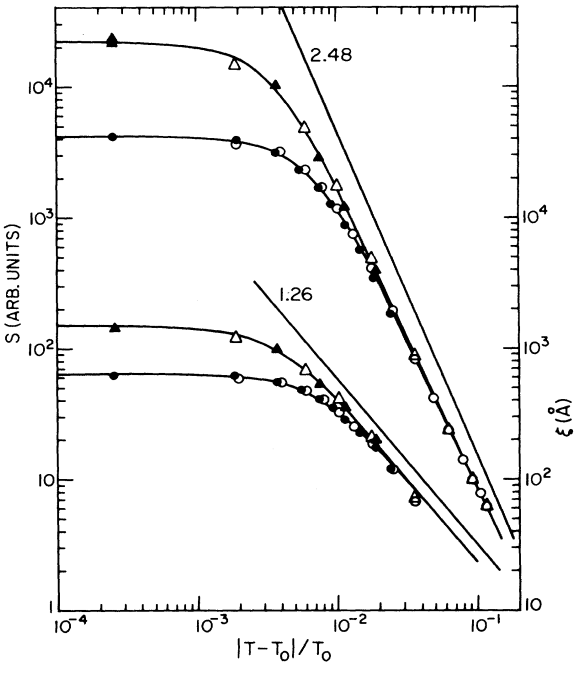

FIG. 3. Susceptibility S (upper two curves) and correlation length ξ vs reduced temperature for two samples which did not contain enough water to exhibit a two-phase region. T_0 is the average of the temperature at which the susceptibility reached its maximum value. The data for one run are shown as open $(T < T_0)$ and filled $(T > T_0)$ triangles, and those for the other run are shown as open $(T < T_0)$ and filled $(T > T_0)$ circles. The solid curves are the results of a model discussed in the text, and the straight lines correspond to exponents equal to twice the Ising values.

by a variety of paths. The two of interest[8] here are (a) the path in the plane tangent to the coexistence surface but not parallel to the critical line and (b) the path parallel to the critical line. Case (a) should result in unrenormalized exponents and is achieved by fixing the concentration of one of the species in a binary mixture.[8] We believe an approach in the tangent plane was maintained by adjusting the guaiacol concentration to its (x dependent) critical value, and that the path followed experimentally in each run by change of the temperature with x fixed becomes tangential to the critical line as $x \rightarrow x_0$.

In an approach of type (a), the two independent fields (here X and T) are equivalent asymptotically,[9] with a divergence of the type $|T-T_c|^{-\gamma}$ being of the form $|X-X_c|^{-\gamma}$ if X is varied at fixed T. In the present case, these are presumably unique values of Δ and X on the critical line for each value of T, $\Delta_c(T)$ and $X_c(T)$, respectively. The fundamental assumption is that if the experimental path followed is such that $\Delta - \Delta_c(T) = 0$, at least asymptotically, the X dependence of χ will be of the form[8-11] $|X_c(T)-X|^{-\gamma}$ with $\gamma = 1.24$. To express this in terms of T, we identify X with x and use data shown in Fig. 1, i.e., the measured values of $T_l(x)$ and $T_u(x)$, to obtain $X_c(T)$ as

$$X_c(t_0) - X_0 = [1-(1-4\Gamma t_0)^{1/2} - 2\Gamma t_0]/2\Gamma^2 A^2. \qquad (1)$$

Here $t_0 = (T_0 - T)/T_0$, $\Gamma = C/A^2 = -0.88$, and A and C are defined by $[T_u(x) - T_l(x)]/T_0 = 2A\,(x-x_0)^{1/2}$ and $[T_u(x) + T_l(x)]/2T_0 = 1 + C(x-x_0)$, respectively. Thus the susceptibility is given by

$$\chi(x,t_0) = \chi_0\{A^2(x_0-x) + [1-(1-4\Gamma t_0)^{1/2} - 2\Gamma t_0]/2\Gamma^2\}^{-\gamma} + \chi_B, \qquad (2)$$

where χ_B is any background which may be present.

In the one-phase region, $x < x_0$, Eq. (2) predicts that a saturating divergence with a maximum at $T = T_0$ will be observed if T is varied with x fixed. This agrees with our results, and the solid curves for the susceptibility shown in Fig. 3 are Eq. (2) with $T_0 = 63.06\,^\circ\mathrm{C}$, x, χ_0, and χ_B adjusted to fit, and γ fixed at 1.24. χ_B was very small ($\lesssim 0.5$). The same equation with no background, with γ replaced by ν (fixed at 0.63), and χ_0 replaced by ξ_0, but with x fixed at the values found fitting the susceptibility, provided a nearly perfect description of the correlation range data as is also shown in Fig. 3.

$$\chi = \chi_0[(1-\Gamma\Delta t)(\Delta t\tilde{t} + \tilde{t}^2 + 2\Gamma\tilde{t}^3 + 5\Gamma^2\tilde{t}^4 + \cdots)]^{-\gamma} + \chi_B, \qquad (3)$$

where $\Delta t = [T_u(x) - T_l(x)]/T_0$ and $\tilde{t} = [T_l(x) - T]/[T_0(1-\Gamma\Delta t)^2]$. Since the data are confined to $\tilde{t} \lesssim 0.1$, the terms of higher order than $\tilde{t}^2$ play a relatively minor role. As $\Delta t \rightarrow 0$, Eq. (3) thus predicts a gradual transition to a doubled exponent. In the limit $\Gamma \rightarrow 0$ Eq. (3) reduces to the result which would be obtained by the expansion of $X_c(T)$ about its minimum and retention of only the quadratic term. The full expression was used because it provided a better description of the data.

Each of the eleven data sets for the susceptibility of samples with $x > x_0$ were fitted by Eq. (3) with χ_0 replaced by $\chi_0(1+bt_0)$ to allow for the temperature dependence of the coupling between the critical fluctuations and the scattered intensity. All the data were consistent with $b = 0.7$, and this was imposed. The parameters adjusted for each run were χ_0, χ_B, and $T_l(x)$. χ_B was small ($\lesssim 0.5$), and the fitted values for $T_l(x)$ equaled the observed phase separation temperatures to within experimental accuracy. The results of these fits are shown by the solid lines in Fig. 2, and the results of fitting the correlation-range data to Eq. (3) with ν fixed at 0.63 are also shown. In this case no background was included, and the values of $T_l(x)$ found in the fitting of the susceptibility data were imposed. Thus, only ξ_0 was adjusted for each run. For the sake of consistency, the weak temperature dependence $(1+bt_0)$ was also imposed on the fits to the susceptibility data for samples with $x < x_0$. This improved the fits but the values for χ_0 changed by less than 3%.

In addition to predicting the temperature dependence of χ and ξ, the model predicts that χ_0 and ξ_0 should be the same for all runs except for the possible analytic dependence on T_l and x. We find this to be the case with $\xi_0 = (1.22\ \text{Å})(1-1.4t_l)$, where $t_l \equiv [T_0 - T_l(x)]/T_0$. In the case of χ_0, we extract the dependence of the coupling between concentration fluctuations and scattered intensity on T and x, which should be $(1+bt_l)(\partial\epsilon/\partial\psi)^2$, with $b = 0.7$. Here ϵ is the dielectric constant of the mixtures, and ψ is the mole fraction of guaiacol. The results for χ_0 are then described to within experimental accuracy by $\chi_0 = 0.019(1+0.8t_l)$. Thus all of the measurements are accounted for by this simple model, which is a striking confirmation of the simplicity and utility of the geometric picture of phase transitions.

The light scattering studies were carried out at the University of California, Santa Barbara. This work was supported by the National Science Foundation, Grant No. DMR82-10884, the U. S. Department of Energy, Grant No. DE AC02-76ER 02203, and the U. S. Army Research Office, Grant No. DAAG29-83-K-0076.

[a] Current address: Experimental Pathology Group, Los Alamos National Laboratory, Los Alamos, N.M. 87545.

[1] See, for example, R. E. Goldstein and J. S. Walker, J. Chem. Phys. **78**, 1492 (1983), and references therein.

[2] S. S. Leung and R. B. Griffiths, Phys. Rev. A **8**, 2670 (1973).

[3] J. S. Walker and C. A. Vause, Phys. Lett. **79A**, 421 (1980), and J. Chem. Phys. **79**, 2660 (1983).

[4] J. S. Walker and C. A. Vause, in *Eighth Symposium on Thermophysical Properties*, edited by J. V. Sengers (American Society of Mechanical Engineers, New York, 1982), Vol. 1, p. 411.

[5] P. S. Pershan and J. Prost, J. Phys. (Paris), Lett. **40**, L27 (1979).

[6] A. R. Kortan, H. von Känel, R. J. Birgenau, and J. D. Litster, Phys. Rev. Lett. **47**, 1206 (1981), and J. Phys. (Paris) **45**, 539 (1984).

[7] H. R. Haller, C. Destor, and D. S. Cannell, Rev. Sci. Instrum. **54**, 973 (1983).

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

[9] R. B. Griffiths, in *Critical Phenomena in Alloys, Magnets and Superconductors*, edited by R. E. Mills, E. Ascher, and R. I. Jaffee (McGraw-Hill, New York, 1971), p. 377.

[10] M. J. Buckingham and W. M. Fairbank, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland, Amsterdam, 1961), Vol. 3, p. 80.

[11] M. E. Fisher, Phys. Rev. **176**, 257 (1968).