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# Two-exponential correlation functions near the critical point of a micellar system

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The critical behavior of the dodecilammonium chloride plus water plus KCl system has been studied by static and dynamic light scattering. The line of critical points intercepts a surface corresponding to first-order phase transitions at low concentrations of KCl and low temperature, thus leading to the existence of a critical end point. The correlation length and osmotic susceptibility experimental data can be well described by simple scaling laws with three-dimensional Ising critical exponents for all the salt concentrations. This suggests that approaching the surface of first-order phase transitions does not affect the nature of the liquid-liquid critical point, in agreement with the predictions of Fisher and Barbosa [Phys. Rev. B **43**, 11 177 (1991)]. Far from the critical temperature $T_c$ single-exponential correlation functions are found at all the salt concentrations studied. However, as $T_c$ is approached a new slower relaxation mode appears and becomes dominant near $T_c$. This behavior is independent of [KCl] and thus of the proximity to the first-order transition surface. The two-exponential decay has been analyzed in terms of the asymmetric *H* model of Hohenberg and Halperin [Rev. Mod. Phys. **49**, 435 (1977)], which allows one to separate the background and critical contributions. The contribution of the critical concentration fluctuations can be very well described in terms of the mode-coupling theory. The analysis of the relative weight of the two contributions has allowed us to conclude that background and critical contributions are very weakly coupled. [S1063-651X(98)03108-0]

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## I. INTRODUCTION

In recent years, photon correlation spectroscopy has become a popular technique for studying the dynamics of fluid mixtures near a liquid-liquid critical point [1]. In the case of nonmicellar systems, the results usually show single-exponential correlation functions [2]. The decay rate $\Gamma(T,q)$ ($q$ being the wave vector and $T$ the temperature) of the correlation function or the corresponding diffusion coefficient $D(T)=\Gamma(T,q=0)/q^2$ is usually associated with the concentration fluctuations. The $q$ and $T$ dependence of $\Gamma(T,q)$ is frequently described in terms of mode-coupling theory [3].

Despite that it is now well established that critical micellar systems belong to the three-dimensional (3D) Ising universality class [4], the critical behavior of their static properties appears to be somewhat peculiar due to the fact that the range of validity of simple scaling laws for the order parameter is smaller than for nonmicellar systems [5]. The low value of the Ginzburg number has been associated with the large value of the leading amplitude of the correlation length in these systems [6]. The behavior of the apparent critical exponents in terms of the size of the micelles has already been discussed in detail [7,8].

Quite frequently, the correlation functions obtained by photon correlation spectroscopy for critical micellar systems have been claimed to show also single-exponential decays and the diffusion coefficients have been analyzed in terms of mode-coupling theory [9,10]. Moreover, the decay rate frequently has been obtained from the experimental data through the cumulants method, i.e., from the information contained in the short-time part of the correlation function.

In recent studies of critical microemulsions Rouch, Tartaglia, and Chen [11] and Hamano *et al.* [12] have reported nonexponential correlation functions and have described them in terms of the so-called droplet model. However, Stauffer has criticized their conclusions [13]. Miura, Meyer, and Ikushima [14] have found two-exponential functions for the $^3$He+$^4$He mixtures. Hair *et al.* [15] and Yajima *et al.* [16] reported a similar behavior for polymer blends near a critical point. Bimodal correlation functions are also expected for binary mixtures near the gas-liquid critical point [17].

In a recent work we have also found bimodal correlation functions for a critical ionic micellar system: dodecilammonium chloride (DAC) plus water plus KCl (0.3*M*) [18]. The results have been analyzed following the predictions obtained by Hohenberg and Halperin for the so-called *H* model for asymmetric fluids [19]. A method similar to that of Hair *et al.* [15] has been followed in order to obtain the critical and background contributions to the order parameter. Good agreement with the mode-coupling predictions was found. Moreover, it was found that the coupling between the background and the critical contributions was rather weak. Anisimov *et al.* [20] have addressed the two-exponential decay of dynamic light scattering near vapor-liquid critical points of binary mixtures and discussed in detail the conditions under which weak or strong coupling between the contributions to the dynamic light scattering are to be expected. Moreover, the theory allows one to calculate the relative amplitudes of the two relaxation modes for a given system if enough information about static (e.g., density and refractive index) and dynamic (e.g., thermal conductivity and viscosity) properties is available.

As pointed out previously [5,18,21], the DAC plus water plus KCl system has a complex phase diagram. Since the

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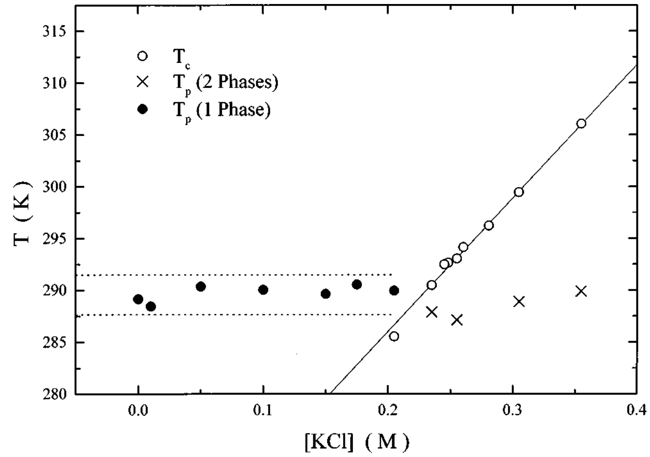

FIG. 1. Phase diagram for the DAC+water+KCl system. ○, critical temperatures $T_c$; ●, precipitation temperatures $T_p$. The horizontal lines represent the temperature interval within which $T_p$ was reproducible in the one-phase system.

critical line (i.e., the $T_c$ vs [KCl] line) intercepts the first-order phase transition line at a fixed surfactant concentration, corresponding to the formation of a pure solid surfactant phase (i.e., the line of so-called Krafft points [22]), a critical end point (CEP) is expected at low KCl concentrations and low temperature. It was also shown that the critical exponents corresponding to static properties (order parameter, density, correlation length $\xi$, and osmotic compressibility $\chi$) did not change when the CEP was approached, in accordance with the predictions of Fisher and Barbosa [23]. However, it was observed that the range of validity of the asymptotic scaling laws for the order parameter is reduced when the CEP is approached [5].

The DAC plus water plus KCl system represents a good opportunity to study whether the approach to a CEP has any influence on the critical dynamics of fluid systems. It is the purpose of this paper to address this point.

The rest of this paper is organized as follows. Section II gives some details of the experimental procedures. Section III describes the static light-scattering results obtained for the critical mixture corresponding to two salt concentrations and the dynamic light scattering for four critical samples. Section IV includes a summary of the theoretical predictions of the *H* model and a discussion of the critical dynamics of the present systems. Finally, Sec. V summarizes the main conclusions.

## II. EXPERIMENT

We have used the same chemicals as in a previous work [18]. Light-scattering measurements were performed on a modified temperature controlled Malvern model 7032 system (256 channels), with a Coherent model 300 $\mathrm{Ar}^+$ laser operating at 514.5 nm and with an angular range 20°–150°. The wave vector is defined as $q=(4\pi n/\lambda)\sin(\theta/2)$, where $\lambda$ is the vacuum wavelength of the light, $n$ is the refractive index of the medium, and $\theta$ is the scattering angle. The sample cell was thermostated using a Tronac PTC-41 proportional controller with a TCP-25 probe and the temperature was measured *in situ* with a calibrated platinum thermometer. The long-term stability of the cell was better than 3 mK. The measuring cell was placed in an isorefractive index bath. The performance of the light-scattering apparatus was tested every week using a toluene sample (afterpulsing effects appeared always well below the time window of interest for our experiments) and poly(styrene) latex samples of well defined average size (Polysciences, Germany). For temperatures close to the critical one the influence of multiple scattering was checked by repeating measurements with three different path lengths: 3, 10, and 25 mm. Furthermore, no appreciable depolarized component corresponding to multiple scattering has been detected. Only measurements with negligible double scattering were retained for analysis.

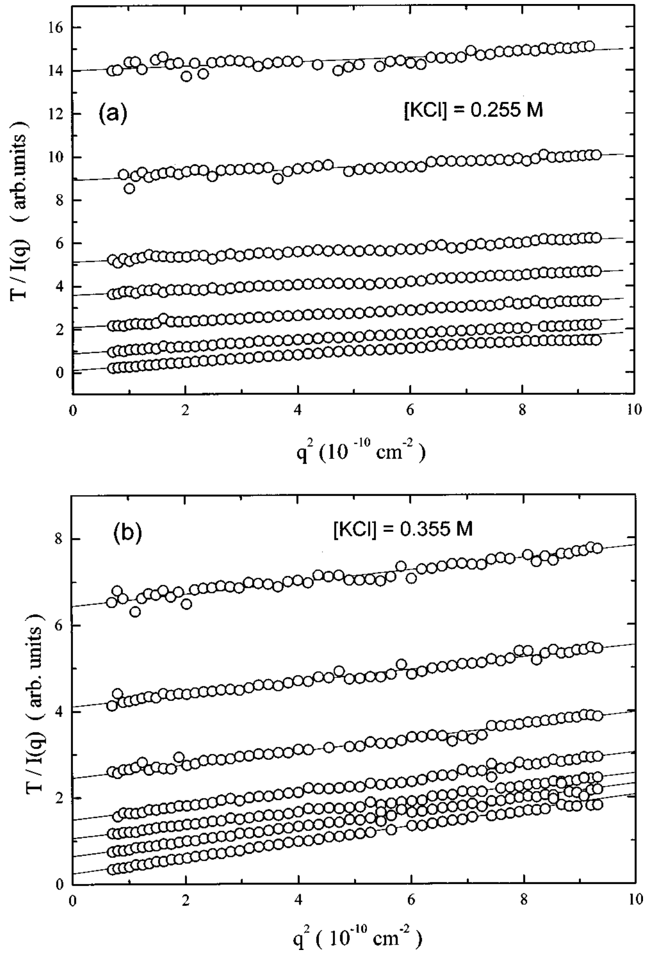

FIG. 2. Static light-scattering results. Ornstein-Zernike plots for critical mixtures corresponding to two different salt concentrations: (a) [KCl]=0.255*M* and (b) [KCl]=0.355*M*.

The viscosities $\eta$ were measured using an Ubbelhode and a rolling ball viscometer and the data were corrected to zero-shear conditions. Since viscoelastic effects may appear near the critical point of colloidal systems [24], measurements in a Bohlin VE rheometer were also carried out. In this paper we will discuss data only in the temperature range in which no flat region appears in the $\eta(\dot{\gamma}\rightarrow 0)$ vs $T$ curve ($\dot{\gamma}$ represents the shear rate). The temperature stability of the viscosity measurements was $\pm 1$ mK for the viscometers and $\pm 10$ mK for the rheometer.

The critical coordinates $T_c, w_c$ ($w_c$ represents the weight fraction of DAC in the sample) were measured both visually

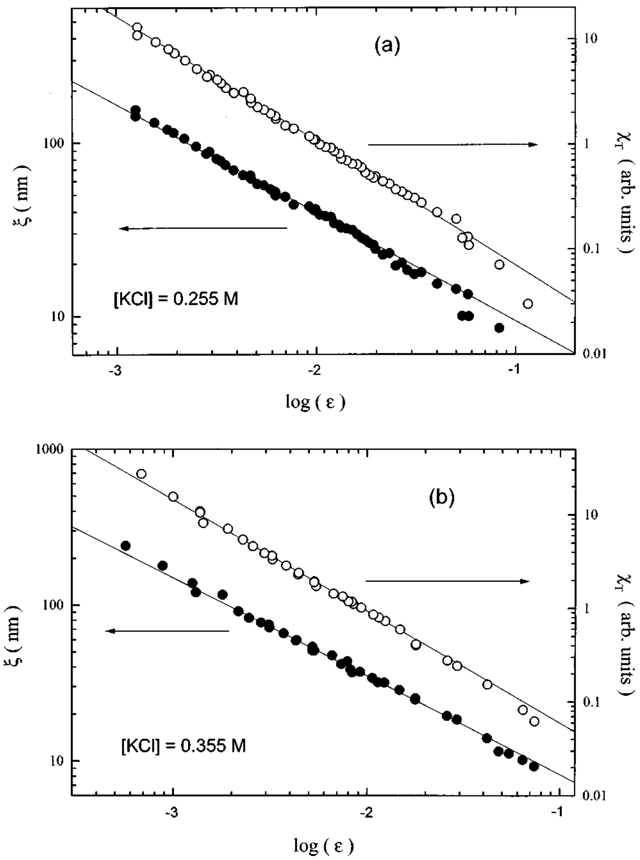

FIG. 3. Test of the scaling laws for the correlation length $\xi$ and the osmotic susceptibility $\chi_T$ for the critical samples corresponding to two salt concentrations. Decimal logarithms are used in the abscissa.

[5] and from turbidity measurements [21]. Good agreement was found between both methods.

The samples were prepared in a dust-free environment, filtered through 0.2-$\mu$m Millipore membranes just before use and then sealed. All the cells were individually tested for dust presence at temperatures well above $T_c$.

## III. RESULTS

### A. Critical coordinates

Figure 1 shows the values of $T_c$ for different molar concentrations of salt. The critical weight fraction of DAC was found to be very close to 1%, as in Ref. [5]. The figure also includes the region at which DAC precipitates. On the right-hand side of the figure ($[\mathrm{KCl}]>0.23$) the continuous line corresponds to the precipitation from a two-phase liquid system, more specifically, from the phase with the highest concentration of DAC (which is the less dense [25]) and hence they do not correspond to the precipitation from a mixture with $w=w_c$. In this region, the values of the precipitation temperatures $T_p$ for a given sample are well reproducible within $\pm 30$ mK. However, on the left-hand side of Fig. 1 ($[\mathrm{KCl}]<0.21$) the precipitation occurs from a one-phase system and a large tendency to undercooling was found. The dashed lines indicate the upper and lower limits of $T_p$ at which precipitation takes place.

Although this behavior makes it impossible to define precise coordinates for the CEP, it is clear that the study of the critical behavior of the system for critical samples corresponding to different values of [KCl] will reveal any effect of the proximity of the CEP in the dynamic properties of the system.

### B. Static light scattering

In a previous paper [21] we have studied the critical behavior of $\xi$ and $\chi$ for some samples with four KCl concentrations in the range $0.255<[\mathrm{KCl}]/M<0.305$. Since one of the main aims of this work is to compare the critical behavior of the system far from and near the first-order transition surface, we report here the static light-scattering results of a mixture with $[\mathrm{KCl}]=0.355M$, for which $T_c=305.908\ \mathrm{K}\pm 0.003\ \mathrm{K}$, i.e., around 18 K above the $T_p$ line shown in Fig. 1, and for $[\mathrm{KCl}]=0.255M$, for which $T_c=292.849\pm 0.005$ K, i.e., around 1 K above the $T_p$ line.

If one neglects the small Fisher exponent [26], the intensity of the light scattered at wave vector $q$ is given by the

TABLE I. Static light-scattering results. Shown are the best-fit parameters for the correlation length $\xi$ and the osmotic susceptibility $\chi_T$ to simple scaling laws.

| [KCl] ($M$) | $(T-T_c)_{\max}$ (K) | $\xi=\xi_0\varepsilon^{-\nu}$ $\xi_0$ (nm) | $\nu$ | $T_c$ (K) |
|---|---|---|---|---|
| 0.355 | 3.6 | 1.92±0.03 | 0.630±0.003 | 305.908±0.003 |
| 0.305 | 3.0 | 2.31±0.12 | 0.63 ±0.01 | 299.331±0.008 |
| 0.265 | 3.2 | 2.4 ±0.4 | 0.63 ±0.03 | 294.81 ±0.04 |
| 0.258 | 3.1 | 2.3 ±0.3 | 0.63 ±0.02 | 293.94 ±0.03 |
| 0.255 | 3.8 | 2.22±0.05 | 0.624±0.05 | 292.879±0.005 |

| [KCl] ($M$) | $(T-T_c)_{\max}$ (K) | $\chi_T=\chi_{T,0}\varepsilon^{-\gamma}$ $10^{-4}\chi_{T0}$ (arb. units) | $\gamma$ | $T_c$ (K) |
|---|---|---|---|---|
| 0.355 | 3.6 | 3.83±0.01 | 1.20 ±0.01 | 305.872±0.005 |
| 0.305 | 3.0 | 4.1 ±0.4 | 1.24 ±0.02 | 299.330±0.007 |
| 0.265 | 3.2 | 2.8 ±0.8 | 1.24 ±0.05 | 294.81 ±0.02 |
| 0.258 | 3.1 | 3.2 ±0.3 | 1.23 ±0.02 | 293.94 ±0.01 |
| 0.255 | 3.8 | 4.60±0.09 | 1.19 ±0.01 | 292.840±0.004 |

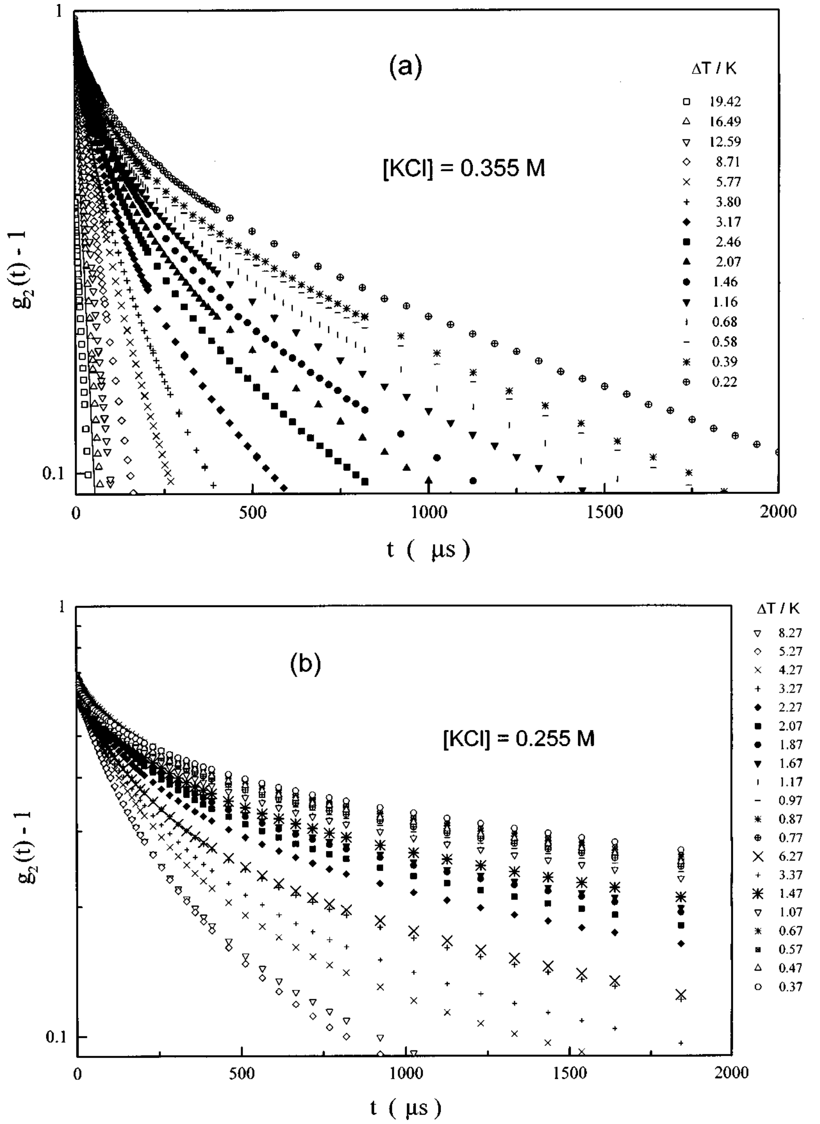

FIG. 4. Temperature dependence of the correlation function for the critical mixtures corresponding to two values of [KCl]: (a) 0.355*M* and (b) 0.255*M*. Notice that while a single exponential decay is found at temperatures far from $T_c$, the correlation functions become nonexponential for $|T-T_c|<8$ K.

Ornstein-Zernike structure factor

$$I(q)=\frac{I(q=0)}{(1+q^2\xi^2)}. \tag{1}$$

The $I(q)$ values were obtained from the raw data by normalization with the intensity scattered by pure toluene under the same experimental conditions. The temperature dependences of $I(q=0)$ and $\xi$ are described in the asymptotic critical region by

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

$$\xi=\xi_0\varepsilon^{-\nu}, \tag{3}$$

$$\chi_T=\chi_{T,0}\varepsilon^{-\gamma}, \tag{4}$$

where $I_B$ is a noncritical background intensity, $\nu$ and $\gamma$ are critical exponents, and $\varepsilon$ is the reduced temperature

$$\varepsilon=\frac{T-T_c}{T_c}. \tag{5}$$

After correcting the raw data for turbidity and for the change of the scattering volume with the scattering angle, we followed the method described by Aschauer and Beysens [6] and Sinn and Woermann [27] to obtain $I(q=0)$, $\xi$, and $\chi_T$ (in arbitrary units). Scattering data at 325.15 K have been used for determining $I_B$. The results are consistent with a $q$ and temperature-independent $I_B$ for $|T-T_c|<20$ K.

Figure 2 shows that the data closely follow Eq. (1) and no signature of double scattering is observed for low values of $\varepsilon$ and $q$. Figure 3 shows the scaling behavior of $\xi$ and $\chi_T$. Table I gives the results of the fits to Eqs. (3) and (4) for the present sample and for those previously reported [21]. As it can be observed, the values of the critical exponents $\nu$ and $\gamma$ remain very close to the 3D Ising predictions ($\nu=0.63$ and $\gamma=1.24$) and are unambiguously different from both the mean field and the Fisher renormalized values. It can also be

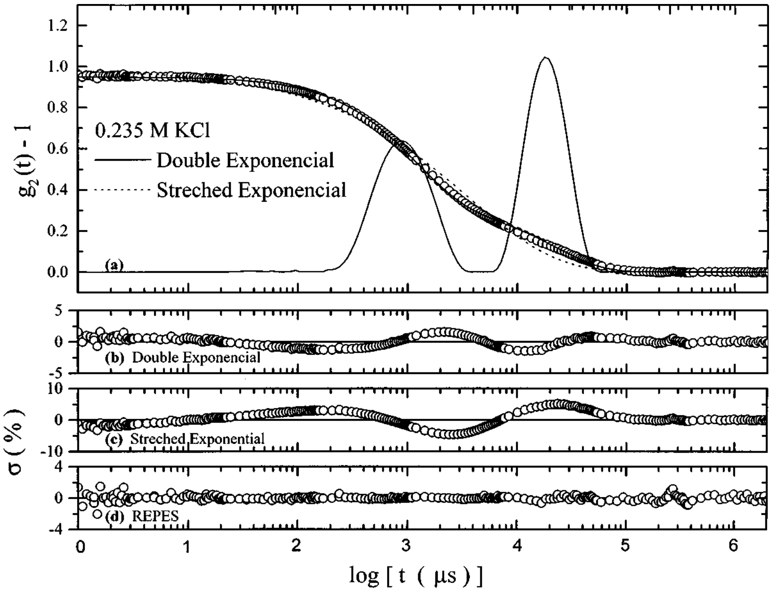

FIG. 5. (a) Comparison between one of the experimental correlation functions and the fits to a double and a stretched exponential. The distribution of relaxation times obtained from the REPES regularization algorithm is also shown. (b) and (c) Residuals obtained from the fits shown in (a). (d) Residuals obtained from the REPES regularization algorithm. The data correspond to the critical mixture for [KCl] $=0.235$ and $T-T_c=0.5$ K. Decimal logarithms are used in the abscissa.

observed that the maximum values of $|T-T_c|$ for which the simple scaling laws can be applied remain roughly independent of [KCl]: $\varepsilon<0.02$. This value is almost tenfold the value obtained from the analysis of the order parameter [5].

### C. Dynamic light scattering

Previously we have reported results for the system $[\mathrm{KCl}]=0.305M$ [18]; here we have extended the study to the rest of the systems contained in Table I. The second-order intensity correlation function $g^{(2)}(t)$ has been calculated from the experimental temporal correlation function $G(t)$ through [28]

$$g^{(2)}(t)=\frac{G(t)}{B}, \tag{6}$$

where $B$ is the experimental base line. The Siegert relation has been used for calculating the first-order field correlation function $g^{(1)}(t)$ [28],

$$g^{(2)}(t)-1=\beta|g^{(1)}(t)|^2, \tag{7}$$

where the coherence factor $\beta$ is a $t$-independent constant, usually treated as an adjustable parameter for each $G(t)$ set of data. Figure 4 shows the normalized $g^{(2)}-1$ (hereinafter the correlation function) for different temperatures and for the systems with the highest and one of the lowest KCl concentrations. In all cases the decay of $g^{(2)}-1$ was followed up to values of $t$ large enough to reach the base line. It can be observed that, as for the system with $[\mathrm{KCl}]=0.305M$ [18], single-exponential correlation functions are obtained for temperatures well above $T_c$. However, as $\varepsilon$ decreases, $g^{(2)}-1$ becomes clearly nonexponential, as can be observed in Fig. 5 for the sample with $[\mathrm{KCl}]=0.235M$ for $|T-T_c|=2$ K and $\theta=30°$. The figure also shows the residuals obtained when fitted to a stretched exponential

$$g^{(1)}(t)=A\ \exp[-(\Gamma t)^{\delta}], \quad 0<\delta\leqslant 1 \tag{8}$$

as has been done by Rouch, Tartaglia, and Chen [11]. It also shows the residuals for the fit to two exponentials

$$g^{(1)}(t)=A_{\mathrm{fast}}\ \exp[-(\Gamma_{\mathrm{fast}}t)]+A_{\mathrm{slow}}\ \exp[-(\Gamma_{\mathrm{slow}}t)], \tag{9}$$

as suggested by Hair *et al.* [15], Ackerson and Hanley [17], and Onuki [29]. Equation (9) also arises in a natural way from the theoretical treatment of Anisimov *et al.* [20]. As it can be observed, the residuals still show some systematic trends, though they are slightly smaller than in the case of the stretched exponential.

In polymer systems $g^{(2)}-1$ is frequently analyzed in terms of a continuous distribution of decay rates $A(\Gamma)$ [1],

$$g^{(2)}-1=\beta\left|\int_0^{\infty}A(\Gamma)\exp[-(\Gamma t)]dt\right|^2. \tag{10}$$

Taking into account that micellar systems always present some degree of polydispersity, it seems reasonable to expect a distribution of Γ's. $A(\Gamma)$ was obtained from $g^{(2)}-1$ by Laplace inversion using the regularized positive exponential sum (REPES) algorithm described by Jakes [30]. Figure 5 shows that the residuals are smaller than in the previous cases and are randomly distributed. It should be noted that the values of $\Gamma$ at which the peaks of $A(\Gamma)$ are centered are coincident with those obtained from Eq. (9). Moreover, the relative weight of the different contributions to $g^{(2)}-1$ obtained from Eqs. (9) and (10) also agree within their estimated uncertainty. In all the cases a single-exponential decay is observed for temperatures far away from $T_c$, while a second process appears as $T_c$ is approached. The slow component becomes dominant as $\varepsilon\rightarrow 0$.

As an example Fig. 6 shows the decay rate of the fast mode for the samples corresponding to $[\mathrm{KCl}]=0.355M$ and

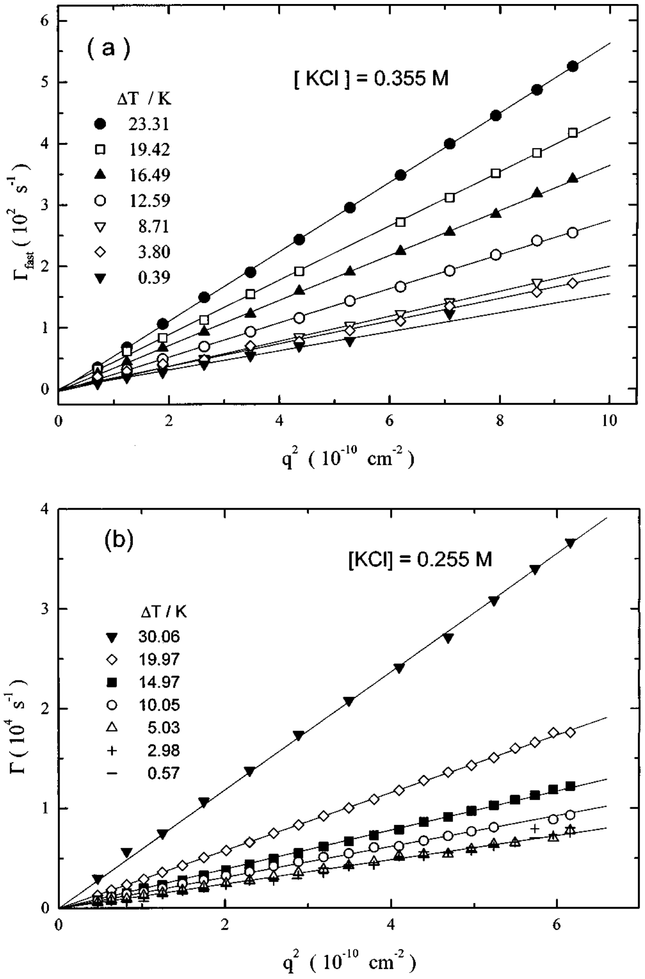

FIG. 6. Wave-number dependence of the decay of the fast component of the correlation function. The symbols correspond to different temperatures for the critical mixtures with different values of [KCl]: (a) 0.355*M* and (b) 0.255*M*. Notice the diffusive character of $\Gamma_{\mathrm{fast}}$ for all the temperatures.

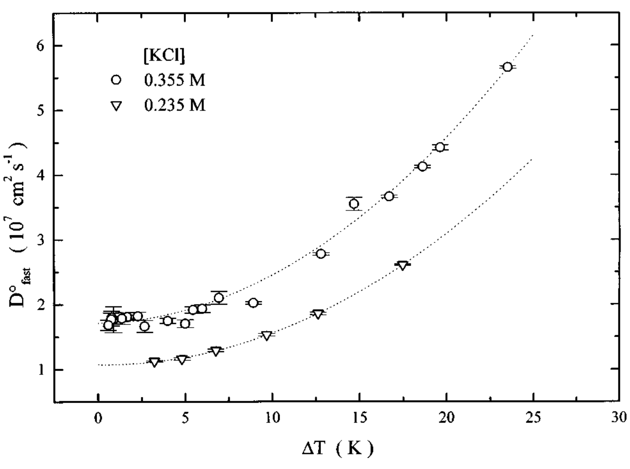

FIG. 7. Temperature dependence of the effective diffusion coefficient calculated from the fast contribution to the correlation function. The data correspond to the critical mixtures for two salt concentrations.

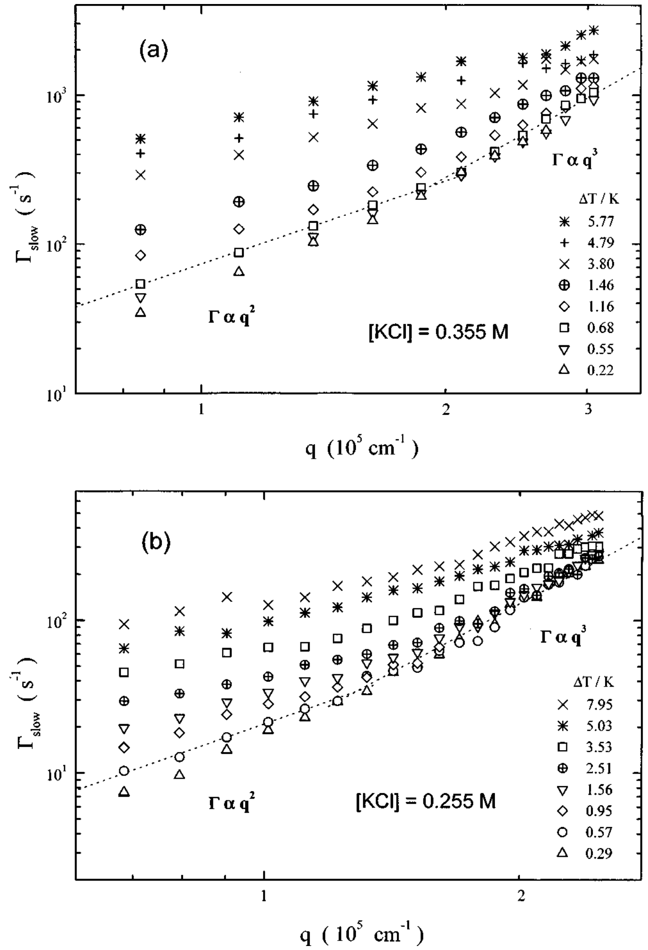

FIG. 8. Wave-number dependence of the decay rate corresponding to the slow contribution to the correlation function. The symbols correspond to different temperatures and to the critical mixtures with two different values of [KCl]: (a) 0.355*M* and (b) 0.255*M*. Notice the crossover from $q^2$ (i.e., diffusive) to $q^3$ behavior. The crossover point moves to higher values of $q$ with increasing the distance to $T_c$.

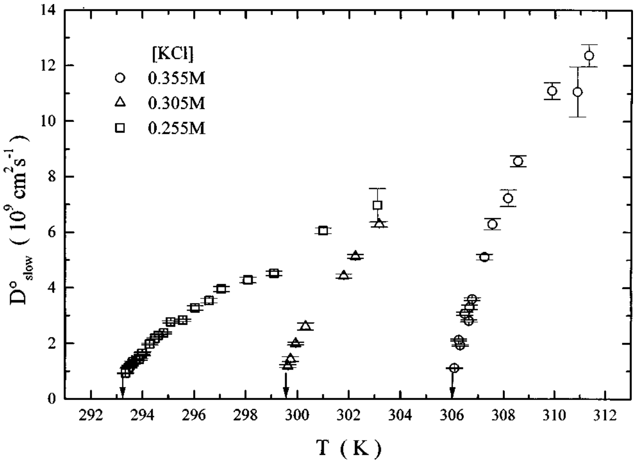

FIG. 9. Temperature dependence of the apparent diffusion coefficient corresponding to the slow contribution to the correlation function. The symbols correspond to data for the critical mixtures for different salt concentrations.

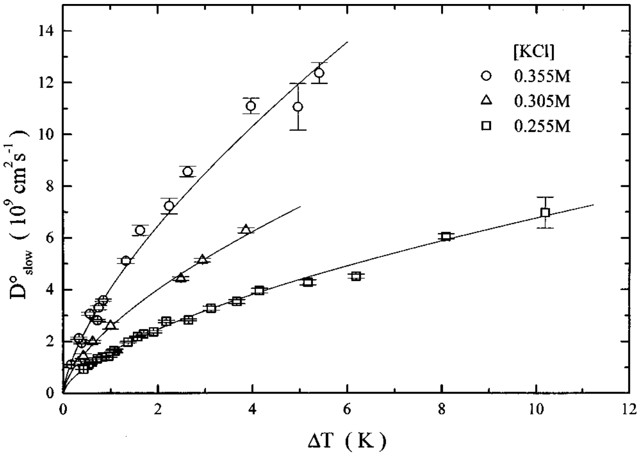

FIG. 10. Same as Fig. 9 expressed in terms of the distance to $T_c$. The lines represent simple scaling laws [Eq. (11)].

$0.255M$. It can be observed that the fast mode has a diffusive character through the whole $(q,T)$ experimental range for which two processes can be detected in the correlation function. We have also included the decay rate for the temperatures far from $T_c$ in which only one relaxation process is observed. This $q^2$ dependence agrees with the predictions of Anisimov *et al.* [20] and Onuki [29]. It is customary to define an apparent diffusion coefficient $D^0 \equiv [D(q=0)]$ related to $\Gamma(q=0,T)$ through $D^0 = \lim_{q\to 0}[\Gamma(q,T)/q^2]$. Figure 7 shows $D^0_{\mathrm{fast}}$ for the two samples with $[\mathrm{KCl}]=0.355M$ and $0.255M$. As it can be observed, for a given $T$, $D^0_{\mathrm{fast}}$ increases with decreasing [KCl]. Far from $T_c$, i.e., in the hydrodynamic region, this behavior is the one usually observed in noncritical ionic micellar systems, where an increase of the ionic strength favors the growth of the micelles [31].

Figure 8 shows $\Gamma^0_{\mathrm{slow}}$ for the same two samples. It can be observed that in all the cases $\Gamma^0_{\mathrm{slow}}$ presents a crossover from a $q^2$ to a $q^3$ dependence, similar to that expected for the contribution from concentration fluctuations [1]. This crossover takes place at higher $q$'s as the temperature of the system is further away from $T_c$. The crossover of $\Gamma^0_{\mathrm{slow}}$ has been predicted by Anisimov *et al.* [20].

Using $\Gamma^0_{\mathrm{slow}}$ one can define a diffusion coefficient $D^0_{\mathrm{slow}}$. Figure 9 shows $D^0_{\mathrm{slow}}$ for three of the systems studied; as it can be observed, the temperature dependence of $D^0_{\mathrm{slow}}$ is quite different from that of $D^0_{\mathrm{fast}}$ and is reminiscent of the one expected for the contribution of concentration fluctuations [32]. In fact, it is possible to describe $D^0_{\mathrm{slow}}$ by a scaling law

$$D^0_{\mathrm{slow}}(\varepsilon) = D^0_{s,0}\varepsilon^{-\nu^*}. \tag{11}$$

Figure 10 shows the excellent agreement of the fits. Values of $0.64\pm0.04 \leqslant \nu^* \leqslant 0.67\pm0.01$ have been obtained for all the samples studied. These values agree rather well with the 3D Ising value $\nu^* = \nu + z_\eta = 0.671$ for the diffusion coefficient corresponding to the concentration fluctuations. The values of $T_c$ obtained from the fits of $D^0_{\mathrm{slow}}$ to Eq. (11) agree with those reported in Table I.

Finally, Fig. 11 shows the results found for the ratio of the amplitudes for the fast and slow relaxation modes. This behavior is similar to that reported by Onuki for the $^3\mathrm{He}+^4\mathrm{He}$ system [29]. It must be recalled that in the limit of incompressible fluids, Anisimov *et al.* [20] predict $A_{\mathrm{fast}} \to 0$, which clearly does not correspond to the present experiments.

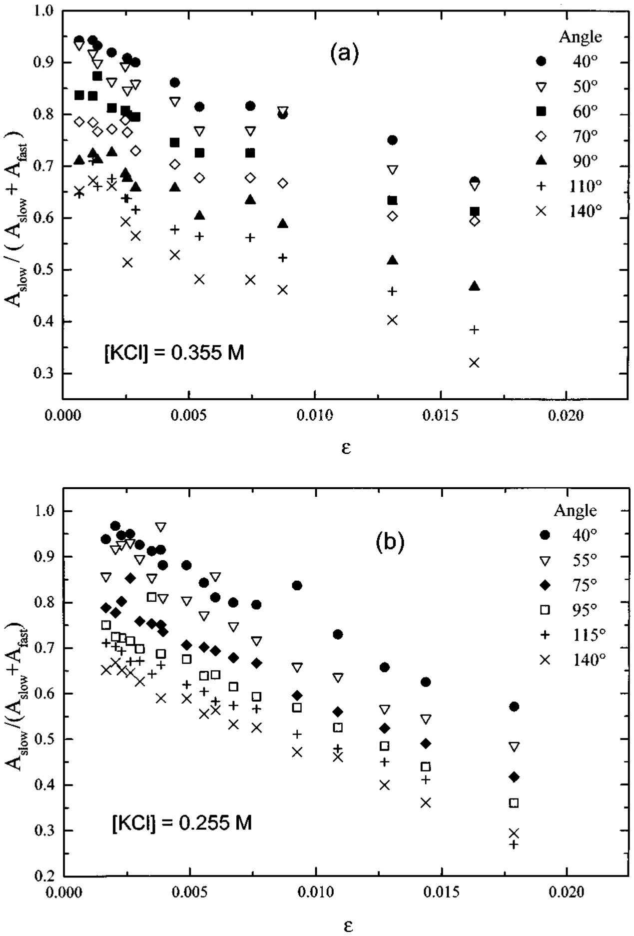

FIG. 11. Temperature and scattering angle dependence of the relative amplitude of the slow component of the correlation function. The symbols represent data for the critical mixtures corresponding to two salt concentrations. The lines are an aid to the eye.

## IV. DISCUSSION

### A. Theoretical background

For a real binary fluid, for which the coexistence curve is asymmetric with respect to the composition axis, the concentration fluctuations at the point $\overline{x}$ are described by the order parameter [19]

$$c(\overline{x}) = [\langle\rho_A\rangle\rho_B(\overline{x}) - \langle\rho_B\rangle\rho_A(\overline{x})]/\langle\rho\rangle^2, \tag{12}$$

where $\rho_A$ and $\rho_B$ are the mass densities of the two species. The binary fluid has an additional long-wavelength diffusive mode $u(\overline{x})$ that in mixtures plays a role analogous to the thermal fluctuation density in binary fluids near the vapor-liquid critical line. It is a linear combination of the $\rho_A$ and $\rho_B$ and the energy density $e(\overline{x})$, chosen such that $u(\overline{x})$ and $c(\overline{x})$ are orthogonal to each other, in the sense that their correlation functions vanish at long wavelengths in equilibrium. Note that $c(\overline{x}) = [\rho_B(\overline{x})/\rho_A(\overline{x})] - \rho_B/\rho$ for small deviations from equilibrium and $c(\overline{x})$ is loosely referred to as the concentration fluctuation. The binary fluid has two long-

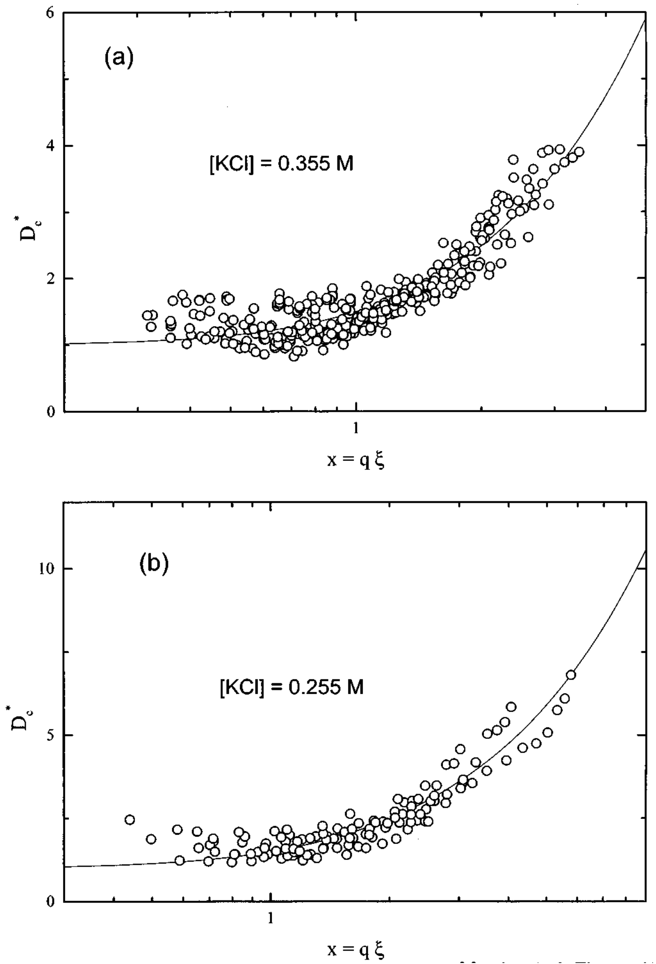

FIG. 12. Reduced diffusion coefficient associated with the concentration fluctuations. The continuous line corresponds to the Kawasaki function arising from the mode-coupling theory. Note that the $D_c^*$ have been calculated using independent experimental values of the viscosity and of the static correlation length. (a) and (b) correspond to two values of [KCl].

wavelength (i.e., $q\to 0$) diffusive modes. These two normal modes are the eigenvalues of the matrix equation

$$\overline{D}q^2=\overline{\Lambda}\,\overline{S}^{-1}q^2 \tag{13}$$

that can be explicitly written as

$$\begin{vmatrix} D_c & D_1 \\ D_2 & D_u \end{vmatrix} = \begin{vmatrix} \Lambda_{cc} & \Lambda' \\ \Lambda' & \Lambda_{uu} \end{vmatrix} \begin{vmatrix} S_{cc}^{-1} & 0 \\ 0 & S_{uu}^{-1} \end{vmatrix}, \tag{14}$$

with the elements of the transport matrix defined according to

$$\Lambda_{i,j}=\lim_{q,\omega\to 0}\frac{\omega}{iq^2}S_{i,j}(q,\omega), \tag{15}$$

where the $S_{i,j}$ are the elements of the static susceptibilities matrix. The indices $i$ and $j$ are either $c$ or $u$, thus making $\overline{S}$ diagonal. In the vicinity of the consolute point only $S_{cc}$ diverges strongly, while $S_{uu}$ does not. On the basis of the mode-coupling theories, it has been found that one of the eigenvalues of $\overline{\Lambda}$ diverges at $T_c$, while the other one remains finite [33]. Furthermore, the diverging part of $\overline{\Lambda}$ is simple $\Lambda_{cc}$, so that in the asymptotic critical region $\overline{\Lambda}$ and $\overline{S}$ may be simultaneously diagonalized.

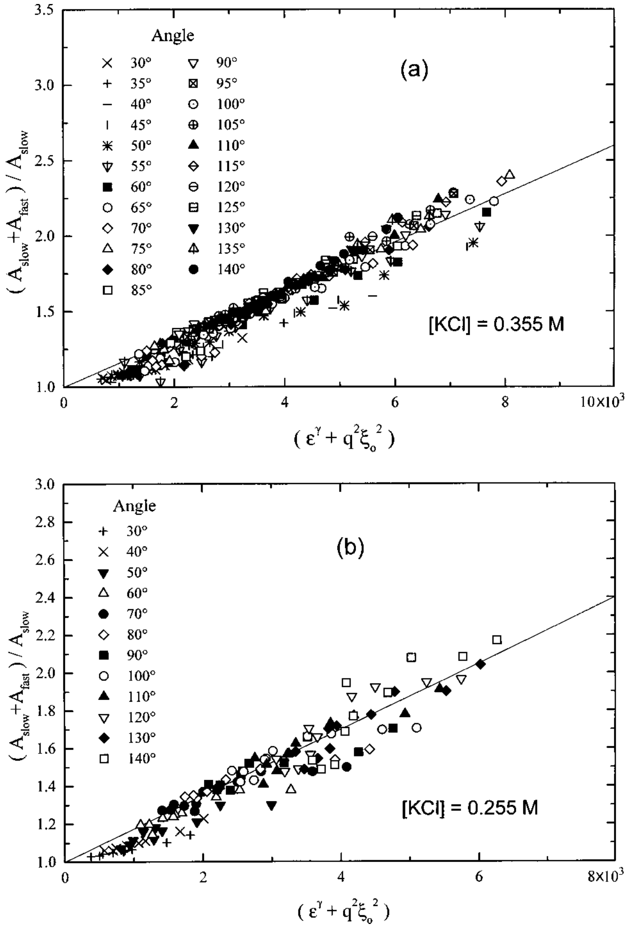

FIG. 13. Comparison of the relative weights of the amplitudes of the two relaxation modes with the predictions of Onuki's theory. (a) and (b) correspond to critical mixtures for two values of [KCl].

### B. Comparison with experiment

In order to compare the predictions of the mode-coupling theory with the experimental data, we have to calculate $D_c=\Lambda_{cc}/S_{cc}$ from the two contributions to the correlation function. The eigenvalues of Eq. (13) are given by

$$\lambda^2-(D_c+D_u)\lambda+D_cD_u-D_1D_2=0, \tag{16}$$

with solutions $\lambda_1=D_{\rm fast}(T)$ and $\lambda_2=D_{\rm slow}(T)$. Since the trace of $\overline{D}$ is invariant under a change of basis, it follows that

$$D_c(q,T)=D_{\rm fast}(T)+D_{\rm slow}(q,T)-D_u(q,T), \tag{17}$$

which relates the diffusion coefficient $D_c$ to the measured fast and slow modes and to a background $D_u$ [14].

As extensively discussed in the literature [34–36], the background corresponds to the value that the diffusion coefficient would have in the absence of any critical anomaly. Therefore, a smooth continuation is expected for the background contribution from the noncritical region to the critical point. The knowledge of the background contribution to any dynamic property near a critical point is fundamental since it is a significant part of the total value of such property [36]. We have calculated $D_u$ using the method described previously [18], which assumes that the background contribution has a diffusive character.

Once $D_u(q,T)$ is calculated, the values of $D_c(q,T)$ calculated from $D_{\text{fast}}$ and $D_{\text{slow}}$ can be compared with the theoretical prediction

$$D^* = D_c \frac{6\pi\eta\xi}{k_B T R_c} = K(x)/x^2. \tag{18}$$

In Eq. (18) $R_c = 1.027$, $x = q\xi$, and $K(x)$ is the Kawasaki function

$$K(x) = \tfrac{3}{4}[1 + x^2 + (x^3 - x^{-1})\tan^{-1}(x)]. \tag{19}$$

Figure 12 shows the experimental results for two KCl concentrations and the predictions of Eq. (19). The agreement is excellent, which clearly shows that the critical behavior of the concentration fluctuations for the present systems does not differ from that of the nonmicellar ones. The systematic deviations that appear at the lowest values of $q\xi$ correspond to points of isotherms with $\Delta T$ close to 8°, for which it is not always easy to obtain a precise separation between the two relaxation modes.

Onuki [29] has shown that in the limit of no coupling between modes, the relative weight of the slow mode is given by

$$\frac{A_{\text{slow}} + A_{\text{fast}}}{A_{\text{slow}}} = 1 + C(\varepsilon^{\gamma} + q^2 \xi_0^2), \tag{20}$$

with $\gamma = 2\nu = 1.24$. $\xi_0$ is taken from the static light-scattering experiments and $C$ is a system-dependent constant. Figure 13 shows that the amplitudes obtained from the experimental correlation functions conform to Eq. (20), which reinforces the previous suggestion [18] that in the DAC plus water plus KCl systems there is a high degree of decoupling between the critical and noncritical contributions to the experimental correlation functions. As in Fig. 12, one can observed similar systematic deviations for low values of the abscissa in Fig. 13. The origin of these deviations lies also in the difficulty of a neat separation of the two contributions to the correlation function when the relative weight of one of them is very small.

## V. CONCLUSIONS

The critical behavior of an ionic micellar system has been studied by static and dynamic light scattering. Decreasing the salt concentration brings the critical point near a surface of first-order transitions. Both the correlation length and the osmotic susceptibility data can be described by simple scaling laws with 3D Ising critical exponents irrespective of the proximity to the first-order transition, in accordance with the predictions of Fisher and Barbosa [23].

Single-exponential correlation functions are observed far from the critical temperature. However, as the critical temperature is approached, the correlation functions become bimodal and the slowest mode becomes dominant near $T_c$. This behavior is in agreement with the predictions of the asymmetric $H$ model of Hohenberg and Halperin [19]. The background and critical contributions have been obtained from the two relaxation modes. The apparent diffusion coefficient calculated from the background contribution shows a smooth continuity from the values calculated far from $T_c$ from the decay rate that characterize the monomodal correlation functions.

The decay rate of the concentration fluctuations shows a crossover from a diffusive (i.e., $q^2$) behavior to a $q^3$ one. The apparent diffusion coefficient corresponding to the critical fluctuations is described very accurately by the predictions of the mode-coupling theory. These conclusions do not depend on the salt concentration, i.e., on the proximity to the surface of first-order transitions. The relative amplitudes of the two relaxation modes follow the predictions of Onuki [29], which suggest that the coupling between the two modes is very weak in the DAC+water+KCl system.

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