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Double-critical-point phenomena in three-component liquid mixtures: Light-scattering investigations

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Measurements of osmotic compressibility (near the lower consolute point, T_L) in two reentrant liquid mixtures [3-methylpyridine (MP)+water (W)+heavy water (HW) and MP+W+NaCl] are presented. The closest approach to the double critical point (DCP) was marked by a sample of loop size $(\Delta T)=250$ mK. Analyzing the data by means of the conventional field variable $t[=|(T_c-T)/T_c|]$ yielded an *exact* doubling of the critical exponent (CE) γ for a $\Delta T=250$ mK. The approach to double criticality (for intermediate ΔT) is described by a *crossover* of the CE from the doubled to its single limit as $t\rightarrow 0$. Recourse to a more appropriate field variable, $t_{\mathrm{UL}}[=|(T_U-T)(T_L-T)/T_UT_L|]$, restores the Ising value of $\gamma(=1.24)$ for any ΔT. The salt-doped mixtures permitted us to observe a doubling of the extended scaling exponent (Δ) and also to scrutinize the ionic critical phenomena. The range of simple scaling in MP+W+HW was found to be extremely large. Switching to a modified variable $t'_{\mathrm{UL}}[=|(T_U-T)(T_L-T)/T^2|]$ led to a remarkable enhancement in the weight of the extended scaling term in both the mixtures—in apparent disagreement with the earlier findings that reported a widening of the asymptotic region. Non-phase-separating samples of MP+W+HW showed the expected saturating divergence preceded by a region of doubled γ as T_D (DCP temperature) was neared. Most of the facets of our investigations can be comprehended in terms of the geometrical picture of phase transitions as well as the Landau-Ginzburg theory as applied to the reentrant phase transitions.

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I. INTRODUCTION

Multicomponent (ternary or quaternary) liquid mixtures display a rich variety of special thermodynamic states such as plait points [1], double critical points [2], tricritical points [3], etc. They provide richer information—compared to binary liquid mixtures— as they allow for a multitude of paths by which a critical point is reached [4,5]. In the recent past, there has been a rapid proliferation [6–14] of investigations directed at unraveling the phenomenon of the reentrant phase transitions (RPT's). Liquid mixtures provide a convenient means to quantitatively verify the analytical and phenomenological predictions concerning the RPT, though there exist numerous systems [2,15–23] that exhibit this intricate phenomenon. The experimental thrust in this area commenced as a sequel to the progressive development and refinement of the lattice-gas models of reentrant miscibility [24–30]. These analytical efforts were supplemented by phenomenological ideas—a compelling case being the analysis of the RPT in terms of the approach to the parabolic line [30–32] of critical points in a multidimensional field space (geometrical picture of phase transitions) [4,5,16].

Modeling of the closed-loop phase diagram (whose upper and lower extrema denote the upper and lower consolute points, T_U and T_L, respectively), was the central theme of the lattice-gas calculations [24–30]. When the closed loop is reduced to a point, the loop size $\Delta T(=T_U-T_L)$ becomes *zero* and a double critical point (DCP) is realized. The critical behavior near an isolated T_U or T_L is well understood [33–36]. The essence of the initial experimental investigations involving RPT in multicomponent liquid mixtures [6–10] was to test the central theoretical prediction that in the vicinity of a DCP, the critical exponents (CE's) should double from their normal Ising values [4,5,16,24–30]. It ought to be stressed that the intent of these endeavors was to explore the *gross* features of the evolution of the critical behavior in the limit $\Delta T\rightarrow 0$. Broadly, it was shown that CE's $[\nu,\gamma,\phi,\theta$, and β for correlation length (ξ), osmotic compressibility (χ), shear viscosity (η), electrical resistance (R), and order parameter, respectively] increased sharply as ΔT was reduced and as T_L (or T_U) was neared [6–12,14]. In these studies, the thermodynamic path was described by the conventional field variable, $t[=|(T_c-T)/T_c|]$, where T_c is T_U or T_L. Most of these results led to the conclusion that a *near* doubling of the Ising-like CE's occurs as $\Delta T\rightarrow 0$, though there was an alarming inference that the *doubled* CE (ν) referred to its mean-field value (0.5) [9,10].

Earlier experiments were aimed at observing an exact doubling of CE's close to a DCP. The crucial facets of the phenomena of RPT and DCP, e.g., the description of the approach to double criticality and the means to recover the universal CE's near and away from DCP, were ignored [11,13,37].

In this paper, we present the findings of a detailed study of RPT in two quasibinary liquid mixtures: 3-methylpyridine (MP)+water (W)+heavy water (HW) and MP+W+salt (NaCl). We measured scattered and transmitted laser light intensity in the neighborhood of T_L for samples of varying ΔT's. A part of this work has been presented earlier in a Brief Report [13].

Our findings shed light on the phenomena of RPT and DCP. For instance, the wide range of t (near T_L) and ΔT that was covered, enabled us to perceive the evolution of critical behavior in reentrant systems in terms of a crossover from the doubled to the single limit of CE's as $t \rightarrow 0$ (for nonzero ΔT's). Besides, an exact doubling of CE (γ) and the extended scaling CE (Δ) was noticed *very* close to the DCP. The use of the field variable $t_{\mathrm{UL}}[=|(T_U-T)(T_L-T)/T_U T_L|]$ retrieves the universal value of CE (γ) for *any* ΔT and captures the essence of the phenomenon of RPT [11,13,37]. The salt-doped system led us to discern the signature of ionic critical phenomena [38], which, in turn, permitted us to examine the response of CE (Δ) to double criticality [39]. Resorting to $t'_{\mathrm{UL}}[=|(T_U-T)(T_L-T)/T^2|]$ revealed a distinct reduction in the region of simple scaling, though this feature is less pronounced in MP+W+HW. Many aspects of this research can be comprehended within the framework of Landau-Ginzburg theory as applied to the case of RPT [40,41] and the geometrical picture of phase transitions [16]. Finally, a range of problems where the singly or multiply reentrant character of multicomponent liquid mixtures can be applied, is discussed.

II. EXPERIMENT

A. Samples

Appropriate amounts [32] of MP (99% Aldrich), W (triple distilled in an all quartz distiller) and HW (isotopic purity 99.6%, BARC, India) were used to obtain the desired ΔT's for MP+W+HW by controlling the quantity X [= the weight of HW divided by the weight of (W+HW)]. In this case X simulates the condition of a thermodynamic field. The reentrant critical line is parabolic in the X-T plane [30–32] and its apex defines the DCP. For each ΔT, the composition of MP must be its critical value (x_c) (referring to T_L). Table I gives the details of the sample preparation for the system MP+W+HW.

The salt-doped samples (MP+W+NaCl) were made using analytical grade NaCl. Salt introduces partial immiscibility in an otherwise miscible MP+W and it plays a role similar to that of pressure in this system. The salt concentration (C) acts as a field variable that governs the ΔT [37,39]. The information regarding the preparation of these samples is provided in Table II. This system has some key advantages [37] over MP+W+HW, which are the following: (i) the quantity of salt required for obtaining any desired ΔT is at least two orders of magnitude smaller than that of HW and hence the quasibinary approximation is upheld firmly; (ii) H^+-D^+ exchange [42,43] is avoided. In addition, the presence of an electrolyte facilitates the examination of ionic critical behavior [38].

The samples were initially filled in cylindrical pyrex glass cells of capacity $\simeq 5$ ml. T_L and ΔT were determined visually [32] in a well-stirred liquid paraffin bath with a temperature stability of ±1 mK. The concentration of MP (x) was adjusted (if necessary) for its critical value (referring to T_L) as guided by the equal volume coexistence. The enormous difficulties encountered in realizing $\Delta T \leq 1$ K stem from the extreme *steepness* of the coexistence surface in the vicinity of the DCP. Other hampering factors are (a) the delicate influence of impurities leached out of the walls of the container (Pyrex/quartz) leading to the shift in ΔT with time, (b) the increasing difficulty in obtaining x_c for smaller ΔT's [12,13]. The additional complication in MP+W+HW is the possible H^+-D^+ isotopic exchange reaction which is progressively significant near the DCP [42,43]. Several empirical methods were employed to overcome these problems [12,13]. Circumventing these obstacles enabled us to investigate three samples of $\Delta T < 1$ K (=250, 600, and 650 mK). These studies represent the *closest* access to the DCP. The coordinates of the DCP for MP+W+HW and MP+W+NaCl are $X_D = 0.1715$, $T_D = 349.80$ K and $C_D = 0.097$, $T_D = 350.70$ K, respec-

TABLE I. Details of the sample preparation for the system MP+W+HW. Typical uncertainty for x_c is ±0.004. X refers to that of fresh samples. Values of x_c and n pertain to the relevant T_L.

No.	x_c	X	T_L (K)	ΔT (K)	n
1	0.290	1.0000	311.53± 0.01	77.50± 0.05	1.377
2	0.310	0.2400	338.51± 0.01	22.60± 0.02	1.375
3	0.313	0.1988	342.79± 0.01	14.02± 0.02	1.374
4	0.315	0.1807	345.70± 0.01	8.20± 0.02	1.373
5	0.317	0.1738	347.74± 0.01	4.20± 0.02	1.373
6	0.318	0.1717	349.15± 0.02	1.30± 0.04	1.372
7	0.318	0.1716	349.50± 0.02	0.65± 0.04	1.372
8	0.318	0.1716	349.68± 0.05	0.25± 0.10	1.372

TABLE II. Details of the sample filling for the system MP+W+NaCl. C is the weight % of NaCl in the mixture. Typical uncertainties for x_c and C are ±0.004 and ±0.001, respectively. Values of x_c and n pertain to the corresponding T_L.

No.	x_c	C	T_L (K)	ΔT (K)	n
1	0.3086	0.405	326.80± 0.01	47.80± 0.02	1.377
2	0.3206	0.230	332.40± 0.01	36.60± 0.02	1.377
3	0.3220	0.099	347.50± 0.01	6.40± 0.02	1.373
4	0.3224	0.098	349.55± 0.01	2.30± 0.02	1.372
5	0.3224	0.097	350.40± 0.15	0.60± 0.30	1.372

tively [32,39]. However, X_D and C_D are highly susceptible to the purity of the chemicals.

After establishing the desired ΔT (and the corresponding x), the samples were transferred from the large visual cells to the light-scattering cells (typical volume 0.3 ml) by means of air-tight syringes, fitted with millipore filters (pore size 0.2 μm). These cells were flame sealed after being frozen in liquid nitrogen. The specifications (T_c and x_c) of each sample were ascertained afresh in the light-scattering cells.

B. Apparatus

The light-scattering setup consists primarily of a He-Ne laser (operating at 632.8 nm), power meters, a photomultiplier tube (PMT), and a photon counter (EG and G ORTEC). The typical power sensed by the samples was 4.8 mW. The incident and the transmitted power were monitored using power meters. The scattered intensity (at 90°) was detected by the PMT (RCA 31034), whose output was fed to a photon counter through a fast preamplifier (EG and G ORTEC). The quantities measured were (i) a fraction of the incident power, (ii) transmitted power, and (iii) scattered intensity (I_E). The sample cell with a path length of $\simeq 8$ mm was placed in a thermostated metallic recess. The temperature stability experienced by the sample is ±3 mK in the range (318–353 K) over 6–8 h. The sample temperature was sensed with the aid of a ruggedized thermistor, anchored to the recess, extremely close to the cell. This thermistor was calibrated against IPTS-68 standards and has an absolute accuracy of ±60 mK [13].

The laser beam was focused at the center of the cell. The incident power and the exposure time of the beam to the sample were optimized to ensure that there was no significant contribution from local heating and temperature gradients, etc. For MP+W+HW, the samples were subjected to the beam for 100 s, whereas for MP+W+NaCl, this time had to be reduced to 60 s (as the heat capacity of the latter is less). The nonlinearity of the detection system was within the combined error bars for the scattered intensity, which is $\simeq 1\%$. The standard precautions regarding the mechanical stability of the optics were adopted.

A typical run scanned the temperature range 1.5 K$\lesssim (T_L - T) \lesssim 25$ K (for MP+W+HW) and 1.5 K$\lesssim (T_L - T) \lesssim 20$ K (for MP+W+NaCl). The duration of each run was 35–45 h and it yielded, on the average, 40–50 data points. At least two reproducible runs were performed for $\Delta T > 650$ mK. All the data were collected in the one phase region as T_L was reached. As the nature of the phenomenon of the RPT is similar regardless of whether one approaches T_U or T_L [10,37], we concentrated on the lower part of the critical line. T_L was determined before and after each run by observing the vanishing of the transmitted beam [44]. Only in one case ($\Delta T = 250$ mK), did we have considerable difficulty in detecting T_L very quantitatively (see Table I). We ascribe this problem to the unusually large ξ and lifetime (τ) of the concentration fluctuations in the close vicinity of the DCP, e.g., ξ could be as large as 50 μm and $\tau \simeq 100$ ms at 1 mK from T_L for this ΔT.

Data very close to a given T_L [$(T_L - T) < 1.5$ K] were not acquired for any ΔT (a) to minimize possible contributions from multiple scattering [45] and gravity effects [34,35], (b) to avoid extremely large ξ ($\mathbf{q}\xi \gg 1$, $\mathbf{q}$ being the scattering wave vector) region. Particularly for the current study, it is not essential to approach T_L (or T_U) very closely—rather, the weight of $(T_L - T)$ with respect to ΔT is more significant [e.g., see Eq. (7)].

III. RESULTS

The corrections for turbidity, background contribution, and variations in the incident intensity were incorporated to the experimentally obtained intensity data (I_E). The corrected I_E ($= I_s$) is described by the following conventional expression [45–47]

$$\frac{I_s}{T} = \frac{\chi_0 t^{-\gamma}}{(1+q^2\xi^2)^{1-\eta/2}}(1+\chi_1 t^{\Delta}+\chi_2 t^{2\Delta}+\chi_3 t^{3\Delta}+\cdots) , \tag{1}$$

where χ_0 is the critical amplitude, γ is the CE, $\chi_1 - \chi_3$ and Δ are the correction-to-scaling amplitudes and exponent, respectively, η is the Green-Fisher CE, and $\xi = \xi_0 t^{-\nu}$. The Ising values of CE's γ, ν, η, and Δ are

1.24, 0.63, 0.03, and 0.5, respectively [48]. The scattering wave vector **q** is equal to $(4\pi n/\lambda)\sin(\theta/2)$, where n is the refractive index of the mixture, λ ($=632.8$ nm) is the wavelength of the incident light in vacuum, and θ, is the scattering angle ($=90°$). n was computed at 293 K using the Lorentz-Lorenz relation as applied to a three-component liquid mixture [49]

$$\frac{n^2-1}{n^2+1}=\sum_i \frac{n_i^2-1}{n_i^2+1}\phi_i \ , \tag{2}$$

where n_i's and ϕ_i's are the refractive indices and volume fractions of the constituent liquids. The temperature coefficient of n for these liquids is $\simeq 0.02\%$ [8], and it had very little influence on the fitting parameters. In the case of MP+W+NaCl, the effect of the presence of the electrolyte on n was estimated using the Tammann-Tait-Gibson model [50] and was found to be negligible ($\leq 0.1\%$) for such small concentrations of the salt (Table II).

The intensity data (I_s) were analyzed using the modified version of the nonlinear-least-squares fit program (CURFIT) [51]. The fit was considered to be good if the minimum in the reduced χ^2 (χ_ν^2) was close to unity and the resulting residuals had reasonably random distribution. The cumulative standard deviation in I_s/T was calculated by the propagation of errors due to the uncertainties in the statistics of counting, reference intensity, transmitted intensity, and temperature.

To begin with, data (for MP+W+HW) were analyzed using Eq. (1) without the correction-to-scaling terms. Those results were presented in our earlier report [13] which showed that Eq. (1) was valid *only* in the two extreme limits of ΔT, viz. $\Delta T=250$ mK and 77.5 K. An unambiguous *doubling* of γ was demonstrated for $\Delta T=250$ mK. However, Eq. (1) is grossly inadequate to account for the evolution of critical behavior as T_L is approached for intermediate ΔT's. This difficulty springs from the fact that there is a *crossover* from the doubled to single limit [Eq. (7)] of the CE (γ) as $t\to 0$ (for a finite ΔT) and it is illustrated in Figs. 1 and 2. This observation and the infirmities in the fit necessitated the recourse to a more apt field variable ($t_{\rm UL}$) to describe the RPT, whose relevance (especially, the recovery of the Ising value of γ for any ΔT) has been highlighted in our earlier work [13,37,39]. In this paper, all the analyses have been carried out with $t_{\rm UL}$ or its corollaries.

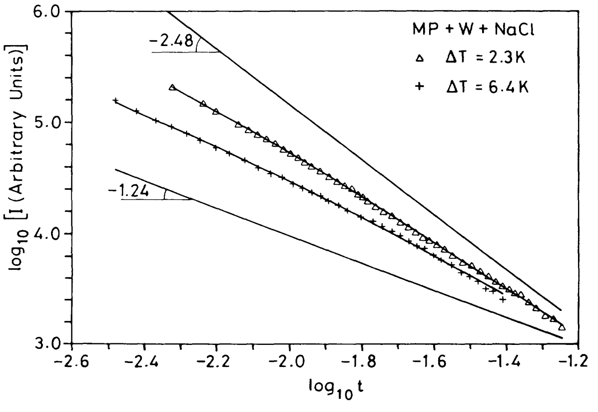

FIG. 1. The monotonic decrease of the CE γ (as $t\to 0$) is illustrated for two intermediate ΔT's. The solid curve is generated by Eq. (3).

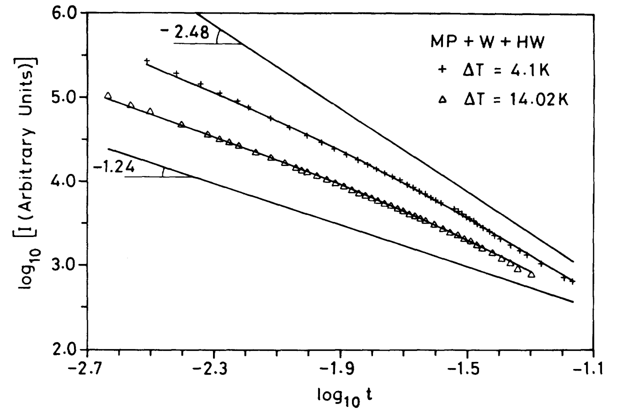

FIG. 2. The monotonic decrease of the CE γ (as $t\to 0$) is illustrated for two intermediate ΔT's. The solid curve is generated by Eq. (4).

A. Data reduction for MP+W+NaCl

The following expression fits the intensity data adequately:

$$\frac{I_s}{T}=\frac{\chi_0 t_{\rm UL}^{-1.24}}{(1+q^2\xi_0^2 t_{\rm UL}^{-1.26})^{0.985}}(1+\chi_1 t_{\rm UL}^{0.5}) \ , \tag{3}$$

where χ_0, ξ_0, and χ_1 were fitting parameters. Initially, the extended scaling term (χ_1) was excluded. Unlike the case of MP+W+HW [13], pure power law yielded progressively smaller γ's as $\Delta T\to 0$, which is a typical index of the existence of correction-to-scaling terms [39]. This aspect of the salt-doped system was dealt with in our earlier Letter [39]. The results of the three-parameter fit (χ_0, ξ_0, and χ_1) are displayed in Table III. Higher-order correction terms were not found to be essential. The parameter ξ_0 was varied independently in steps and χ_0 and χ_1 were free. The persistence of the extended scaling term (especially for successively smaller ΔT's) is evident in Fig. 3 and is articulated in a more quantitative manner in Fig. 4. Figure 5 elucidates the retrieval of universality of γ and Δ for three representative ΔT's.

It is clear that the salt has remarkably shrunk the asymptotic region. The description of the data for all ΔT's by Eq. (3) implies the simultaneous doubling of the *leading* and *extended* scaling CE's (γ and Δ) at the DCP [where $t_{\rm UL}=t_D^2$, $t_D=|(T_D-T)/T_D|$]. Our studies present evidence for the doubling of CE Δ near DCP.

To obtain a situation where the influence of the Δ term might be reduced, we switched to a modified version of $t_{\rm UL}$, i.e., $t'_{\rm UL}[=|(T_U-T)(T_L-T)/T^2|]$ substituted for $t_{\rm UL}$ in Eq. (3) and the corresponding parameters are represented by primes. The choice of this field variable was motivated by earlier reports [52,53] which suggested that $t'[=|(T_c-T)/T|]$ widened the asymptotic region

TABLE III. Results of fitting of the scattered intensity to Eq. (3) for MP+W+NaCl. The standard deviations of the best-fit parameters are $\lesssim 2\%$. A remarkable increase in the weight of the extended scaling term (χ_1') for any ΔT reflects the shrinkage of the pure-power-law region when t_{UL}' is employed in lieu of t_{UL} in Eq. (3).

ΔT (K)	t_{UL}				t_{UL}'			
	χ_0 (units of 10^{-3})	ξ_0 (Å)	χ_1	χ_ν^2	χ_0' (units of 10^{-3})	ξ_0' (Å)	χ_1'	χ_ν^2
47.80± 0.02	5.81	1.56	1.11	1.42	6.71	1.68	2.35	1.46
36.60± 0.02	7.02	1.60	0.18	1.38	7.77	1.68	1.71	1.48
6.40± 0.02	3.98	1.56	9.31	2.17	3.87	1.55	13.42	2.13
2.30± 0.02	3.20	1.53	6.43	1.87	3.14	1.53	9.96	1.88
0.60± 0.30	3.49	1.55	11.25	2.06	3.37	1.54	15.73	1.99

near a conventional critical point. Table III summarizes the results of the data reduction. Surprisingly, there is a marked enhancement in the weight of the correction-to-scaling term (χ_1') in apparent disagreement with the earlier findings concerning t' [53]. Figure 6 emphasizes this observation more acutely.

B. Data reduction for MP+W+HW

Unlike the previous case, the extended scaling term was found to be redundant and the data were analyzed by the following expression:

$$\frac{I_s}{T}=\frac{\chi_0 t_{\mathrm{UL}}^{-1.24\lambda}}{(1+q^2\xi_0^2 t_{\mathrm{UL}}^{-1.26\lambda})^{1-\eta/2}}\ , \qquad (4)$$

where λ is an additional free parameter that ought to be unity from analytical considerations [40,41]. Results of the fit to Eq. (4) are listed in Table IV. The invariance of λ (from unity) for any ΔT is clear from Table IV and this observation is depicted in Fig. 5 for a remarkably broad range of ΔT.

In order to justify the exclusion of the Δ term in the data reduction even when the (T_L-T) range is rather wide ($\simeq$20–25 K), a plot of $It_{\mathrm{UL}}^{\gamma}$ versus t_{UL} is shown in Fig. 7. The randomness of the distribution of the data along with its narrow confinement confirms the pure power-law nature. Furthermore, the inclusion of the first extended scaling term to Eq. (4) led to inconsistencies in the sign of the χ_1 term, with negligible improvement in χ_ν^2 and was therefore discarded.

As in the case of MP+W+NaCl, an attempt was made to analyze these data using Eq. (4) with t_{UL}'. The corresponding results are given in Table IV. There is a distinct decrease in λ for all the ΔT's and the fits were poor when λ was held fixed at 1. This readily guided us to switch to Eq. (3) in terms of t_{UL}'. Table V summarizes the outcome of this analysis and underlines the shrinkage of the asymptotic region, with t_{UL}', as observed in the case of MP+W+NaCl.

Finally, the intensity data of the non-phase-separating mixture ($X<X_D$) was analyzed using the following expression [6,16]:

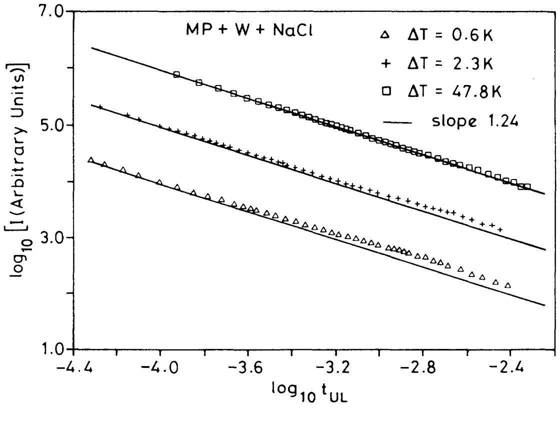

FIG. 3. The inadequacy of the pure power law to quantify the measured scattered intensity (far away from T_L) is displayed. The lines for $\Delta T=47.8$ and 0.6 K have been shifted to improve the clarity of presentation.

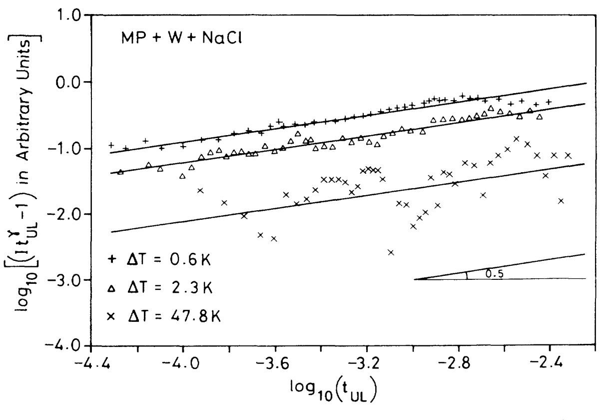

FIG. 4. Double logarithmic graph of the nonasymptotic contribution to the scattered intensity, emphasizing the persistence of the extended scaling term (slope $=0.5$) as $\Delta T\to 0$.

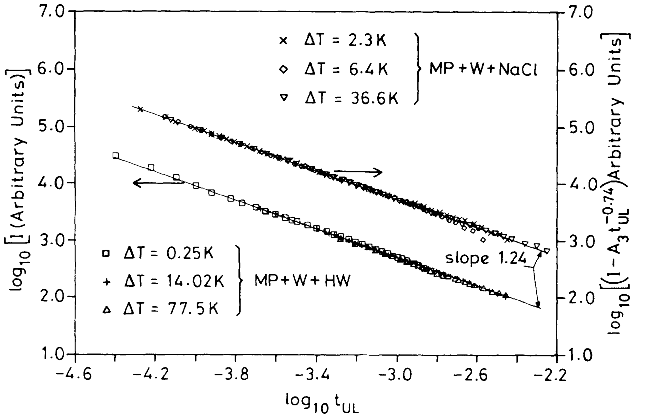

FIG. 5. Pictorial representation of the recovery of the universal CE γ ($=1.24$) for *any* ΔT. The line for MP+W+HW has been shifted for the sake of clarity.

$$\frac{I_s}{T}=\frac{\chi_0[t_D^2+A_1^2(X_D-X)]^{-1.24}}{\{1+q^2\xi_0^2[t_D^2+A_1^2(X_D-X)]^{-1.26}\}^{0.985}}\ , \tag{5}$$

where A_1 is the amplitude of the line of critical points [32]. Table VI gives the results of the fit to Eq. (5), and Fig. 8 demonstrates the power law (with doubled γ) followed by the saturation of I_s as T_D is neared [6,8,9,54,55].

IV. DISCUSSION

A vivid demonstration of the doubling of CE γ (at the DCP) was made possible by probing the DCP exceptionally closely in MP+W+HW ($\Delta T = 250$ mK). This result verifies the central theoretical finding. It can also be

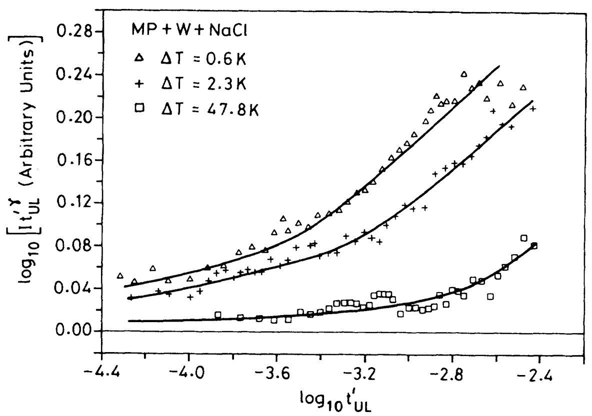

FIG. 6. Log-log plot of the normalized scattered intensity (I_s) multiplied by $t_{\mathrm{UL}}^{\prime\gamma}$ (to neutralize the temperature dependence of I_s) vs t'_{UL}. The progressive importance of the extended scaling term (as $\Delta T \to 0$) is underlined. The solid curve is a guide to the eye.

understood in terms of the tangential approach to the line of critical points [4,5,15,16]. Two vital conditions in these studies which ought to be satisfied are (i) one must have the proper slice (referring to the second-order phase transitions) of the coexistence dome, (ii) the ΔT must be stable during the course of the measurements and hence maintain the constancy of the thermodynamic path.

Though the MP+W+HW system is deemed to be quasibinary in nature [42,43], this assumption needs to be verified. The increase in the value of γ as a result of the Fisher renormalization, a consequence of the ternary (deviation from quasibinary) nature of the system, is given by the following expression [56]:

TABLE IV. Results of the data reduction of the scattered intensity using Eq. (4) for MP+W+HW. The switch to variable t'_{UL} [instead of t_{UL} in Eq. (4)] yields distinctly smaller values of λ, implying a reduced asymptotic region. The standard deviations of the best-fit parameters are $\lesssim 1\%$.

ΔT	t_{UL}				t_{UL}'			
(K)	χ_0 (units of 10^{-2})	ξ_0 (Å)	λ	χ_ν^2	χ_0' (units of 10^{-2})	ξ_0' (Å)	λ'	χ_ν^2
77.50± 0.05	2.25	1.59	0.96	1.46	3.46	1.72	0.94	2.17
22.60± 0.02	1.68	1.97	0.98	0.87	2.40	2.26	0.95	0.82
14.02± 0.02	1.86	1.83	0.99	0.58	2.85	2.11	0.95	0.57
8.20± 0.02	0.93	1.58	1.00	0.53	1.30	1.83	0.97	0.61
4.10± 0.02	3.36	1.90	0.99	2.23	4.71	2.23	0.96	1.83
1.30± 0.04	1.51	1.64	1.00	2.67	2.11	1.92	0.97	2.31
0.65± 0.04	2.60	1.99	0.96	1.52	3.94	2.38	0.92	1.49
0.25± 0.10	0.94	1.45	1.01	2.02	1.31	1.69	0.98	1.98

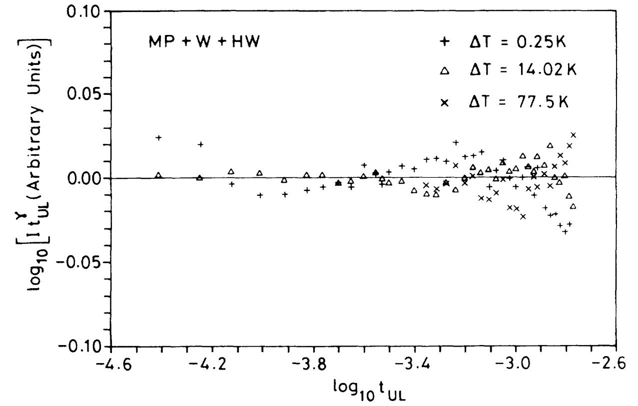

FIG. 7. Log-log plot of the normalized intensity multiplied by t_{UL}^{γ} vs t_{UL}. The random character of this graph coupled with its narrow band justifies the exclusion of the correction-to-scaling term in the expression used for the data reduction [Eq. (4)].

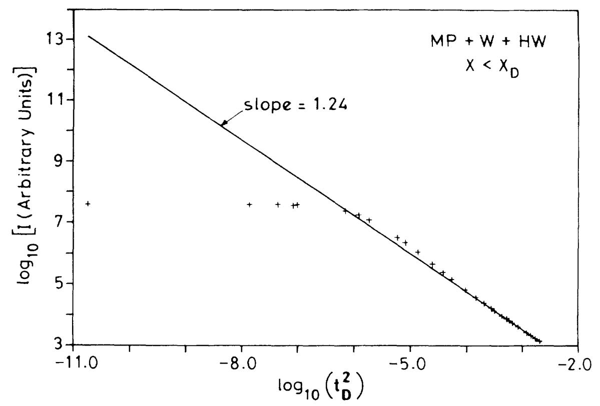

FIG. 8. Graphical presentation of the scattered intensity for a non-phase-separating mixture ($X \lesssim X_D$).

$$\gamma_{\rm fit} = \gamma_I \left[1 + \frac{z}{5}(1+2z^2)\frac{\alpha}{1-\alpha} \right] , \tag{6}$$

where $\gamma_{\rm fit}$ and γ_I are the effective and Ising values of γ, α ($=0.11$) is the CE of heat capacity, and z is the dilution parameter [43,56]. $z = f|(T_c^0 - T_c)/T_c|$, where T_c^0 and T_c are the critical temperatures of the pure binary mixture and its multicomponent form, respectively, and f is a parameter that assumes values between 0.6 and 0.9 depending upon the system. According to Fisher and Scesney, this is the maximum possible increase of γ due to the ternary nature of the system in the close vicinity of T_c ($10^{-6} \le t \le 10^{-3}$). Far away from T_c this effect may be even less pronounced. In the present case, taking $T_c^0 = 311.53$ K (i.e., for MP+HW), γ cannot increase from its Ising value by more than 0.3% even for a sample of $\Delta T = 250$ mK (the largest $T_c^0 - T_c$) as a result of the Fisher renormalization, which is well within our experimental resolution.

The recourse to field variable t_{UL} was guided by the fact that as one approaches a given T_L (T_U) in the homogeneous phase, one is also approaching the conjugate T_U (T_L). Its choice enabled us to restore the universality of γ for any ΔT. A contrasting situation prevails where a T_L lies above T_U (two coexisting regions separated by a one-phase region) or in the two-phase region of the closed-loop system. In this case, an experimental path that advances to a T_U or T_L recedes from the conjugate T_L or T_U. Geometrically, the former path is directed to a *convex* and the latter to a *concave* critical curve. A decrease from the Ising value for CE ν was observed for an experimental path (t) that probed a concave critical line [57]. However, t_{UL} has the intrinsic capability to distinguish between the two instances and restore the universality of CE's. The increase or decrease of the CE's (for t) can be readily understood by expanding t_{UL} in terms of t, i.e.,

TABLE V. Summary of the data reduction of the scattered intensity using Eq. (3) in terms of t'_{UL} for MP+W+HW. The standard deviations of the best-fit parameters are $\lesssim 2\%$.

ΔT (K)	χ'_0 (units of 10^{-2})	ξ'_0 (Å)	χ'_1	χ^2_ν
77.50± 0.05	1.91	1.62	3.35	2.03
22.60± 0.02	1.38	1.82	4.06	0.93
14.02± 0.02	1.68	1.76	3.44	0.61
8.20± 0.02	0.94	1.62	2.27	0.63
4.10± 0.02	3.09	1.88	2.55	2.26
1.30± 0.04	1.53	1.69	1.83	2.74
0.65± 0.04	1.61	1.63	6.99	1.86
0.25± 0.10	1.09	1.57	0.51	2.11

TABLE VI. Best-fit parameters obtained from the fit of the scattered intensity (for a *non-phase-separating* sample of MP+W+HW) to Eq. (5). The standard deviations of the parameters are $\leq 1\%$.

X	X_D	T_D (K)	A_1	χ_0	ξ_0 (Å)	χ_ν^2
0.171 36	0.1715	349.804	0.1191	0.016	1.54	1.15

$$t_{\mathrm{UL}} = \left[t + \delta \frac{T_c}{\Delta T} t^2 \right] \frac{\Delta T}{T_c^*} , \tag{7}$$

where T_c is T_U or T_L, T_c^* is the conjugate T_L or T_U, and δ is $+1$ or -1 depending upon whether the experimental path is approaching a convex or a concave critical line. The quantity within the brackets [in Eq. (7)] becomes $>t$ for $\delta=+1$ and $<t$ for $\delta=-1$ (at least for intermediate ΔT's). The former leads to an effective increase of the CE [13] and the latter to an effective decrease of the CE [57] from their Ising limits when analyzed using t.

The origin of t_{UL} is even more fundamental and it follows from the Landau-Ginzburg theory as applied to the case of the RPT [40,41]. For instance, the coefficient a in the Landau-Ginzburg free-energy functional is linear in t near a normal, single critical point, with its sign being negative in the ordered (coexisting) phase and positive in the disordered (homogeneous) region [27,40]. Hence, for a system with a closed-loop phase diagram, a has to flip its sign across T_U and T_L. In other words, a needs to be quadratic in t (t_U or t_L), or, more precisely, a polynomial of degree *two*, which is symbolized by t_{UL} [Eq. (7)]. If there are p (>2) such transitions (multiple reentrance) [58], then a will be a polynomial in t of degree p. If one wants to recover the universality of CE's in such cases, the corresponding polynomial in t has to be employed as the field variable [40]. Equation (7) is identical to the expression derived from the geometrical picture of phase transitions [16].

Attempts were also made to recover the universal CE's by using other unconventional field variables like t_D and $|X-X_D|$ [8,57]. However, these field variables differ from the actual experimental path (t) except at the DCP.

The shrinkage of the asymptotic region in the salt-doped system can be deemed a consequence of the presence of an electrolyte. It should be recognized that in the present case the Coulombic interaction is not the primary factor for phase separation, unlike that of a conventional ionic fluid [38,59]. By now, it has been well established that the ionic fluids exhibit classical (mean-field) critical behavior [23,38,60,61]. This feature has been attributed to the existence of long-range intermolecular interactions and their role in suppressing the critical fluctuations. Another way of visualizing the ionic critical phenomena is the proximity of the Ginzburg temperature (T_G) to T_c and hence the entire experimental t range being in the mean-field regime [61]. If this argument is correct, then the reduction of the pure-power-law region by the addition of salt may be a signature of ionic critical behavior. This conclusion is somewhat subtle in view of the fact that the quantity of salt added is extremely small (Table II) and the resulting inverse Debye screening length <1 nm. Further work is necessary to resolve this issue in a system where a very large amount of salt is required for effecting phase separation and the Coulombic interaction is still not the primary factor in phase separation.

The inadequacy of the pure power law (in terms of t'_{UL}) to describe the critical behavior in a reentrant system (in contrast to the case using t_{UL}) is in apparent disagreement with the earlier inferences [52,53] that the use of t' extends the asymptotic region. Since t and t' differ merely by an algebraic factor, their impact depends on the signs of the exponents and amplitudes, too. Hence their effect on the critical behavior could be dissimilar for different properties and is possibly system dependent. In any case, the use of t'_{UL} has facilitated an easy examination of the behavior of the extended scaling term near the DCP.

The persistence of critical fluctuations in non-phase-separating mixtures ($X \lesssim X_D$) is described by the power law ($t^{-2\gamma}$) followed by the saturation of χ in the vicinity of T_D (Fig. 8). This situation provided a vital test for the geometrical picture of phase transitions [Eq. (5)]. It can be referred to as a superdouble critical state [8,54,55]—analogous to the *supercritical* state in fluids. Many anomalous phenomena exhibited by aqueous solutions of alcohols, pyridines, etc. [58] can be attributed to the proximity of a hidden DCP in a multidimensional field space.

In a nutshell, we examined various aspects of the phenomenon of RPT in two apparently similar but microscopically dissimilar systems. Our findings can be rationalized on the basis of phenomenological theories. However, a rigorous theoretical result on the extended scaling near the DCP is still lacking.

V. OVERVIEW

The research reported here is the simplest manifestation of the RPT exhibited by multicomponent liquid mixtures. In fact, the full potential of these systems (singly or multiply reentrant) has not been exploited as yet [58]. For instance, the following interesting and challenging problems can be readily addressed by employing multicomponent liquid mixtures: (i) The interfacial phenomena, such as the wetting transition [62], prewetting [63], critical adsorption [64], etc. can be demonstrated near *both* T_U and T_L, and their reentrant character can be probed [65]. Furthermore, a marked improvement in the appearance of these phenomena is probable due to the enhancement of the CE's near the DCP. (ii) The non-phase-separating mixtures provide an ideal medium to study the phase separation in the restricted geometry (capillary condensation), since the hindrances from the bulk phase separation are eliminated [65]. Moreover, the sensitivity of *surface* CE's [62] to double criticality can be examined. (iii) Identification and characterization of a quadruple critical point (QCP) that emerges when two *independent* DCP's merge in a multidimensional field space. The quest for this multicritical point merits consideration due to the plausibility of a *quadrupling* of Ising-like CE's near a QCP. The richness of approaching a QCP is further reflected in the realization of *macroscopic* critical phenomena both in terms of length as well as time scales of the critical concentration fluctuations.

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