Observation of Two Length Scales near an Unsymmetrical Tricritical Point

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(Received 19 August 1992)

We have isolated a tricritical point in the system water/*n*-hexane/1-propanol/2-propanol. Two samples of fixed composition exhibiting three-phase regions extending over temperature ranges of 4 and 1 K have been studied extensively by light scattering. Near the critical end points bounding the three-phase regions the structure factor $S(q)$ is not of the Ornstein-Zernike form but is well fitted by $S(q) = \Gamma_1/(1+q^2\xi_1^2) + \Gamma_2/(1+q^2\xi_2^2)$. The second length scale ξ_2 is nondivergent and is independent of the primary length scale.

PACS numbers: 64.60.Fr, 05.70.Jk, 64.60.Kw, 64.70.Ja

Tricritical systems provide sensitive tests of our understanding of critical phenomena, as they present systems with a marginal dimensionality of 3. Previous studies of unsymmetrical tricritical points in fluid mixtures have elucidated their phase behavior [1–6] and investigated the Griffiths sum rules [7] for their scattering properties [8–11]. The scattering studies have been hampered either by imprecise knowledge of position in the phase diagram [8,9,12] or by measurement of the scattered intensity at only two angles [10,11]. Systematic scattering studies near the critical end points bounding the three-phase region have not been reported for any fluid system near a tricritical point.

We have located a tricritical point in the system water/*n*-hexane/1-propanol/2-propanol which is well suited for study by light scattering [13]. It occurs at ~38 °C at atmospheric pressure, and the system scatters weakly enough that multiple scattering is negligible. We have prepared two samples which, upon changing temperature, enter and exit the three-phase region through, or close to, the critical end points. One sample exhibits a three-phase region over the range $\Delta T \equiv T_U - T_L = 3.98$ K, where T_U and T_L are the upper and lower critical end-point temperatures, respectively. The other sample, which is closer to the tricritical point, has $\Delta T = 1.01$ K. We have measured the wave-vector-dependent structure factor $S(q)$ for each sample throughout the three-phase region and into both adjoining two-phase regions. Except in the vicinity of the critical end points, $S(q)$ is of the Ornstein-Zernike form, $S(q) = \Gamma/(1+q^2\xi^2)$, as expected theoretically [14]. However, this fails to hold for either sample near its end points, where an adequate description of $S(q)$ can be obtained only by the introduction of a second length scale. Lacking any theoretical guidance we have fit the data using the simple form $S(q) = \Gamma_1/(1+q^2\xi_1^2) + \Gamma_2/(1+q^2\xi_2^2)$. The second length scale ξ_2 and its associated amplitude Γ_2 are roughly temperature independent as the end points are approached, while Γ_1 and ξ_1 exhibit Ising-like divergences. In both samples, ξ_2 is 4–5 times larger near the lower critical end point than it is near the upper critical end point. The sample with $\Delta T \cong 1$ K has values of ξ_2 which are ~80% larger than those observed in the same phase at the corresponding end point for the $\Delta T \cong 4$ K sample. The results for Γ_1 can be used to construct the first Griffiths sum, $\Sigma_\Gamma = \Gamma_\alpha^{1/2} - \Gamma_\beta^{1/2} + \Gamma_\gamma^{1/2}$, where α, β, and γ refer to the three coexisting phases. The two samples have comparable values for Σ_Γ, but it varies systematically across the three-phase region of either sample, rendering its interpretation problematic.

The tricritical point was isolated using techniques similar to those discussed by Kahlweit and co-workers [6,15]. The ternary system water/*n*-hexane/1-propanol has a broad three-phase region at atmospheric pressure [15], while water/*n*-hexane/2-propanol has none. Mixing the two alcohols allows one to shrink the three-phase region until it ultimately vanishes at the tricritical point. The binary mixtures of the propanols were characterized by the weight fraction of 2-propanol in the alcohol mixture, denoted x_2. (Note that x_2 is not the weight fraction of 2-propanol in the quarternary mixture.) If the ratio of the two alcohols is the same in all coexisting phases of the quarternary mixture, the alcohol mixture may be considered as a single pseudocomponent, and the quarternary system may be considered to be quasiternary. Using gas chromatography, the value of x_2 was found to be identical in all coexisting phases of the $\Delta T \cong 1$ K sample near both critical end points to within 3%, which is the instrumental uncertainty. The quasiternary approximation thus appears to be well justified, though it may fail to hold closer to the tricritical point.

For a given value of x_2, a series of samples was prepared with a fixed water:oil ratio and increasing total alcohol content. Assuming that the set of samples so generated intersects both the upper and lower critical tie lines as temperature is varied, observation of the phase behavior of these samples allows one to determine the temperature width of the three-phase region, ΔT. Near a tricritical point, ΔT is predicted to scale as $a_4^{3/2}$, where a_4 is any thermodynamic *field* used to measure distance from the tricritical point [16]. Since x_2 has the same value in all three phases it acts as a field, and we may choose $a_4 \sim x_{2t} - x_2$. As illustrated in Fig. 1, the temperature difference between the upper and lower critical tie lines scales as $\Delta T = A(x_{2t} - x_2)^{\beta_t}$ with $A = 253 \pm 66$ K,

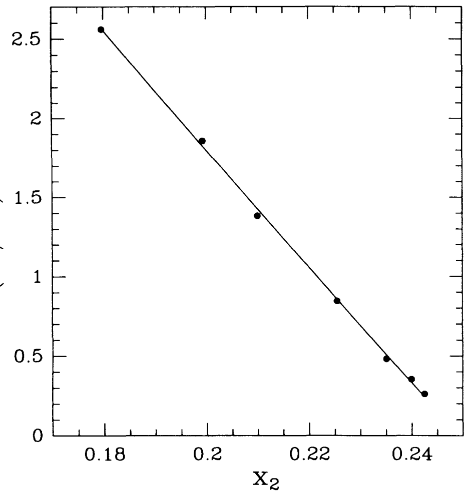

FIG. 1. Dependence of the temperature difference $\Delta T = T_U - T_L$ on x_2, the weight fraction of 2-propanol in the alcohol mixture, as the tricritical point is approached. The solid line is the result of a fit to the data which yields $\beta_t = 1.55 \pm 0.12$ and $x_{2t} = 0.250 \pm 0.002$.

$\beta_t = 1.55 \pm 0.11$, and $x_{2t} = 0.250 \pm 0.002$, which is the fit shown by the solid line. This result for β_t is consistent with that found in a variety of other tricritical systems [1-6]. We estimate the coordinates of the tricritical point to be $T_t = 37.8 \pm 0.25\,°C$, $x_{\text{water}} = 0.254$, $x_{\text{hexane}} = 0.213$, $x_{1\text{-propanol}} = 0.400$, and $x_{2\text{-propanol}} = 0.133$.

A sample which exhibits both an upper and a lower critical end point has a unique composition for any given value of x_2. This composition is that through which both the lower and upper critical tie lines pass as temperature is varied. It was determined by using gas chromatography to measure the compositions of the end points of the critical tie lines and, thus, that of their intersection. The composition of the $\Delta T \cong 4$ K sample, in weight fractions, is $x_{\text{water}} = 0.2997$, $x_{\text{hexane}} = 0.2229$, $x_{1\text{-propanol}} = 0.3914$, and $x_{2\text{-propanol}} = 0.0861$ ($x_2 = 0.1803$). The sample was prepared without filtration and flame sealed in a borosilicate glass ampule of inner diameter 15.3 mm. It is at the critical composition for both lower and upper critical end points, as expected. The other sample was prepared to have the composition $x_{\text{water}} = 0.2691$, $x_{\text{hexane}} = 0.2220$, $x_{1\text{-propanol}} = 0.3944$, and $x_{2\text{-propanol}} = 0.1145$ ($x_2 = 0.2250$). It was treated identically except that it was filtered to remove any dust. This sample is at the critical composition for the lower end point but is slightly off critical for the upper end point. Its value of ΔT is 1.01 K, larger than the 0.83 K expected based on its value of x_2. We speculate that this is due to loss of the more volatile 2-propanol during filtration. Both samples have been stable over several years, in terms of their phase behavior and scattering properties, while their end-point temperatures have changed $\lesssim 90$ mK over this period.

Static light scattering measurements were performed between the angles of 2.5° and 127° using apparatus described previously [17]. Throughout the course of such measurements, the sample under study was immersed in temperature controlled circulating water stable to 0.3 mK and having gradients $< 15\ \mu$K/cm. The samples were equilibrated at each temperature with frequent stirring by means of Pyrex encapsulated magnetic stir bars. Equilibration generally occurred within 3 h of the final stirring. The refractive indices needed to determine the scattering wave vectors were determined as functions of temperature by differential refractometry.

Measurements made as a function of height in each phase showed $S(q)$ to be independent of position within our resolution. Variation of incident laser power revealed no power dependence for $S(q)$. Incident powers were $\lesssim 25\ \mu$W near T_L and $\lesssim 1$ mW near T_U. We estimated double scattering using the method of Shanks and Sengers [18]. It was never more than 6% of the single scattering and had no significant effect on the fit results. Consequently, the data were not corrected for double scattering. We did correct the data for the effect of collecting a small fraction of light scattered at the angle complementary to that being measured, which is caused by weak reflections at the cell walls. These effects were $< 5\%$ and also had no significant effect on the results.

Except near the end points, $S(q)$ is described quite well by the Ornstein-Zernike (OZ) form, $S(q) = \Gamma/(1 + q^2\xi^2)$. However, as either critical end point was approached marked deviations were observed in the critical phases, while the noncritical phase remained OZ-like. Initially, the data were adequately characterized by the addition of a background, Γ_2, to the OZ form, $S(q) = \Gamma_1/(1 + q^2\xi^2) + \Gamma_2$. Upon closer approach to an end point this form was generally inadequate, and a second independent length scale was required. This was included through fitting by the form $S(q) = \Gamma_1/(1 + q^2\xi_1^2) + \Gamma_2/(1 + q^2\xi_2^2)$.

Figure 2 shows data for $S^{-1}(q)$ vs q^2 (an OZ plot) for data taken 14 mK below T_U in the β phase (middle phase) of the $\Delta T \cong 4$ K sample. The departure from a simple OZ form, which would yield a straight line, is obvious. Forcing such a fit resulted in a reduced chi squared, χ_ν^2, of 293. Addition of a background decreased χ_ν^2 to 7.3, while inclusion of a second length scale further decreased χ_ν^2 to 1.0. The solid line in the figure shows this fit. As judged by the F test, the probability of the extra parameters being spurious is below 10^{-12}. The inset shows the dependence of χ_ν^2 on ξ_2 with all other parameters readjusted. Similar results are obtained in the other critical phases, near both end points for both samples, over periods from 3 to 100 h after stirring. Values of ξ_2 obtained over a year apart agree well, giving us added confidence that this effect is not an artifact. We also observe a second length scale in the critical phase above T_U in both samples, but only a background is apparent in the critical phase below T_L. The background persists at least

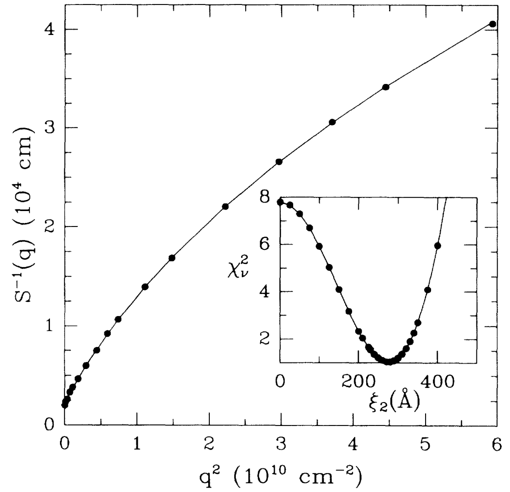

FIG. 2. Example of an Ornstein-Zernike plot, $S^{-1}(q)$ vs q^2, for light scattering data taken 14 mK below T_U in the β phase of the $\Delta T \cong 4$ K sample. Deviations from Ornstein-Zernike (OZ) behavior, which would yield a straight line, are obvious. The solid line shows the result of fitting the data to the sum of two OZ terms and results in the values $\Gamma_1 = (4.18 \pm 0.10) \times 10^{-4}$ cm^{-1}, $\xi_1 = 2455 \pm 49$ Å, $\Gamma_2 = (1.91 \pm 0.01) \times 10^{-5}$ cm^{-1}, $\xi_2 = 276 \pm 17$ Å. Inset: The variation of the reduced chi-squared parameter χ_ν^2 as the second length scale ξ_2 is varied with the other parameters readjusted. It reveals a very deep minimum at $\xi_2 = 276$ Å.

300 mK below T_L for the $\Delta T \cong 1$ K sample, but we only observed it within 6 mK of T_L for the $\Delta T \cong 4$ K sample.

Figures 3 and 4 summarize our observations of the form of the structure factor. The figures are schematic diagrams of the three-phase curves for the $\Delta T \cong 4$ K sample (Fig. 3) and the $\Delta T \cong 1$ K sample (Fig. 4). The phases are denoted α, β, γ in order of increasing density, while $\alpha\beta$ refers to the critical phase for temperatures above T_U and $\beta\gamma$ refers to that below T_L. Different symbols are used to indicate the observed form of $S(q)$ in each of the phases at each temperature investigated. Plotted in this fashion, the similarities between the properties of the two samples are readily apparent.

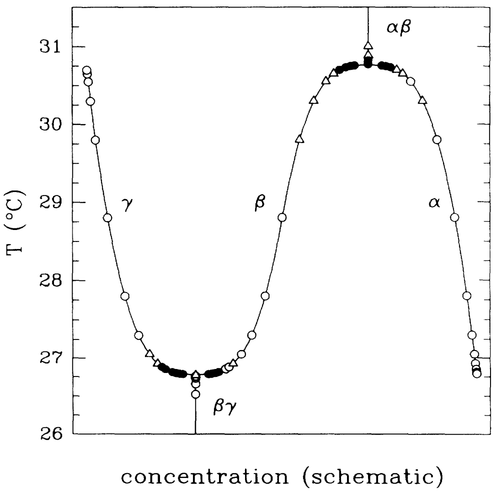

FIG. 3. Schematic plot showing the variation of the form of the structure factor with temperature in the $\Delta T \cong 4$ K sample. The symbols indicating the observed form of the structure factor are as follows: ○, single OZ; △, single OZ plus background; ●, sum of two OZ forms.

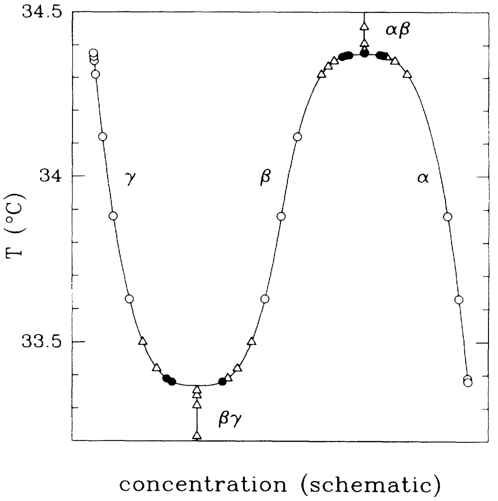

FIG. 4. Schematic plot showing the variation of the form of the structure factor in the $\Delta T \cong 1$ K sample. Symbols have the same meaning as in Fig. 3.

Table I presents average values of the second length scale ξ_2 in each of the critical phases near both end points for the two samples. Whereas the values of ξ_2 in the β and γ phases near the lower critical end point agree within their uncertainties for each sample, this is typically not the case near the upper critical end point. We have found no quantitative relationship between ξ_2 and other system parameters, but it is interesting to note that Γ_1, Γ_2, and ξ_2 are all largest near T_L. The second length scale obviously increases as the tricritical point is approached; however, no clear scaling relation is evident.

It would be natural to associate Γ_2 and ξ_2 near one end point with the critical fluctuations of the other end point, especially in the β phase, whose properties are singular at

TABLE I. Average values of the second length scale ξ_2, in angstroms, in the various phases of the two samples. The error bars are statistical uncertainties only, and do not reflect possible systematic errors.

Phase		$\Delta T \cong 4$ K	$\Delta T \cong 1$ K
Near T_U:	$\alpha\beta$	180 ± 4	335 ± 43
	α	124 ± 6	321 ± 16
	β	266 ± 5	437 ± 13
Near T_L:	β	1046 ± 84	1686 ± 289
	γ	936 ± 47	1388 ± 354

both end points. However, our data do not support this interpretation. For example, near T_L in the β phase of the $\Delta T \cong 4$ K sample, $\Gamma_2 \cong 6.8\times10^{-3}$ cm^{-1} and $\xi_2 \cong 1046$ Å, while the values of Γ_1 and ξ_1 extrapolated from the upper critical end point are $\Gamma_1 \cong 3.4\times10^{-7}$ cm^{-1} and $\xi_1 \cong 58$ Å. Similarly, in the β phase near T_L of the $\Delta T \simeq 1$ K sample, $\Gamma_2 \simeq 1.8\times10^{-2}$ cm^{-1} and $\xi_2 \cong 1686$ Å, compared to $\Gamma_1 \cong 8.4\times10^{-6}$ cm^{-1} and $\xi_1 \cong 139$ Å extrapolated from the upper critical end point.

While the presence of a second length scale makes the interpretation of the Griffiths sum rules problematic, we have nonetheless used our results for Γ_1 to investigate the first Griffiths sum, Σ_Γ. As the tricritical point is approached, Σ_Γ has been predicted to approach a constant value in extended mean-field theory [10,19] and to diverge like a_4^{-1} in a renormalization-group calculation [20]. We find that Σ_Γ varies significantly throughout the three-phase region of either sample, decreasing by roughly a factor of 2 as temperature is increased from somewhat above T_L to somewhat below T_U. The two samples show comparable values, but the ratio of Σ_Γ for the $\Delta T \cong 1$ K sample to that for the $\Delta T \cong 4$ K sample varies from ~ 1.5 to ~ 1.0 depending on where in the three-phase regions the measurements are made. This result does not offer any support for a divergence, but it can scarcely be considered a confirmation of extended mean-field theory, either.

Non-Ornstein-Zernike structure factors have also been observed in the isotropic liquid "sponge" phase investigated by Roux *et al.* [21]. This phase occurs in a bilayer-forming system of water/oil/surfactant, and it is unclear to us what, if any, connection exists between this system and our own. However, it is at least conceivable that our results are indicative of some vestigial surfactant-type behavior on the part of the alcohols which becomes apparent only near the end points. Clearly, significant theoretical and experimental progress will be required before tricritical phenomena can be considered to be fully understood.

This research was supported by NSF DMR 90-18089. One of the authors (R.M.D.) gratefully acknowledges the support of an IBM Graduate Student Fellowship.

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