

Critical behavior of a cationic-surfactant–water–salt system near and far from the Krafft temperature

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The cationic micellar system dodecylammonium chloride + water + KCl has been studied by light scattering near the critical point for different concentrations of salt. For the lowest value of salt concentration, the critical point is rather close to the Krafft line, and therefore there is a critical mixture in equilibrium with two noncritical phases: vapor and pure solid surfactant. Both the correlation length and osmotic susceptibility data for the critical mixtures can be accurately described by the usual three-dimensional Ising exponents for all values of the concentration of KCl (c_{KCl}). This is in agreement with theoretical predictions that indicate that approaching a critical end point does not affect the critical exponents. Two off-critical mixtures have also been studied, and their behavior has been found to be compatible with the linear model equation of state.

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I. INTRODUCTION

Surfactant solutions exhibit a variety of complex phases depending on the composition, temperature, and coexisting salt [1]. Cationic surfactants in aqueous salt solutions have been shown to form rodlike micelles of high molecular weight [2]. As a consequence one frequently finds highly asymmetric liquid-liquid coexistence curves that resemble those of polymer-solvent systems [3].

A few years ago some controversy was raised about whether microemulsions and micellar systems near a critical point belonged to the three-dimensional (3D) Ising universality class. In effect, several experiments were reported that lead to critical exponents different from those usually found in liquid-liquid critical points in binary mixtures of simple liquids [4]. Moreover, Fisher pointed out that, due to the rescaling of the correlation length of this type of systems with the size of the micelles, effective critical exponents, different from the 3D Ising ones, might be found under certain conditions [5]. Recent experimental work has shown that micellar systems belong to the Ising class [6,7].

Rather frequently the micellar systems include water, a salt, and a surfactant, therefore actually being ternary systems. In the case of liquid-liquid equilibrium, it is generally found that the salt concentration is the same in the coexisting phases, thus allowing the system to be treated as pseudobinary [6,7]. However, the influence of the salt concentration upon the critical temperature opens the possibility that, near the critical point, the critical exponents become renormalized as described by Fisher [8]. Such a renormalization has been found in some microemulsion and micellar systems [3,9,10], while in other cases the experimental results can be described by the nonrenormalized 3D Ising critical exponents [6,11,12]. As pointed out by Jayalakshmi and Beysens [10], in general, a purely numerical analysis of the experimental data does not allow Ising and Fisher renormalized exponents

to be distinguished. However, based on physical arguments, some authors have used the renormalized exponents in order to analyze the experimental data [9,10].

In most cases simple scaling equations have been used to describe the experimental data [6,7,9–12]. Both static and dynamic light scattering results for micellar systems lead to values of the critical amplitude of the correlation length, ξ_0 , of the order of 1–2 nm [3,7,12], a value which is much larger than the one found for mixtures of simple liquids [13]. Since the Ginzburg criterion depends on ξ_0^{-6} it seems reasonable to expect that the range of validity of simple scaling always will be smaller than in simpler liquid mixtures [14]. It is well known that the use of simple scaling always outside their range of validity leads to effective critical exponents that differ from the 3D Ising ones. This might lead to values of the exponents ν and γ close to the Fisher renormalized ones even for relatively smaller values of ϵ ($\epsilon = |T - T_c|/T_c$), for which simple scaling holds for mixtures for simple fluids.

A further element that complicates the analysis is the fact that it is not clear which concentration variable must be used to define the order parameter. As already mentioned, ionic micellar systems show highly asymmetric coexistence curves, similar to those of polymer-solvent systems. We have found [15] that the use of an effective concentration variable proposed by Sanchez [16] makes the coexistence curves of micellar systems more symmetrical, and extends the range of validity of simple scaling.

In a study of the coexistence curves of dodecylammonium chloride (DAC) + water + KCl we have found that, within the precision of the experiments, the use of the Fisher renormalized critical exponents does not lead to any improvement with respect to the unrenormalized ones [15]. Therefore more work seems necessary in order to settle this point from an experimental point of view.

The molar concentration of KCl (c_{KCl}) has a noticeable influence on the lower critical solution temperature (LCST) of the DAC + water + KCl; in fact, the critical temperature decreases almost linearly with c_{KCl} [15]. For

samples with $c_{\text{KCl}} > 0.3 \text{ M}$ and $w \simeq 1\%$, a decrease in T drives the system from a single-phase to a two-phase liquid-liquid equilibrium state. After further decrease in T , one reaches a value T_K at which a pure-surfactant solid phase appears in equilibrium with the two liquid phases. T_K is called the Krafft temperature. Since $|T_c - T_K|$ decreases with c_{KCl} , there is a value c_{CEP} for which the Krafft line [i.e., the (T_K, c_{KCl}) line] intersects the critical line. At the point at which both curves coincide, the critical mixture is in equilibrium with two non-critical phases (vapor and pure surfactant). For lower salt concentrations the system does not show any liquid-liquid equilibrium, but a solid-liquid one. Since the critical micellar concentration for this system is very low (approximately 10^{-6} M), for very low salt concentrations, the equilibrium system at $T < T_K$ is essentially formed by pure solid surfactant and a water-salt solution. Figure 1 shows the critical line and the Krafft line; in addition to the data reported previously [15] additional measurements have been included in order to determine the intersection better. From these results, the coordinate of such a critical end point (CEP) were estimated to be $T_{\text{CEP}} = 292.230 \text{ K}$, $w_{\text{CEP}} = 1.04\%$, and $c_{\text{KCl,CEP}} = 0.242 \text{ M}$, w being the weight fraction of the surfactant. For $c_{\text{KCl}} < 0.242 \text{ M}$ the liquid-liquid equilibrium is hidden by the first order solid-liquid equilibrium. The coexistence curve data confirm that the approach of the critical line (CL) to the CEP does not change the values of the critical exponent β , in agreement with other experimental [17]

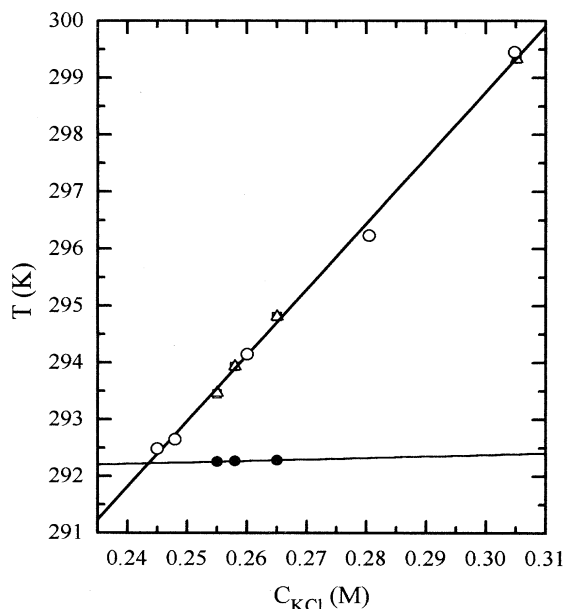


FIG. 1. Critical (T_c) and Krafft (T_K) temperatures for the DAC + water + KCl system as a function of the salt concentration, c_{KCl} . The critical surfactant concentration for each value of c_{KCl} was taken from Ref. 15. \bullet , Krafft temperature. Critical temperatures: \circ , from coexistence curves; Δ , from the analysis of osmotic compressibility data (the points arising from the analysis of correlation length data overlap with the triangles).

and theoretical [18,19] results. However, we found that the range of validity of simple scaling laws was reduced as the LCST approached the CEP [15].

In this paper we will report static light scattering data for the DAC + water + KCl system in the critical region, and for several salt concentrations. The objective is twofold. On one side we will check whether correlation length data allow us to distinguish between Ising and Fisher renormalized exponents. On the other hand we will confirm the constancy of the ν and γ exponents as the CEP is approached.

The rest of this paper is organized as follows. Section II includes some experimental details. Section III gives the results that are discussed for both critical and off-critical isochores. Finally, Sec. IV summarizes the main conclusions of the work.

II. EXPERIMENT

Light scattering experiments were performed on a Malvern K7032 instrument using an Ar^+ laser operating at 514.5 nm. In order to ensure appropriate temperature control ($\pm 0.005 \text{ K}$) the measuring cell was modified, and a Tronac PTC-41 proportional controller with a TCP-25-S probe was used. The temperature was measured with a calibrated platinum resistance thermometer, whose agreement with the IPTS-90 is at least ± 0.01 over the temperature interval of the present measurements. The precision of the measurements was $\pm 1 \text{ mK}$.

DAC was synthesized and purified as in previous work [15]. The water was double distilled and deionized (Milli-Q, $\Omega > 18 \text{ MS}$). KCL was Carlo Erba RPE, purity $> 99\%$, and was dried under vacuum at 100°C shortly before use. The mixtures were prepared by weight on an analytical balance of precision $\pm 0.1 \text{ mg}$, thus the precision of the surfactant weight fraction is at least $\pm 0.1\%$. Dust-free samples were prepared by filtration through $0.2\text{-}\mu\text{m}$ membranes just before use.

III. RESULTS AND DISCUSSION

A. Critical compositions

The scattered intensity as a function of the scattering vector q of a mixture in the critical region is given, if one neglects the very small Fisher exponent η [20], by the Ornstein-Zernike structure factor

$$I(q) = I_{q=0} / (1 + q^2 \xi^2), \quad (1)$$

where $q = 4\pi n \sin(\theta/2) / \lambda$, λ being the vacuum wavelength of the incident light, n the refractive index of the sample, θ the scattering angle, $I_{q=0}$ the intensity at $q=0$, and ξ the correlation length. $I(q)$ values were obtained from the raw experimental data by normalization with the intensity scattered by pure toluene under the same experimental conditions. The temperature dependences of $I_{q=0}$ and ξ are described by

$$I_{q=0} = I_0 (1 + \varepsilon) \varepsilon^{-\gamma} + I_B, \quad (2)$$

$$\xi = \xi_0 \varepsilon^{-\nu} \quad (3)$$

where I_B is a noncritical background intensity.

After correcting the raw data for turbidity and for the variant of the scattering volume with the scattering angle, we followed the method described by Aschauer and Beysens [11] and Sinn and Woermann [21] for obtaining $I_{q=0}$, ξ , and χ_T (in arbitrary units). Scattering data at 318 K have been used for determining the background corrections. The results are consistent with a tempera-

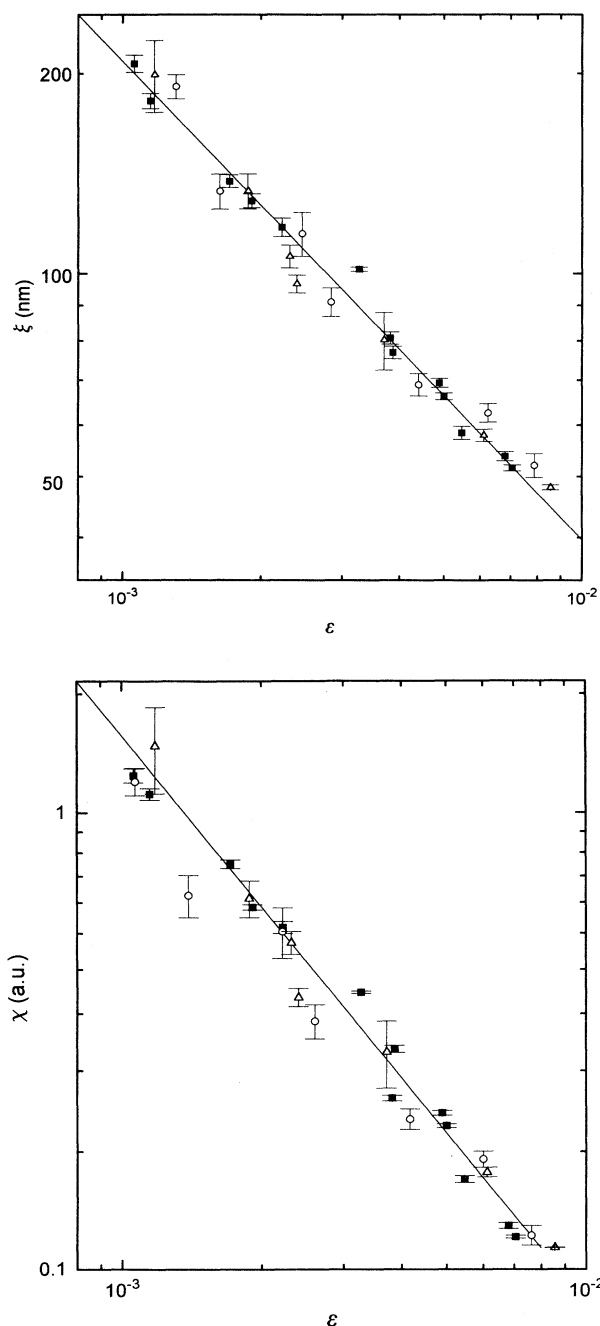


FIG. 2. Scaling behavior for the critical mixtures corresponding to three salt concentrations c_{KCl} : ■, 0.305 M; ○, 0.265 M; △, 0.258 M. The slope of the straight lines correspond to the 3D Ising values for the critical exponents ($\nu=0.63$ and $\gamma=1.24$).

ture independent background contribution I_B for $|T-T_c| < 20$ K. Figure 2 shows ξ and χ_T for critical concentrations corresponding to three different salt concentrations. The fits of ξ and χ_T to simple scaling laws like Eq. (3) lead to the critical exponents γ and ν which are collected in Table I. It must be remarked that for our system the background correction does not lead to any significant change in the critical exponents (e.g., $\nu=0.63\pm 0.01$ is found for $c_{\text{KCl}}=0.305$ M when I_B was neglected), while the critical amplitudes are changed by approximately 10% in the case of ξ_0 and less than 2% in the case of χ_0 . This seems to indicate that the background effects in the present system are smaller than in other micellar systems reported in the literature [12].

As can be observed, values of γ are reasonably close to the 3D Ising prediction, $\gamma=1.24$, for all the c_{KCl} concentrations. Similar values were found by Wilcoxon [12] ($\gamma=1.13$) and Sinn and Woermann [21] ($\gamma=1.14-1.17$) for nonionic surfactant systems, and by Aschauer and Beysens [11] for a microemulsion ($\gamma=1.18$). This value is quite different from the renormalized value $\gamma^*=\gamma/(1-\alpha)=1.39$, found by Rouch *et al.* [9] (α is the heat-capacity critical exponent $\alpha=0.11$). Similar conclusions can be drawn for the exponent ν , for which the theoretical value for the 3D Ising model is $\nu=0.63$. Again the values given in Refs. [11], [12], and [21] are 0.62, 0.64, and 0.63–0.67, respectively. The results agree reasonably well with the relationship $\gamma=(2-\eta)\nu$, where $\eta=0.03$ is Fisher's exponent [22].

The amplitude of the correlation length obtained ($\xi_0=2.6$ nm) is similar to those found in other micellar and microemulsion systems [9,11,12], and is an order of magnitude larger than in binary mixtures of simple liquids [17,2]. The value of ξ_0 may be of interest when discussing the size of the region in which critical fluctuations dominate the behavior of the system. For the critical isochore, such a region is given by the Ginzburg number

$$|T-T_c|=G_i \equiv \Lambda(1_0/\xi_0)^6, \quad (4)$$

where Λ is an amplitude which has been found to be of the order of 0.01 in simple liquids. Since G_i is proportional to ξ_0^{-6} a significant increase in ξ_0 might alter the crossover region dramatically, unless the interparticle distance l_0 changes as much as ξ_0 . Our coexistence curve data for the present system [15] indicate that the range of validity of simple scaling was small compared with other

TABLE I. Simple scaling analysis of the experimental results for the DAC + water + KCl system at different concentrations of salt (c_{KCl}). Critical exponents and amplitudes for the correlation length ξ (ν and ξ_0), and the osmotic susceptibility χ (γ and χ_0).

c_{KCl} (M)	w (%)	ξ_0 (nm)	ν	$10^4\chi_0$ (a.u.)	γ
0.305	0.95	2.6 ± 0.2	0.62 ± 0.2	2.8 ± 0.2	1.24 ± 0.1
0.265	1.01	2.7 ± 0.5	0.62 ± 0.03	2.8 ± 0.8	1.24 ± 0.05
0.258	1.03	2.7 ± 0.3	0.62 ± 0.02	3.2 ± 0.3	1.23 ± 0.02
0.255	1.01	2.8 ± 0.3	0.62 ± 0.02	3.0 ± 0.3	1.24 ± 0.02

liquid mixtures. In Fig. 2 we have shown data for the ε range for which constant values of the critical exponents ν and γ are found. This reduces roughly to $(T - T_c) < 4$ K (i.e., $\varepsilon < 0.013$), which is similar to the range found for mixtures of simple fluids. This seems to indicate that the range of simple scaling is slightly larger when approaching the critical point from the one-phase side than from the two-phase one. The use of correction to scaling terms in Eqs. (2) and (3) does not lead to any improvement, and is not statistically justified (Student t test).

It can be observed that the critical exponents do not show any significant change when the CEP is approached by reducing c_{KCl} . This result agrees with the prediction of Fisher and Barbosa [19] that the proximity of a CEP does not modify the universal values of the critical exponents.

Dorshow, Bunton, and Nicoli [22] measured the diffusion coefficient and the apparent hydrodynamic radius, R_h^{app} for mixtures of DAC + water + NaCl at different salt concentrations. This system presents a phase diagram similar to Fig. 1, and R_h^{app} was measured for c_{NaCl} above and below the salt concentration corresponding to the intersection of the two-phase and Krafft lines [$c_{\text{NaCl}} = 0.22$ M, $T_{\text{CEP}} = 16.5^\circ\text{C}$]. They found that R_h^{app} increased sharply as T was decreased for c_{NaCl} values smaller than 0.22 M, and suggested that this behavior could be interpreted in terms of the critical slowing down characteristic of the approach to a critical point. For the results corresponding to $c_{\text{NaCl}} = 0.20$ M this would represent a behavior reminiscent of a liquid-liquid critical point frustrated by the appearance of the solid phase at the Krafft point.

Dorshow, Bunton, and Nicoli [22] used a surfactant

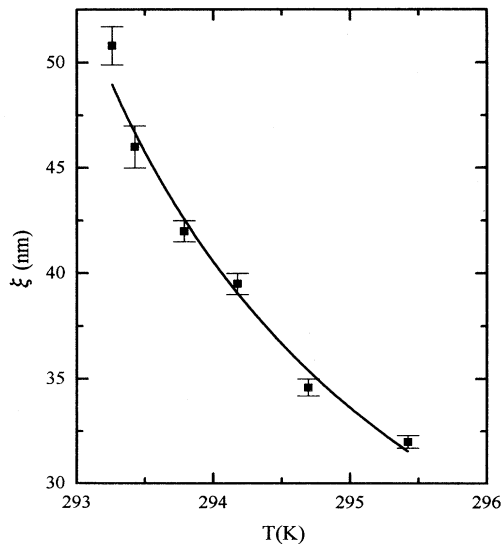


FIG. 3. Temperature dependence of ξ for a mixture corresponding to a salt concentration $c_{\text{KCl}} = 0.235$ M (lower than the corresponding to the CEP) and DAC weight fraction $w = 1.04\%$. The line corresponds to a simple scaling behavior with the 3D Ising value for ν , and the critical temperature calculated from the extrapolation of the critical line of Fig. 1.

concentration independent of c_{NaCl} , and for $c_{\text{NaCl}} = 0.20$ M it might be slightly off-critical, therefore we have considered it interesting to check whether such critical effects were present in DAC + water + KCl for $c_{\text{KCl}} < 0.242$ M. We measured the correlation length for the critical mixture corresponding to $c_{\text{KCl}} = 0.235$ M. Extrapolation of the critical line of Fig. 1 indicates that the critical temperature (T'_c) for $c_{\text{KCl}} = 0.235$ M would lie around 1.4° below the Krafft temperature (for the system of Dorshow, Bunton, and Nicoli [22] the critical temperature would be approximately 4° below the Krafft line).

Figure 3 shows that the results present a critical-like increase for $|T - T'_c| < 6^\circ$. Moreover, their behavior in terms of $\varepsilon' = |T - T'_c|/T'_c$ can be described with $\nu = 0.61 \pm 0.08$, that is compatible with 3D Ising values for the critical exponent. This is consistent with the suggestion of Ref. [22]; however, it must be pointed out that the critical effects seem to be felt in R_h^{app} at values of $|T - T'_c| < 25^\circ$, while almost no effect is detected in the correlation length this far from T_c . Similar precritical effects far from T_c have been claimed to exist for dielectric properties [23] and C_p [24] for some binary mixtures of nonmicellar fluids.

B. Off-critical compositions

Due to the uncertainty in the salt concentration of the critical concentration for DAC + water + KCl, resulting from the scatter in the data for the T_c versus c_{KCl} curve in Ref. [15], we have measured two more mixtures for $c_{\text{KCl}} = 0.30$ M, with DAC concentrations very close to that discussed above.

Two kinds of analysis have frequently been used in the literature for off-critical mixtures. One makes use of the concept of pseudospinodal [25], and the other one is based on the so-called linear model [26] that gives the equation of state of the system near the critical point in a parametric form.

On the basis of the concept of pseudospinodal temperature, T_{ps} , it has been customary to express the temperature dependence of ξ and χ as power laws similar to Eq. (3) but with ε defined in terms of T_{ps} instead of T_c . With this kind of analysis, our off-critical data can be described with the 3D Ising critical exponents ν and γ . However, since no physical interpretation of T_{ps} is rigorous, we will not pursue this analysis further, but instead will analyze the data in terms of the linear model [27]. According to this model, it is possible to write, for the correlation length,

$$\xi^2 = \xi_0^2 (V_m / V_{m,c}) \{ [w_c(1-w_c)] / [w/(1-w)] \}^2 \times \{ r^{-\gamma} / [1 + d_2 \theta^2] \}, \quad (5)$$

where V_m and $V_{m,c}$ are the molar volumes of the off-critical and critical mixtures, respectively, d is a universal constant [$d_2 = (2\beta\delta - 3)/(1 - 2\beta) = 0.377$], and r and θ are parametric variables that describe the state of the mixture (composition and temperature) with respect to the critical point. We have calculated them from $(T - T_c)$ and $(w - w_c)$ following Moldover [28]. For a

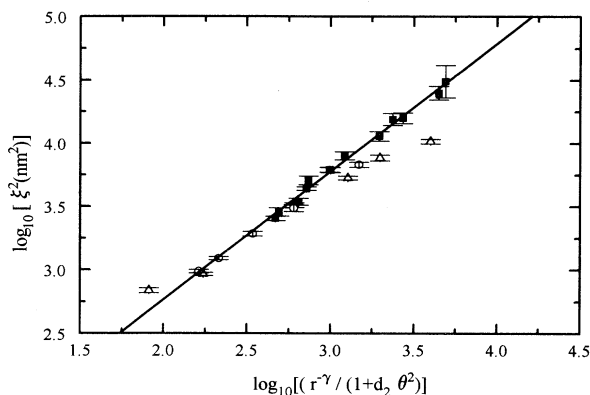


FIG. 4. Test of the validity of Eq. (6) (linear model equation of state) for describing the off-critical results in the vicinity of the critical point for $c_{\text{KCl}}=0.30$. Symbols correspond to different weight fractions of DAC (in percent): \blacksquare , 0.95; \circ , 1.00; \triangle , 0.89.

pseudobinary system, the linear model can be written

$$\varepsilon(r, \theta) = r(1 - b^2 \theta^2) \quad (6)$$

$$w - w_c = \pm g \theta r^\beta, \quad (7)$$

where g is related to the nonuniversal amplitude of the coexistence curve B_0 through

$$g = (B_0/2)(b^2 - 1)^\beta, \quad (8)$$

and the \pm applies to each of the branches of the coexistence curve.

$V_m(T)$ data are not available for our mixtures, therefore it is not possible to carry out a rigorous test of the validity of Eq. (5). Since the available experimental data

are concentrated in a narrow region around the critical point, we have assumed $V_m/V_{m,c} \cong \text{const}$, thus making it possible to test the above model. Figure 4 shows that the results for the three isochores for $c_{\text{KCl}}=0.30$ M collapse on a single straight line. Even though there is some scattering in the results, it may be explained in terms of the simplification mentioned above, thus we can consider that Fig. 4 confirms the validity of Eq. (5) for describing the present results.

IV. CONCLUSIONS

The correlation length and the susceptibility data for critical samples of the DAC + water + KCl system confirm that this cationic micellar system can be described with the usual 3D Ising exponents. Nevertheless the range of validity of simple scaling seems to be lower than in mixtures of simple liquids, which is in agreement with the Ginzburg criterion for systems with large values of the critical amplitude of the correlation length ξ_0 .

For the lowest concentrations of KCl, where the critical point is close to the Krafft line, the results agree with theoretical predictions according to which the proximity of a critical end point should not affect the values of the critical exponents. The results for two slightly off-critical mixtures can be described accurately with the 3D Ising exponents and the linear model equation of state.

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