International Journal of Thermophysics, Vol. 20, No. 6, 1999

Nonexponential Behavior Near the Critical Point of an Ionic Micellar System[1]

A. Martin,[2] A. G. Casielles,[2] F. Ortega,[2, 3] and R. G. Rubio[2]

The coexistence curves of the system dodecylammonium chloride + water + KCl have been obtained for different salt concentrations. We found that the asymptotic behavior of the order parameter can be describe using extended scaling and the usual Ising value for the $\beta = 0.325$ exponent. The static light scattering data for the critical composition are also compatible with the Ising value $\nu = 0.63$. Dynamic light scattering results have been obtained near the liquid-liquid critical point. The correlation functions have been found to be single-exponential for temperatures well above critical, while a second decay process at longer times becomes evident for $T - T_c < 4$ K. These correlation functions can be fitted to the sum of two exponential functions. The diffusion coefficient associated with concentration fluctuations has been calculated from both relaxation modes. It has been analyzed in terms of the predictions of the mode-coupling theory. These results, together with correlation length and viscosity data, are in good agreement with the calculations.

KEY WORDS: coexistence curve; critical phenomena; light scattering; micellar solution.

1. INTRODUCTION

The behavior of micellar systems near a critical point has attracted much attention in the last years [1]. Although some experiments lead to critical exponents different to those of the three-dimensional (3D) Ising model, recent experimental work has shown that micellar systems belong to the Ising class [2].

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[1] Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22-27, 1997, Boulder, Colorado, U.S.A.

[2] Departamento de Quimica Fisica I, Facultad de Ciencias Quimicas, Universidad Complutense, 28040-Madrid, Spain.

[3] To whom correspondence should be addressed.

0195-928X/99/1100-1765$16.00/0

Ionic micellar systems are particularly interesting. They are actually ternary systems containing water, a salt, and a surfactant. In the case of liquid–liquid equilibrium, it is generally found that the salt concentration is the same in the coexisting phases; in this case, the system can be seen as pseudobinary. Furthermore, by tuning the ionic strength, one can modify the phase behavior of the system. More specifically, one can reduce the difference between the critical point temperature and the Krafft temperature (T_k), where the pure surfactant solid is in equilibrium with the solution. In the limit $|T_c - T_k| \to 0$, the critical point becomes a critical end point (CEP). Recent experiments and theoretical work indicate that the proximity of a CEP does not affect the critical behavior of the system undergoing a second-order phase transition [3, 4].

In most cases simple scaling equations have been used to describe the experimental data [2, 5, 6]. Both static and dynamic light scattering results for micellar systems lead to values of the critical amplitude of the correlation length, ξ, of the order of 1 to 2 nm, a value which is larger than the one found for mixtures of simple liquids [5, 6]. Since the range of validity of simple scaling laws depends on $1/\xi^6$ (Ginzburg's criterion), it seems reasonable to expect it to be smaller than in simple liquid mixtures [7]. The use of simple scaling laws outside their range of validity can lead 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 small values of ($\varepsilon = |T - T_c|/T_c$), for which simple scaling holds for mixtures of simple fluids.

The critical dynamics of simple binary mixtures has also been studied in detail, and the experimental results show remarkable agreement with the predictions of mode-coupling and renormalization group theories of dynamic critical phenomena [8]. As described by Hohenberg and Halperin [9], the key factor for the critical slowing-down of the order parameter fluctuations is the nondissipative coupling between the order parameter and the transverse part of the momentum density.

For binary liquid mixtures, the decay of the order parameter fluctuations $\Gamma(q)$ is most frequently obtained from photon correlation spectroscopy experiments. Although the theory predicts the existence of two relaxation modes near a consolute point [9], there is a very limited number of experiments reporting non-single-exponential correlation functions $\Gamma^{(2)}(q, t)$ [10–12].

In order to shed light to some of the questions mentioned above, we have chosen an ionic micellar system: dodecylammonium chloride (DAC) + water + KCl. The system shows an upper critical solution temperature (UCST). This critical temperature increases with increasing [KCl], but the critical concentration does not seem to change significantly and it is kept

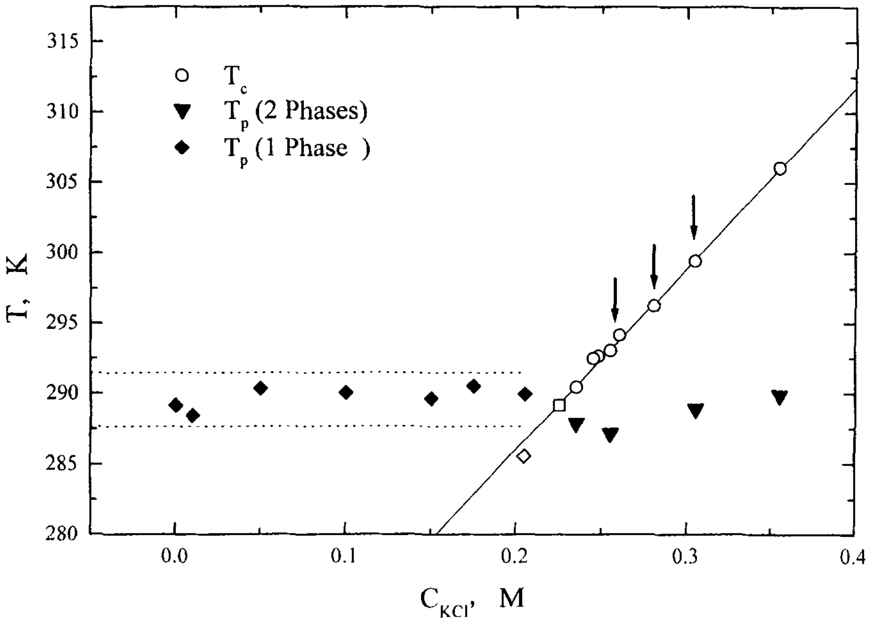

Fig. 1. Critical (T_c) and Krafft (T_K) temperatures for the DAC + water + KCl systems as a function of the salt concentration, [KCl]. The open circles represent the phase separation temperature. The solid line is a linear fit. The open square represents the approximate coordinates of the CEP. Filled symbols are the Krafft temperatures.

constant around 1.0 wt% of DAC. Figure 1 shows the relative position of the critical line for different salt compositions with respect to the Krafft line. The arrows in Fig. 1 show the three path concentrations that were chosen in order to carry out both the static and the dynamic light scattering measurements. Some off-critical compositions were also measured in order to test the predictions of the linear model.

The rest of the paper is organized as follows: Section 2 gives some details on the experimental procedure and the data and the methods followed for the data analysis, and a discussion of the results is given in Section 3.

2. EXPERIMENTAL

The coexistence curves at 0.1 MPa were obtained by the point-by-point method described elsewhere [13]. The composition of the samples was determined by weight with a precision of ±0.5 mg. The samples were placed in a water bath, and the temperature was kept constant and measured to within 1 mK.

The effect of pressure on the T_c was measured with a technique described previously [14]. The precision was 0.01 MPa over the complete pressure range.

Both static and dynamic 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 (±0.5 mK), 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 platinum resistence thermometer.

DAC was synthesized and purified as in previous work [15]. The water was double distilled and deionized (Milli-Q; $\Omega > 18$ MS) KCl was Carlo Erba RPE, purity >99%. The mixtures were also prepared by weight with the same mentioned precision. All of the light scattering samples were filtered through a 0.2-μm-pore size membrane just before use.

3. RESULTS AND DISCUSSION

3.1. Coexistence Curves

We measured the coexistence curves of the system at different salt concentrations. Figure 2 shows the phase separation temperature versus the weight fraction of DAC. For a binary mixture near an upper critical solution point temperature (UCST), the shape of the coexistence curve according to the renormalization group (RG) can be described as

$$\Delta\lambda = B_0 \varepsilon^{\beta}(1 + B_1 \varepsilon^{\Delta} + B_2 \varepsilon^{2\Delta} + \cdots) \tag{1}$$

where $\beta = 0.325 \pm 0.001$ and $\Delta = 0.50 \pm 0.02$ are critical exponents; $\varepsilon = (T - T_c)/T_c$; and B_0, B_1, and B_2 are critical amplitudes.

Table I collects the results of the fit with Eq. (1). As an example, Fig. 3 shows the results for [KCl] = 0.305 and 0.280*M*. It can be seen that there is fairly good agreement between the data and Eq. (1) with fixed values of the critical exponents. The range of validity of simple scaling is small ($\varepsilon < 10^{-4}$) compared with other nonmicellar systems [16], and it seems to decrease as the CEP is approached. Any attempt to fit the curves outside that range leads to effective β values that may be *even larger* than the mean field value.

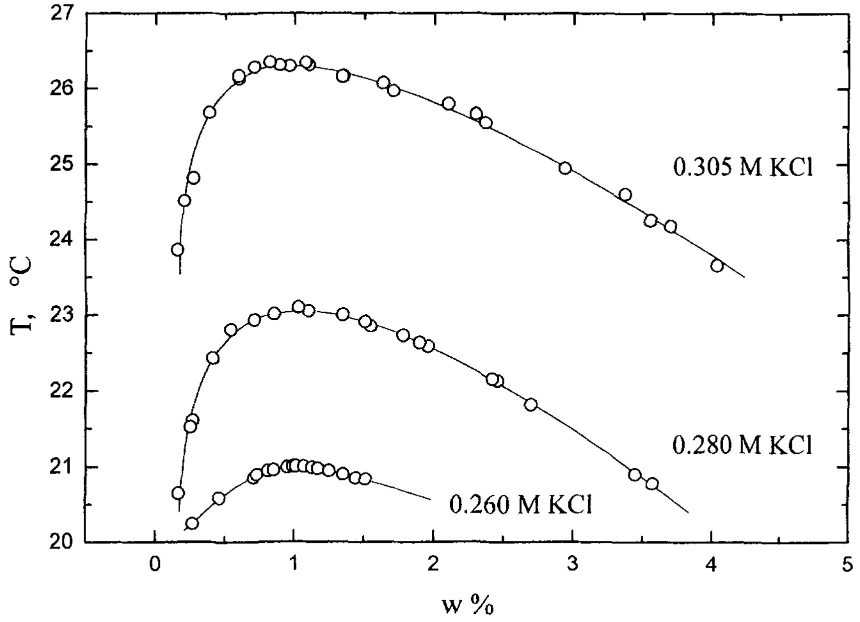

Fig. 2. Coexistence curves for the system DAC + water + KCl as a function of the salt concentration. Open circles are the experimental points. The solid curves are the fits to Eq. (1).

The dependence of T_c on the pressure was studied. In all cases a linear behavior was found, with a slope $dT_c/dp = (-20 \pm 1)$ mK · bar^{-1}, which is independent of the salt concentration. This value, together with the critical amplitudes, the results of static light scattering, and the density measurements, allows us to confirm the validity of the two-scale universality hypothesis for ionic micellar systems, obtaining a value of $R_\xi = 0.27 \pm 0.03$.

Table I. Results of the Fit of the Order Parameter ($\Delta\lambda = \Delta\omega$) of the System DAC/KCl/$H_2O$ Using Eq. (1)

[KCl] (M)	T_c (K)	B_0	B_1	B_2
0.305	299.448 ± 0.004	6.32 ± 0.03	29.59 ± 0.16	−105 ± 2
0.280	296.202 ± 0.003	6.44 ± 0.02	25.42 ± 0.13	−89.8 ± 1.4
0.260	294.155 ± 0.002	2.73 ± 0.01	105.0 ± 0.5	−291 ± 12

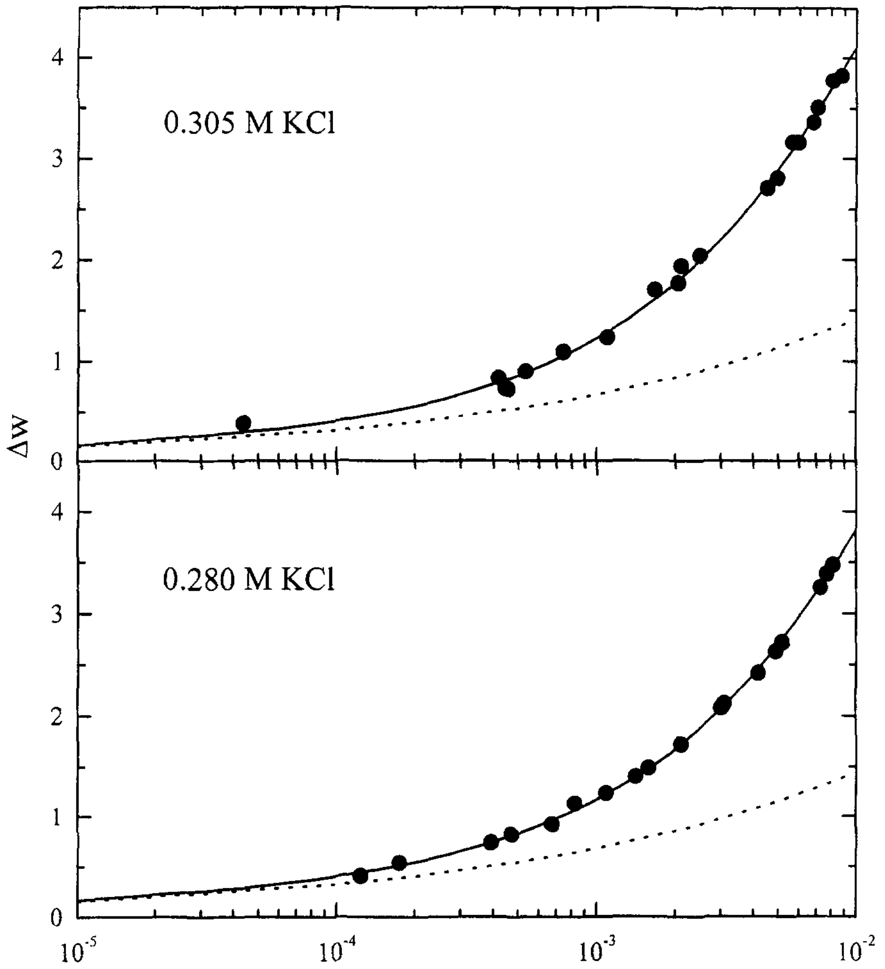

Fig. 3. Order parameter for the system DAC + water + KCl. Symbols are experimental data. The dashed lines represent fits to simple scaling. Solid lines represent the fits to Eq. (1).

3.2. Static Light Scattering

The total scattered intensity data as a function of the scattering vector for mixtures of critical composition were analyzed in terms of the Ornstein–Zernike approximation [17],

$$\frac{I_s(q)}{I_0} = \frac{AT\chi_T}{1+q^2\xi^2} \tag{2}$$

Table II. Results of the Fit of the Correlation Length [$\xi(T)$] of the System DAC/KCl/H_2O using an Equation Similar to Eq. (1)

[KCl] (M)	$(T_c - T)_{\max}$ (K)	ξ_0 (nm)	ν	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	0.631 ± 0.010	299.331 ± 0.008
0.255	3.8	2.22 ± 0.05	0.624 ± 0.005	292.849 ± 0.005

where $q = 4\pi n \sin(\Theta/2)/\lambda$, λ is the wavelength of incident light in vacuum, n is the refractive index of the sample, Θ is the scattering angle, I_0 is the incident light intensity, T is the absolute temperature, ξ is the correlation length, and χ_T is the osmotic susceptibility. The A constant accounts for the optical properties of the mixture.

The temperature dependences of χ_T and ξ are described by the power laws

$$\begin{aligned} \xi &= \xi_0 \varepsilon^{-\nu} \\ \chi_T &= \chi_{T,0} \varepsilon^{-\gamma} \end{aligned} \tag{3}$$

where ν and γ are universal critical exponents, and ξ_0 and $\chi_{T,0}$ are the characteristic critical amplitudes. After correcting the data for turbidity, we follow the method described by Sinn and Woermann [18] to obtain ξ and χ_T (in arbitrary units).

The fits of the ξ and χ_T data using Eq. (3) up to $\varepsilon \leqslant 10^{-3}$ lead to the values of critical exponents which are collected in Tables II and III. These values of ν and γ are in good agreement with the 3D-Ising prediction ($\gamma = 1.241$ and $\nu = 0.63$) for all the critical mixtures.

The amplitude ξ_0 is similar to that found in other micellar systems [6, 19] and is one order of magnitude larger than the values usually found for binary mixtures of simple liquids. The range of ε for which constant values of the critical exponents ν and γ are found seems to be similar to the range

Table III. Results of the Fit of the Osmotic Susceptibility [$\chi_T(T)$] of the System DAC/KCl/H_2O Using an Equation Similar to Eq. (1)

[KCl] (M)	$(T_c - T)_{\max}$ (K)	$\chi_{T_0} \cdot 10^{-4}$ (a.u.)	γ	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
0.255	3.8	4.60 ± 0.09	1.19 ± 0.01	292.840 ± 0.004

found for mixtures of simple liquids, and hence, apparently, it is larger than the range obtained from the order parameter data.

In addition to the previous experiments some samples corresponding to off-critical compositions were also measured. This allows us to test the predictions from the so-called linear model [20]. According to this model one can describe the correlation length as follows:

$$\xi^2 = \xi_0^2 \frac{V_{\mathrm{m}}}{V_{\mathrm{m,c}}} \left[\frac{w_c(1-w_c)}{w(1-w)}\right]^2 \frac{r^{-\gamma}}{1+d_2\theta^2} \tag{4}$$

where V_{m} and $V_{\mathrm{m,c}}$ are the molar volumes of the off-critical and critical mixtures, respectively, d_2 is a universal constant, and r and θ are parametric variables that we have calculated from the critical temperature and composition. Figure 4 shows that the results for the three isopleths for [KCl] = 0.305*M* collapse on a single straight line, confirming the validity of Eq. (4). Similar results were found for other values of [KCl].

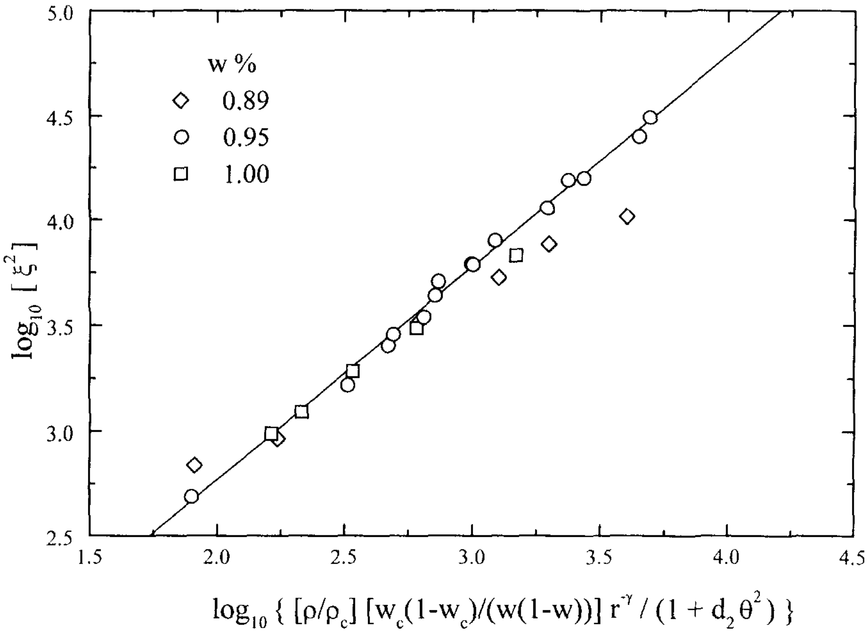

Fig. 4. Test of the validity of Eq. (4) (linear model equation of state) for describing the off-critical results in the vicinity of the critical point for [KCl] = 0.305*M*. Symbols correspond to different weight fractions of DAC (percentage).

3.3. Dynamic Light Scattering

Dynamic light scattering allows us to measure the temporal autocorrelation function for the thermally induced concentration fluctuations. Experimentally, we obtain the intensity–intensity autocorrelation function $g^{(2)}(t)$. For an ergodic system, $g^{(2)}(t)$ is related to the field–field correlation function, $g^{(1)}(t)$, through the equation

$$g^{(2)}(t) - 1 = \beta \; |g^{(1)}(t)|^2 \tag{5}$$

Figure 5 shows the normalized intensity correlation function $(g^{(2)} - 1)$ for some temperatures far from and near T_c and at an scattering angle $\Theta = 90°$. The data collected in this figure show two regimes. Far from the critical temperature the experimental correlation functions are single exponentials. However, as T approaches T_c, the correlation functions can

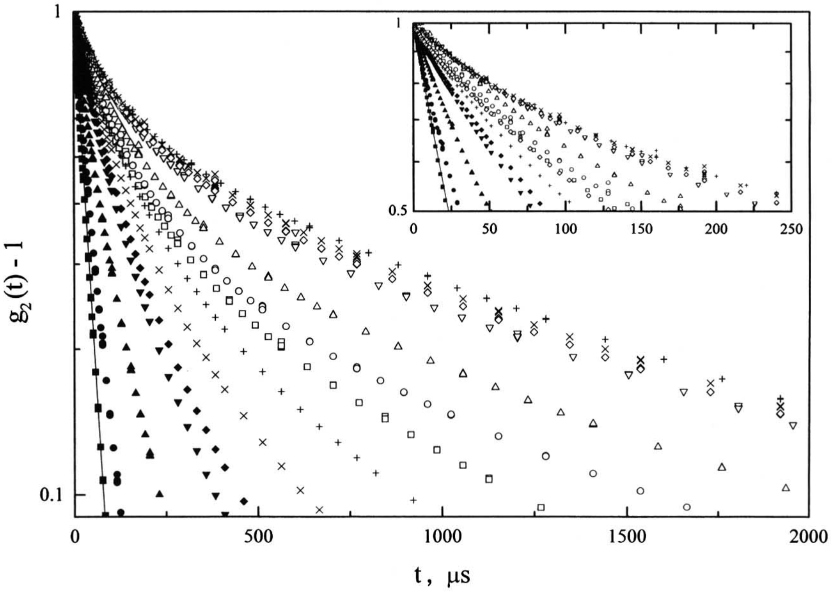

Fig. 5. Experimental correlation functions for the DAC + water + KCl (0.305*M*) system at different temperatures and a fixed scattering angle of 90°. Only some of the experimental data are shown for the sake of clarity. Note that for temperatures far from the critical value, the correlation function shows a single-exponential decay, while near T_c there are two decays. The inset shows the short-time behavior in detail. The line corresponds to the fit to Eq. (9) for $\Delta T = 18.28$ K. ΔT (K): ■, 18.28; ●, 13.41; ▲, 8.53; □, 3.83; ○, 2.92; △, 2.46; ▽, 0.98; ◇, 0.60; ×, 0.40; + 0.29. The data shown for ΔT (K) ≈ (▽) 12.618, (◆) 7.63, (×) 7.09, and (+) 6.01 are those obtained at the laboratory of Prof. D. Woermann (Cologne, Germany).

no longer be described by a single-exponential function. Following the procedure of Rouch et al. [21], we tried to fit the results using a stretched exponential, but the residuals still showed systematic trends. Therefore, we used a double-exponential as did Hair et al. [10] and Onuki [22]:

$$g^{(2)}(t) - 1 = \beta[A_{\text{fast}} e^{-\Gamma_{\text{fast}} t} + A_{\text{slow}} e^{-\Gamma_{\text{slow}} t}]^2 \tag{6}$$

where Γ_{fast} and Γ_{slow} are the decay rates and A_{fast} and A_{slow} are the corresponding amplitudes.

In order to rule out that the fast contribution appearing in our results near T_c is due to multiple scattering, we carried out measurements for $|T - T_c| < 0.3$ K using cells with three path lengths: 25, 10, and 3 mm. We found that within the experimental uncertainty there was no significant change in the relative weight of the two relaxation processes.

The decay rates (Γ_{fast} and Γ_{slow}) obtained by fitting the experimental autocorrelation function using Eq. (6) are shown in Fig. 6. It can be observed that the fast mode has a diffusive character through the whole (T, q) experimental range for which two processes are observed. For the sake of comparison, Fig. 6a also shows the decay rate for the temperature farthest away from T_c. The q^2 dependence of Γ_{fast} allows one to define a diffusion coefficient $D_{\text{fast}}(T, q) = \Gamma_{\text{fast}}(T, q)/q^2$. It must be remarked that there is a smooth transition between the diffusion coefficient D° obtained from the single-exponential correlation functions measured at temperatures far away the critical one and $D_{\text{fast}}(T)$ for the temperature interval in which two processes can be separated.

Figure 6b shows that Γ_{slow} presents a diffusive character only for low q's. The maximum value of q for which a q^2 behavior is observed decreases as T approaches T_c. For high values of q, Γ_{slow} shows a q^3 dependence. This kind of crossover has been extensively discussed in the literature for the decay rate of critical fluctuations [22].

It should also be mentioned that the values of the decay rates corresponding to the fast peaks are similar to those corresponding to the dynamics of micelles in noncritical mixtures, i.e., far from T_c. On the other hand, the values of Γ_{slow} are of the same order of those usually assigned to the concentration fluctuations in near-critical micellar systems.

The mode-coupling theory predicts that the decay rate of the critical fluctuations can be described to the lowest order in the solutions as

$$\Gamma_c(q, T) = q^2 D_c K(x)/x \tag{7}$$

where $D_c = R_c k_B T/(6\pi\eta\xi)$ and $K(x) = (3/4)[1 + x^2 + (x^3 - x^{-1}) \tan^{-1}(x)]$ is the Kawasaki universal function with $x = q\xi$. In the preceding expressions, $R_c = 1.027$.

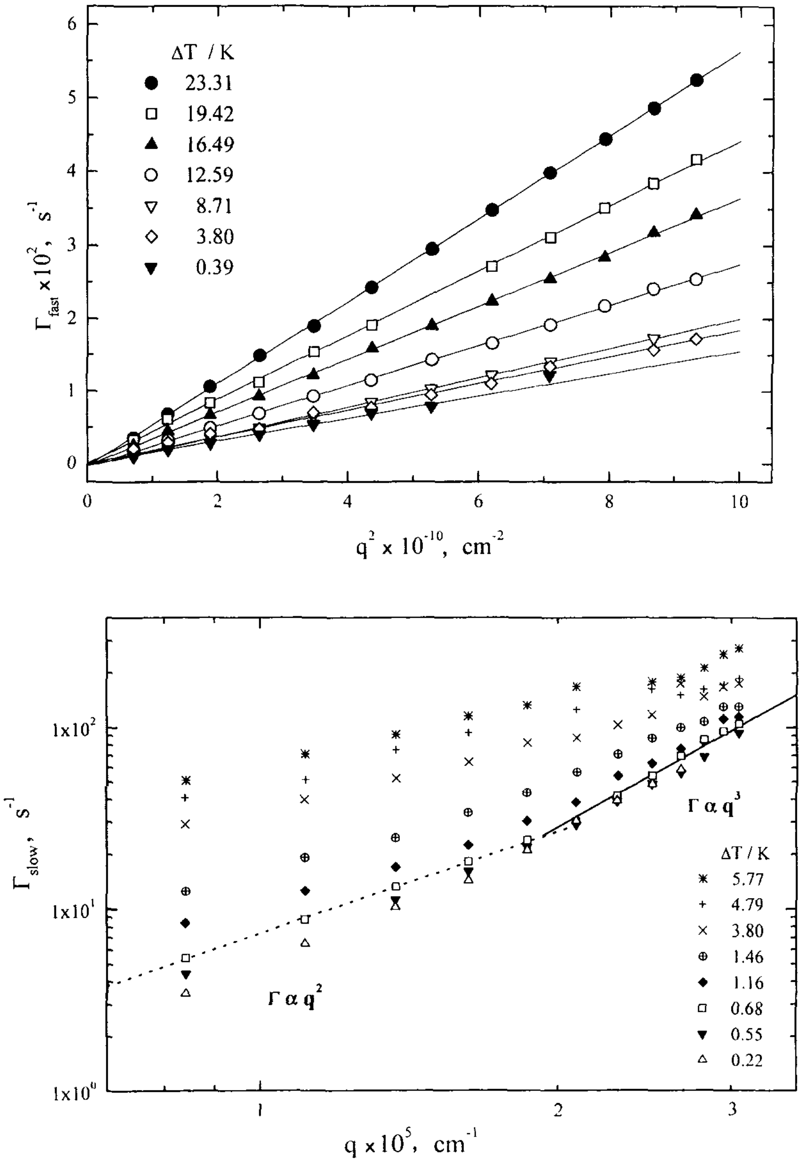

Fig. 6. (a) Decay rate corresponding to the fast relaxation mode for two temperatures within the interval for which two modes can be resolved. For the sake of comparison the results for a temperature far from critical (where single-exponential behavior is found) are also included. (b) Decay rate corresponding to the slow relaxation mode. Note that, within the experimental range, there is a crossover from a q^2 to a q^3 behavior. Lines are aids for the eye.

In order to probe the validity of Eq. (7) we must calcute D_c. D_c is related to the measured fast and slow modes and to a background contribution D_u, which corresponds to the value that the diffusion coefficient would have in the absence of any critical perturbation. We can calculate D_u, knowing that due to the critical slowing-down, D_c should be zero at T_c. With the value of D_u at T_c and assuming that it does not depend on q (pure diffusive character), we can compute D_c for all the other temperatures and q's. We have described in detail this procedure in a previous paper [24].

The calculated values of D_c can be compared with the predictions of the mode-coupling theory. To do so, it is customary to reduce the diffusion coefficient associated with the decay rate as

$$D^* = D_c(6\pi\eta\xi/k_B TR_c) = K(x)/x^2 \qquad (8)$$

Figure 7 shows the fairly good agreement between the results and the predictions given by Kawasaki's function.

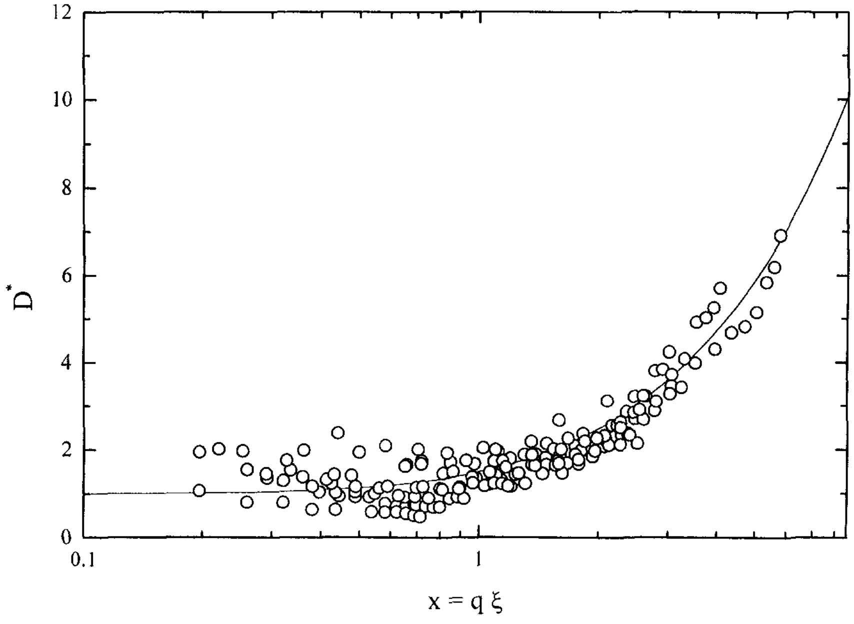

Fig. 7. Reduced diffusion coefficient associated with the concentration fluctuations. The solid line corresponds to the Kawasaki function arising from the mode coupling theory. Note that the D^* has been calculated using independent experimental values of the viscosity and of the static correlation length.

It is worth noting that we found that D_{fast} is much larger than D_{slow}. As a consequence, over most of the T and q values, we have $D_u \approx D_{\text{fast}}$ and therefore $D_c \approx D_{\text{slow}}$ (this is so from a numerical point of view, but from the physical point, both modes contain part of the critical fluctuations). A complete decoupling of the hydrodynamic modes would allow one to interpret the two contributions in Eq. (6) directly in terms of critical and noncritical contributions, a result similar to that of Onuki [22] for $^3\text{He} + {}^4\text{He}$ mixtures. It is not possible to establish a relationship between the high degree of decoupling of the modes and the proximity to the CEP.

ACKNOWLEDGMENTS

This work was supported in part by CICYT, under Grants MAT95-1686E and PB-96/609, and by Fundación Areces. We are grateful to Servicio de Espectroscopia for making the light scattering facility available.

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