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ABSTRACT

We report the critical behavior of osmotic compressibility (χ_T), that was deduced from turbidity, in an ionic fluid mixture comprised of tetra-n-butylammonium picrate in a low dielectric solvent, 1-dodecanol. The liquid-liquid phase separation in this system is driven, predominantly, by Coulombic interactions. Measurements covered the reduced temperature, $\mathbf{t}$, range $7 \times 10^{-5} \leq \mathbf{t} \leq 7 \times 10^{-2}$. The critical behavior of χ_T indicates a *crossover* from the mean field to the Ising critical exponent, as the critical temperature (T_c) is approached.

KEY WORDS: critical phenomena; ionic fluids; liquid-liquid transition; turbidity.

1. INTRODUCTION

Recently, it has been shown that the critical behaviour of ionic fluid mixtures, where the liquid-liquid phase separation is driven, primarily, by Coulombic interactions, is described by classical critical exponents (**CE**'s) – even very close to the critical temperature (T_c) [1-5]. This finding is in sharp contrast to that observed in neutral fluids and fluid mixtures whose **CE**'s belong to Ising universality class [6]. In neutral fluids, the intermolecular forces are short ranged, whereas in ionic fluids, the interionic interactions are long ranged [2].

The restricted primitive model (**RPM**), that represents the ionic fluid as a distribution of charged hard spheres in a dielectric continuum, exhibits a phase separation driven by Coulombic forces [1,7,8], corresponding to a dimensionless concentration C^*=ca^3 and temperature $T^*=4\pi\epsilon_0\epsilon a k_B T/Z^2e^2$, with c the number density of ions, a the hard sphere diameter, ϵ the dielectric constant of the solvent, ±Ze the ionic charge and other symbols have their usual meaning. Most recent Monte-Carlo simulations [9] provide $C_c^* \simeq 0.03$ and $T_c^* \simeq 0.06$. Hence, for 1:1 electrolytes (with $a \sim 0.8$nm) in solvents of low ϵ ($\sim$4), a phase separation driven by Coulombic interactions is possible near room temperature.

While the theoretical efforts concerning Coulombic phase separation [7,8] are still evolving, the experimental evidence from three separate studies [3-5] strongly suggested mean field type **CE**'s. These investigations involved the measurements of order parameter [3], correlation length (ξ) [4] and osmotic compressibility (χ_T) [4,5]. In all three cases the data were consistent with a mean field description even for reduced temperature, $\mathbf{t} = \mid (T - T_c)/T_c \mid$, $\sim 10^{-4}$ and did not invoke the need for a *crossover* to Ising behavior (as $\mathbf{t} \rightarrow 0$), though this possibility could not be excluded within experimental uncertainties [3,4].

Thus, it is unclear from the earlier investigations [3-5] whether the critical phenomena associated with Coulombic phase separation belong to mean field universality class or involves a *crossover* to Ising behavior extremely close to T_c. To answer this question, we investigated the critical behavior of χ_T (extracted from turbidity measurements) in the ionic mixture of tetra-n-butyl ammonium picrate (TBAP) and 1-dodecanol (DD), henceforth referred to as TPDD. DD is a low dielectric solvent ($\epsilon \sim 4.6$ at T_c) and hence the phase separation is predominantly due to Coulombic interactions [1,2]. In all the measurements, T_c was approached from the one phase region.

2. EXPERIMENTAL

Tetra-n-butyl ammonium picrate (TBAP) was synthesized [10] by the *slow* neutralization of tetra-n-butyl ammonium hydroxide with picric acid and purified by repeated recrystallization from methanol solution. The dried and fiber free salt melted at $91 \pm 1°C$. Solvent DD (98%, Aldrich) was filtered prior to using in the sample preparation. The critical concentration of the mixture was determined using the equal volume coexistence criterion and its value in terms of mole fraction of TBAP is 0.147±0.002 (corresponding to a weight fraction of 0.304). The samples were contained in cylindrical quartz turbidity cells with polished flat windows and gas tight teflon stopper. The cells had beam path length (l) 1cm or 5cm. The samples were heated and homogenized before quickly mounting in a well stirred water bath which is maintained initially at a temperature much above T_c. The temperature of the bath was controlled to better than ±2mK. The bath temperature was measured using a calibrated thermistor. The bath water was filtered periodically.

The optical arrangement [10] consisted of a He-Ne laser (λ=632.8nm) of power 1mW and other essential optical components. The incident beam was split partially (30%) using a beam splitter to monitor the laser intensity fluctuations. The resulting beam that was weakly foccused at the cell position was made to pass through the polished bath windows at normal incidence. Spatially filtered incident and transmitted intensities were measured using photo diodes in conjuction with conventional electronic circuitry that have linear intensity-voltage characteristics. To eliminate the effect of incident laser intensity fluctuations, instantaneous voltage referring to transmitted intensity was divided by that due to incident intensity using a precision analog voltage divider. This voltage ratio (V_T), that is stable to better than 0.1% after the thermal equilibriation of sample, was measured using a 6 1/2 digit multimeter.

At each temperature, the transmission loss due to bath and reflection losses at bath windows were corrected by dividing V_T with sample cell by that without cell (which can be moved away from the beam by means of a micrometer arrangement) and this ratio is denoted by I_T. To further eliminate the contributions from non critical back ground turbidity (τ_B), reflection and transmission losses at the cell windows, I_T at any temperature was normalized by I_T at a reference temperature ($=I_R$) which was the farthest temperature of measurement ($T - T_c > 30$K) where the critical part of the turbidity (τ_c) is below the accuracy of measurement. Thus the resulting quantity represented by I_T/I_R is the critical part of transmitted intensity and τ_c is calculated using the expression, $\tau_c = -l^{-1}\ln(I_T/I_R)$. The phase separation (for l=1cm) is detected by the appearence of the spinodal ring [11] followed by vanishing of the transmitted beam. All the results presented here are extracted from the l=5cm data. The T_c of l=5cm sample was deduced by comparing the turbidity values to those of l=1cm sample.

3. RESULTS

The turbidity of the sample is the integral of the scattered light intensity (I_s) over all angles per unit length [12]. Taking Ornstein-Zernike (OZ) form [11,12] of I_s, τ_c is given by the following expression due to Puglielli and Ford [12]

$$\tau_c = \frac{\pi^3 k_B T}{\lambda_0^4}\left(\frac{\partial n^2}{\partial x}\right)_T^2 \chi_T f(\alpha) \tag{1}$$

where f(α) is the OZ correction factor, n is the concentration (x) dependent refractive index of the mixture and λ_0 is the vacuum wave length of the incident light. For **CE** η=0, f(α) has the form, $f(\alpha) = (2\alpha^2 + 2\alpha + 1)\alpha^{-3}\ln(1 + 2\alpha) - 2(1 + \alpha)\alpha^{-2}$, with $\alpha = 2(2\pi n\xi_0 \mathbf{t}^{-\nu}/\lambda_0)^2 = \alpha_0 \mathbf{t}^{-2\nu}$, where ξ_0 is the prefactor of correlation length, $\xi = \xi_0 \mathbf{t}^{-\nu}$, ν is the **CE** of ξ and $\mathbf{t}$ $\{=\mid (T - T_c)/T_c \mid\}$ is the reduced temperature. For x=x$_c$ (the critical concentration), χ_T has the scaling form [11], $\chi_T = \chi_0 \mathbf{t}^{-\gamma}(1 + \chi_1 \mathbf{t}^{\Delta_1} + \chi_2 \mathbf{t}^{2\Delta_1} + ...)$, where χ_0 is the critical amplitude, γ is the **CE**, χ_1, χ_2,... etc. are correction-to-scaling amplitudes of χ_T, and Δ_1 ($\simeq$0.5) is the correction-to-scaling exponent. The temperature dependence of τ_c can be described by the following expression,

$$\tau_c = \frac{Tf(\alpha)\tau_0 \mathbf{t}^{-\gamma}}{T_c}\left(1 + \tau_1 \mathbf{t}^{0.5} + \tau_2 \mathbf{t} + ...\right) \qquad (2)$$

where $\tau_0 = (\pi^3 \chi_0 k_B T_c/\lambda_0^4)\ (\partial n^2/\partial \mathrm{x})^2_{T_c}$, and $\tau_1{=}\chi_1$, $\tau_2{=}\chi_2$, ... etc.

Figure 1 displays the behavior of τ_c (using l=5cm sample) over the $\mathbf{t}$ range $7\mathrm{x}10^{-2} \geq \mathbf{t} \geq 10^{-4}$ for TPDD mixture. A simple scaling expression, Eq. (2) with τ_1, τ_2, ... etc. =0, is inadequate to describe all the data. This is manifested by the strong preference for Ising values of γ and ν (1.24 and 0.63 respectively) by the data near T_c (dotted line in Fig.1) and a mean field effective γ (=1.0) for $\mathbf{t} > 2\times10^{-2}$ (dashed line in Fig. 1). Eq. (2) with the first correction term (τ_2, ...etc. =0) and Ising **CE**'s adequately describes all the data as shown by the continuous line in Fig.1. The dotted line for Ising **CE**'s without correction terms is indistinguishable from the solid line for $(T-T_c)\leq$1K. Alternatively, the evolution of critical behavior in this case can be perceived as a *crossover* of **CE**'s from their mean field to the Ising limit as T_c is neared. The main results of data analysis are provided in Table I.

4. DISCUSSION

The *crossover* feature in TPDD mixture can be more readily visualized using Fig.2. From Eq.(2), it is straightforward to show that the inverse of OZ corrected turbidity ($\mathrm{f}(\alpha)/\tau_c$) is linear in T^{-1} for γ=1. Fig.2 displays this remarkable feature in the far away region. The departure from straight line behavior indicates the *crossover* from classical to non classical **CE** and the corresponding temperature denotes the *crossover* temperature (T_{x}) – that gives the lower limit for the validity of classical **CE**'s. Similarly, the X-intercept gives the fictitious mean field T_c ($T_{c,mf}$). For a *true* mean field type system $T_{c,mf} = T_c$. Thus Fig.2 firmly establishes the classical to non-classical *crossover* in χ_T for TPDD mixture. This type of crossover phenomenon is observed in polymer blends [13] as well as in $Na - NH_3$ solution [14] which again is ionic in the dilute phase but is metallic in the concentrated phase.

We conclude that the critical behavior of a Coulombic fluid is better described in terms of a *crossover* from mean field to Ising **CE**'s rather than either *true* mean field or Ising **CE**'s. Our finding is in agreement with the earlier theoretical prediction [8] that **RPM** should develop an Ising critical point.

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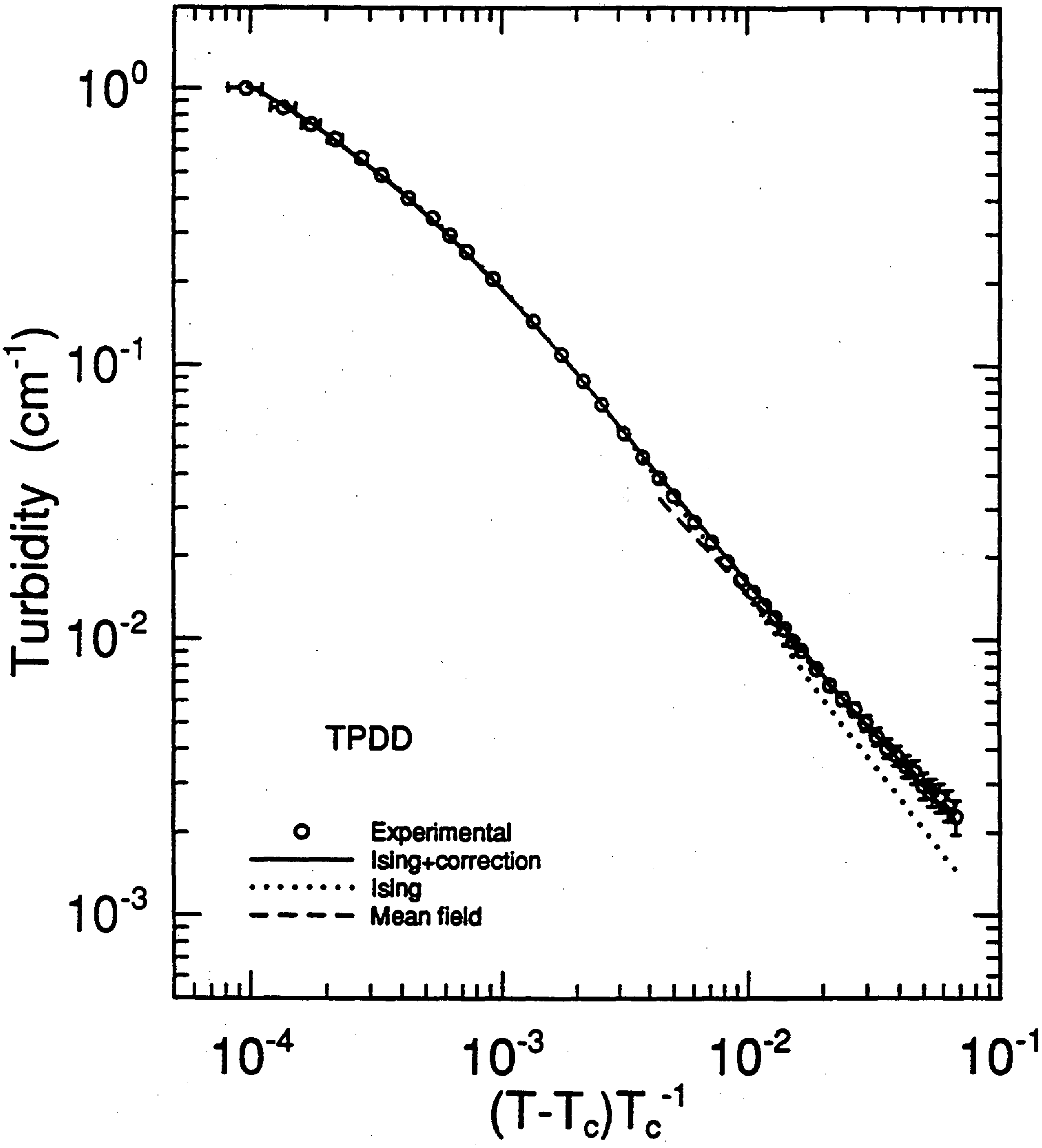
Table I. Summary of data analysis using Eq.(2) for TPDD mixture. T_c was fixed at its experimental value. CE γ was fixed at its theoretical value 1.24 or 1.0 corresponding to ν equals to 0.63 or 0.5 respectively.

$\mathrm{T}_c(K)$	$\tau_B \times 10^3(cm^{-1})$	t range	$\alpha_0 \times 10^5$	γ	$\tau_0 \times 10^5$	τ_1
332.012 ±0.003	3.57	$10^{-4} - 7 \times 10^{-2}$	4.48 ±0.16	1.24	1.556 ±0.027	2.92 ±0.21
		$10^{-4} - 7 \times 10^{-3}$	5.94 ±0.21	1.24	1.818 0.076	0
		$10^{-2} - 7 \times 10^{-2}$	0.152 ±0.066	1.0	5.604 0.161	0

FIGURE CAPTIONS

Fig. 1. Background corrected turbidity of a critical mixture of TPDD (l=5cm). The solid and dotted lines demonstrate the true Ising behavior near T_c.

Fig.2. Reciprocal of Ornstein-Zernike corrected turbidity, $f(\alpha)/\tau_c$, as a function of inverse temperature for TPDD system. *Crossover* behavior is directly evident. $f(\alpha)$ refers to the best fit value using Eq.(2). The inset depicts the pure Ising behavior near T_c. The values of T_x and $T_{c,mf}$ are 333.0K and 332.3K respectively.



Turbidity (cm^{-1})
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
$(T-T_c)T_c^{-1}$
TPDD
○ Experimental
Ising+correction
Ising
Mean field

Fig. 1

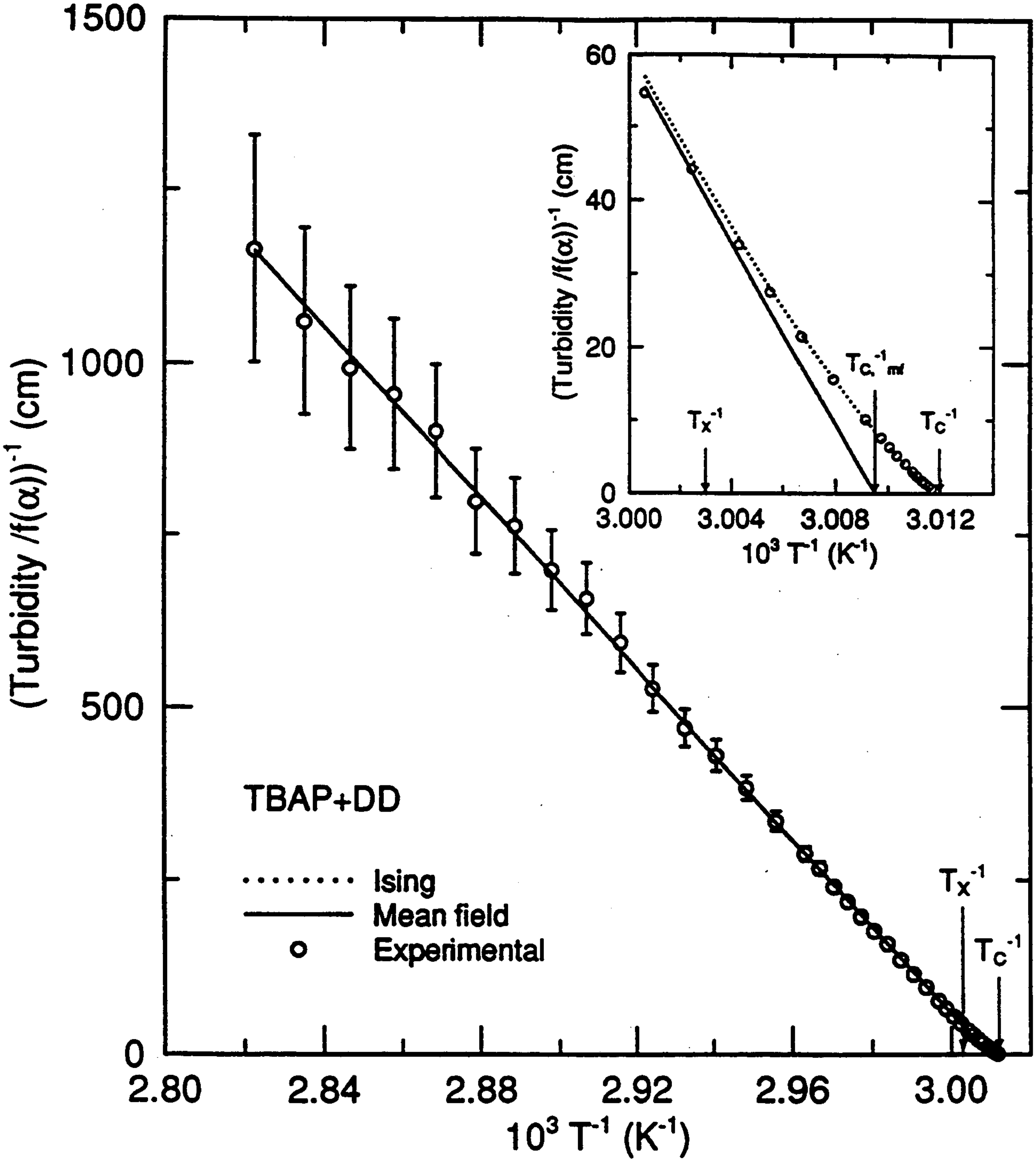

1500
1000
500
0
(Turbidity /f(α))⁻¹ (cm)
2.80
2.84
2.88
2.92
2.96
3.00
10³ T⁻¹ (K⁻¹)
TBAP+DD
Ising
Mean field
Experimental
Tx⁻¹
Tc⁻¹
60
40
20
0
3.000
3.004
3.008
3.012
Tc,⁻¹mf

Fig. 2

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