PHYSICAL REVIEW E VOLUME 49, NUMBER 2 FEBRUARY 1994

Dynamic critical phenomena in water-butoxyethanol mixtures studied by viscosity and light-scattering measurements

D. Lombardo and F. Mallamace*
Dipartimento di Fisica dell'Università di Messina, I-98166 Vill. S.Agata, Cassella Postale 55, Messina, Italy

N. Micali
Istituto di Tecniche Spettroscopiche del Consiglio Nazionale delle Ricerche, I-98166 Vill. S.Agata, Cassella Postale 55, Messina, Italy

G. D'Arrigo
Dipartimento di Fisica, Università di Roma La Sapienza, Piazza Aldo Moro 2, I-00185 Roma, Italy

(Received 13 April 1992; revised manuscript received 1 March 1993)

We have used shear viscosity and dynamic light scattering to study the critical behavior in a water-butoxyethanol (C_4E_1) mixture as a function of temperature. The data of viscosity and of the relaxation rate are analyzed in terms of the mode-coupling theory, taking into account background effects on the transport coefficient. From experimental data we measure both the short-range correlation length ξ_0 and the Debye cutoff length q_D^{-1}, whose values confirm the micellarlike structural picture proposed for such a water-alcohol mixture. Furthermore, we find evidence for a crossover from critical to single-particle behavior in the light-scattering data. The crossover temperature T_x is found to be such that $q_D\xi(T_x)\simeq 1$. For both the measured quantities, i.e., viscosity and linewidth, the parameter q_D plays the determinant role in the critical dynamics of the system.

PACS number(s): 64.70.−p, 66.20.+d, 82.70.−y

I. INTRODUCTION

Simple monohydric alcohols (C_nE_0) and alkoxyethanols (C_nE_1) constitute the short-chain polyoxethylene alkyl ethers $C_nH_{2n+1}(OCH_2CH_2)_mOH$ (C_nE_m) that for large m and n are well known nonionic surfactants, which in water solutions form a micellar phase [1]. Furthermore, adding a mineral oil, they show a complex phase behavior which includes microemulsions. Many experimental studies, such as viscosity [2], density and specific heat [3], mutual diffusion coefficients [4], and ultrasound propagation (absorption and velocity) [5,6], performed in water solutions of such short-chain alcohols, show peculiar behaviors (in many physical properties) that can be associated with the formation of supramolecular aggregates. In particular, depending on the carbon chain length the C_nE_0 and C_nE_1 systems provide a sequence of amphiphiles ranging from those that form simply associating nonideal solutions to those that form structured liquids, such as micelles and liquid crystals [7,8]. On these bases, careful investigations of these systems appear to be very useful in order to clarify the effect of amphiphilic molecule length (and in particular the requirement of a minimal length) on the formation of surfactant structures.

Several experiments have given indications of the surfactantlike behavior of the simplest ethoxylated alcohols as C_4E_1 (butoxyethanol) and C_6E_2 [8,9]; in fact, the presence of micellarlike structures in water mixtures above an amphiphile mole fraction X of about 0.018 has been conjectured. The behavior of the partial molar heat capacity [9] of a C_4E_1-water solution (with a well-defined maximum at a concentration of C_4E_1 of about 0.018) is similar to those observed in water solutions of known surfactants (e.g., sodium octanoate and sodium dodecyl sulfonate) at their critical micellar concentration (CMC) [9]. This characteristic concentration, above which aggregation phenomena are present, has been also found by ultrasonic experiments. For $X=0.018$, sound-velocity data show well-defined peaks [10,11] and the ultrasonic absorption data point out two relaxation processes: one connected to the amphiphilic association (relaxation frequency $f<5$ MHz) and the other one to the amphiphile-water hydrogen bonding ($f\sim 40$ MHz). Such a low relaxation frequency was observed only in alkoxy ethanols of hydrophobic tail length C_4 or longer. The formation in water-C_4E_1 solutions of micellar structures is also supported by both a phase diagram and a CMC-like curve quite similar to those observed in long C_nE_m nonionic surfactant solutions. As far as the phase diagram is concerned, C_4E_1 presents a closed loop of solubility analogous to that of C_nE_m compounds, with an upper critical and a lower critical solution temperature (LCST). In fact, upon increasing T, it shows a phase transition with a lower critical solution temperature T_C at critical concentration X_C.

However, direct confirmations of the presence of micellar aggregates in this mixture have been recently obtained by small-angle neutron scattering (SANS) [12] and light-

---

*Author to whom correspondence should be addressed. Electronic address: MALLAMAC AT IMEUNIV (EARN Bitnet) scattering (elastic and quasielastic) data [13] obtained as a function of temperature ($-10 \leq T \leq 45\,^{\circ}\mathrm{C}$) in the concentration range $0.015 \leq X \leq 0.09$ (X is expressed as molar fraction of butoxyethanol) where ultrasonic attenuation exhibits peak values. On the other hand, viscosity [14] and Brillouin [15] measurements performed in the same experimental conditions, T and X, support this (structural) point of view.

Starting from these results, and having found the miscibility curve and the lower critical solution temperature, we report here a study of the behavior of the shear viscosity and of the relaxation rate of the fluctuations $\Gamma(k,t)$ carried out by means of dynamic quasielastic light scattering (QELS) in the critical region. The aim is to point out that the amphiphilic character of the butoxyethanol (C_4E_1), with well-defined micellar structures (whose dimensions, as shown by SANS, increase slowly with temperature), plays a decisive role in controlling the critical dynamics in the whole temperature range explored. The data analysis is performed in the framework of the mode-coupling theory of critical phenomena [16–19], which emphasizes the effects of the background contribution on the transport coefficient [20–24]. Furthermore, according to this model, we stress that the Debye cutoff parameter q_D, which can be measured far from the critical region, governs in fact all the critical dynamics of the water-butoxyethanol (C_4E_1) mixture, as it represents the significant parameter for both the divergence of the viscosity and the order-parameter correlation time.

In addition, considering the obtained value of q_D^{-1} and the presence of micellar structures, we clarify the behavior already pointed out by ultrasound data [15,25] which, differently from molecular LCST binary mixtures (where the critical divergence manifests at 15–20 °C below T_C), in our solution this anomaly emerges at a few degrees ($\sim 5\,^{\circ}\mathrm{C}$) from T_C. Usually, for a pure fluid or in a binary molecular mixture the short-range correlation length ξ_0 and the Debye cutoff length q_D^{-1}, governing the critical behavior of the shear viscosity, have the same order of magnitude (a few angstroms) comparable to the range of the intermolecular potential [26,27]. Instead, it has been shown that in microemulsions [28] and in micellar solutions [29] ξ_0 can be fairly large (some tens of angstroms) and q_D^{-1}, according to the Fisher theoretical model [30], should be of the order of the size of the micellar droplets. In fact, in this model the Debye cutoff length is closely linked to the diameter of the micelles (for our system ~ 20 Å; a value obtained from SANS data [12] far from the critical region). As in the case of a critical binary mixture, $q_D\xi$ can be deduced from viscosity data by extrapolating to the critical region data obtained in the noncritical one [26,31]. In a critical system (binary, such as an ordinary mixture or a micellar system, or ternary, such as a three-component microemulsion) close to the critical point, the long-range correlation length ξ diverges like $\xi = \xi_0 \epsilon^{-\nu}$, where $\epsilon = |T - T_C| / T_C$ is the reduced temperature and ν is the critical exponent (for microemulsions ν is replaced by ν^*, a renormalized exponent). In particular, in a critical micellar suspension, when ξ is such that $\xi q_D \gg 1$, the system should behave like an ordinary critical liquid mixture close to a plait point, with $x = k\xi$ the relevant scaling variable, where k is the wave number of the order-parameter fluctuations. When the system is far from the critical temperature, ξ and q_D^{-1} may acquire the same order of magnitude, and thus the critical phenomenon ceases to exist. In this regime, the system (microemulsions or micellar solutions) behaves like a disperse solution consisting of interacting droplets whose dynamics is driven by Brownian motion. In agreement with the result obtained for ternary systems (microemulsions) this can be named the "crossover phenomenon." For temperatures around and below this crossover, x will no longer play the role of a scaling variable, temperature being the most important parameter, and the dynamic behavior of the system can be represented by an ordinary colloidal suspension. Close to the critical region, above the crossover, the transport coefficient can be written as a sum of the regular background contribution, which the system shows far from the critical region, and a nonlocal frequency-dependent critical contribution. In order to specify the micellar picture proposed for our system from the above experimental results, we explore a large temperature domain (more than 30 °C below T_C) with the idea that the observation of this crossover from a single particle to a cooperative critical behavior can constitute a definitive confirmation that the simplest ethoxylated alcohols have a surfactant behavior.

II. EXPERIMENT

The butoxyethanol used in this experiment was of high-purity grade (99.99%) and was purchased from Jannsen Chemical. Triply distilled deionized gas-free water was used and the samples were prepared by weight in the proper quantity. Great care was taken to avoid contamination. All the samples were filtered before the measurements. Immediately after preparation, the samples were put into a cylindrical optical cell or in the viscometer. To avoid unwanted stray-light contributions at small forward angles we used a 27-mm-diam high-precision optical round glass cell; we also used a refractive-index-matching bath continuously filtered in order to have flare-free measurements. In these conditions the measured optical background in the scattered light was negligible. The scattering cell and the viscometer were thermostated, within ±2 mK, in the range 0–49 °C, using a proportional temperature controller monitored by a calibrated platinum resistor connected to a high-precision resistance bridge. The measurements were performed after a suitable time in order to ensure the thermodynamical equilibrium of the samples.

Since many different works [32–35] report critical concentrations ranging between $0.04 < X_C < 0.07$, we have accurately studied the phase diagram of the mixture, from the shape of the coexistence curve obtained from light-scattering data. The transition temperature T_P, for each concentration, is assumed to be the temperature for which the scattered intensity has the maximum value. We found that the critical concentration is $X_C = 0.0525 \pm 0.0020$, with a critical solution temperature $T_C = 49.21\,^{\circ}\mathrm{C}$ [14]. These values agree with the findings of recent ultrasound and hypersound measurements [11,15,25]; in particular, the ultrasound absorption X_α has a maximum at X_C. In the inset of Fig. 1 is represented the phase diagram of the mixture. The solutions studied in this work have the following concentrations: $X=0.035$, 0.048, 0.052, 0.07, and 0.09.

The viscosity is measured for the concentration X_C using a standard Ubbelohde viscometer with the reduced temperature ranging from $\epsilon=9.061\times10^{-2}$ up to $\epsilon=6.204\times10^{-5}$. In this temperature range the measured viscosity shows a Newtonian behavior representing the zero-frequency viscosity value $\eta(0)$. In this respect, we tested the system using viscometers with different shear rates (100–500 $\sec^{-1}$). Because the measured viscosity is nearly constant in such a shear rate range, and having indication, from ultrasound absorption [11,15] data, that the relaxation frequency is located at higher values ($\sim$4 MHz), we may assume that the obtained data represent $\eta(0)$. The dynamic viscosity η is obtained from the kinematic viscosity data by multiplying by the density of the studied sample. The density is measured with a high-precision densimeter that gives an absolute uncertainty lower than 10^{-5} g/cm^3. The resulting relative uncertainty in the shear viscosity η can be estimated to be lower than 0.005 cP.

The quasielastic light-scattering measurement was made in the homodyne technique (by photon correlation spectroscopy) by using a 256-channel Malvern 4700 full correlator. As a light source, a 10-mW unimode He-Ne laser operating at 6328 Å was used. A cooled photomultiplier was used in order to obtain negligible dark counts. The optical alignment of our scattering setup was previously tested on standard latex particle water solutions. At the studied concentrations, multiple-scattering effects were not present, as was previously verified by attenuation and polarization tests. We measured the correlation function of the fluctuations $\langle I_S(\tau)I_S(0)\rangle$ of the relative total scattering intensity $I_S(\tau)$, this function being related to the correlation function of the density fluctuations $g^{(1)}(\mathbf{k},\tau)=\langle\Delta\rho(\tau)\Delta\rho(0)\rangle/\langle\Delta\rho^2\rangle$, where τ is the delay time and $\mathbf{k}$ the exchanged wave vector. The background contribution to the $I_S(\tau)$ correlation function was measured in each run by delaying the last few channels of the correlator by a suitable time. In this way a reliable estimate of the uncorrelated contribution was obtained. We derived $g^{(1)}(k,\tau)$ after the subtraction of this "background" and the normalization of its value at $\tau=0$. The first cumulant in the obtained first-order density correlation function gave us the linewidth or the relaxation rate Γ_1. A heterodyne technique was also used in order to test the Gaussian shape of the scattered field, and the results were in agreement with those obtained using the homodyne technique. Measurements have been performed from scattering angles $\theta=90°$, 50°, 30°, 25°, which corresponds to values of the scattering wave vector $k=1.979$, 1.183, 0.7247, and 0.606×10^5 cm^{-1}.

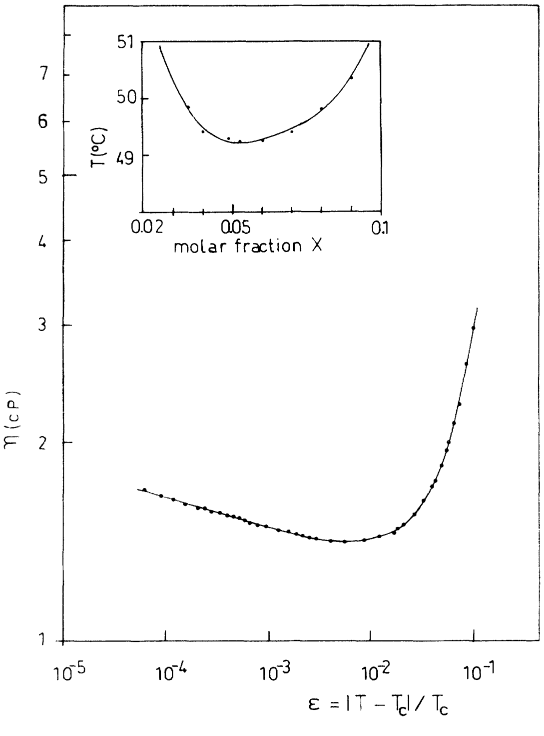

FIG. 1. Shear viscosity as a function of the reduced temperature ϵ. Continuous line is the best fit with Eq. (2) that takes into account the background contribution. In the inset is represented the phase diagram of the mixture.

In the full temperature domain that we studied, even very close to the phase-separation temperature and for all concentrations, the obtained correlation functions were always fitted with very good accuracy and without systematic deviations to a single exponential curve. We also verified that the relaxation rates Γ have the proper k^2 dependence ($\Gamma=Dk^2$, where D is the mass diffusion coefficient).

III. RESULTS AND ANALYSIS

We shall first address the nature of the viscosity behavior in order to obtain definitive insight on its divergence near T_C, and on the quantity ξq_D coming from the background contribution. This latter quantity is important for the following discussion of the light-scattering linewidth data, because the background contribution in the viscosity is related, as pointed out by the mode-mode–coupling theories, to the background of $\Gamma(k,t)$ through the Debye cutoff wave number q_D. For both viscosity and linewidth data our analysis is performed in terms of the mode-mode–coupling theory whose complete treatment has been reported by many authors [16–19] and, as recently shown, is well suited to study the critical behavior of supramolecular aggregates such as micelles and microemulsions. In particular, it is possible to have deeper insight both into effects of the background contribution coming from the finite extent (tens of angstroms) of the dispersed particle size in these "colloidal suspensions" and into the dominant role of the Debye cutoff wave number in their critical behavior. As shown for microemulsions, this quantity is the significant parameter for both the divergence of the viscosity and the order-parameter correlation time.

A. Viscosity

Near the critical temperature the anomaly of the shear viscosity is experimentally known to be weak (the accessible enhancement is of the order of 10–20 %), and is characterized by an exponent y according to the law

$$\eta \sim \epsilon^{-y} . \tag{1}$$

Many experimental observations give values for the critical index y that span the range $0.032 < y < 0.042$. This large uncertainty ($\pm 15\%$) is presumably due to the fact that the dynamical properties of critical systems (such as diffusion, thermal conductivity, and viscosity) are more difficult to study than static ones. Universality classes defined for static exponents are well accounted from the experimental results; for example, the exponent ν, describing the critical divergence in the fluctuation correlation length ξ, is known with very little uncertainty ($\nu = 0.63$) is a universal exponent [19]).

The mode-coupling approach [16–19] to critical phenomena, considering that the relevant variables of a critical system vary slowly in space and time, employs the idea that hydrodynamic equations can be used to study the decay of fluctuations, accounting for nonlinear interactions between relevant dynamical modes. For a critical mixture, such critical modes are both determined by the local concentration (order parameter) and the transverse velocity field with respect to the wave vector k, with the concentration conductivity α and the shear viscosity η as corresponding transport coefficients. The static susceptibility χ of the order parameter (the osmotic compressibility), the number density ρ, and α determine the mass diffusion coefficient D as $D = \alpha / \rho\chi$. Close to the critical point, the transport coefficients α and η can be written in terms of a regular part (background) α_B and η_B and a nonlocal (k-dependent) critical part α_C and η_C. One has a set of coupled integral equations which relate α_C and η_C to the wave vector k through the k-dependent osmotic susceptibility $\chi(k)$. According to many theoretical results [16,20–24], the shear viscosity can be put in an exponential form, giving the temperature dependence of η near T_C as the product of the background viscosity $\eta_B(T)$ with a power-law divergence:

$$\eta(T) = \eta_B(T)(Q_0\xi)^{\phi} , \tag{2}$$

where Q_0 is a fluid-dependent wave vector; in particular, as shown by Bhattacharjee, Ferrell, and Sengers (BFS) [23] it is given in terms of two different contributions, the Debye cutoff q_D, and a contribution related to the diffusivity background q_C, as

$$\frac{1}{Q_0} = \frac{e^{4/3}}{2}\left[\frac{1}{q_D} + \frac{1}{q_C}\right] . \tag{3}$$

Both the viscosity and linewidth data must be analyzed considering this contribution.

The Debye cutoff q_D was proposed for the first time by Perl and Ferrell [20], whereas q_C was studied by Oxtoby and Gelbart (OG) [21]. This latter wave vector is written by BFS [23] as $q_C = \pi/\xi 2a_0$ (where a_0 is the OG parameter, $a_0 = (8\pi\eta_B\alpha_B\xi)/[k_B T\chi(0)]$ [21]), while, by OG [21] is written as $q'_D = C/\xi a_0 = (2C/\pi)q_C$ (where C is a constant of order unity that is found to be 0.9 [21]). Usually the viscosity data are studied in terms of a more general function $H(Q_0\xi, q_D/q_C)$. The best agreement with the experimental data is obtained for $q_D/q_C \simeq 1$, in the case of gas-liquid critical points (nitrogen and steam analyses by Bhattacharjee *et al.* of Ref. [23]; also ethylene and ethane from Basu and Sengers of Ref. [23]). This value was also adopted by Burstyn *et al.* of Ref. [23] for the liquid-liquid critical point. Although recently others found $q_D/q_C \simeq 3$ for xenon and higher for CO_2 [36], we will assume $q_C \simeq q_D$, i.e., $Q_0 \simeq e^{-4/3} q_D = 0.26 q_D = 0.26 q_C$. Such a choice is consistent with the idea of a cutoff wave vector in the linewidth data numerically coincident with q_C. Kawasaki equations of mode coupling yield $\phi = 8/15\pi^2$. Several authors attempted to obtain a refined theoretical estimate of this exponent [19,23], obtaining values that lie in the range $\phi = 0.062 \pm 0.005$; however, the theoretical value currently adopted is $\phi = 0.054$ [23]. This value is obtained by expanding the mode-coupling equations for critical dynamics up to the second order in $x = 4 - d$, where d is the dimensionality of the system [19]. The exponent ϕ is related to the dynamic scaling exponent $z = 3 + \phi$, which characterizes the asymptotic behavior of the decay rate of the order-parameter fluctuations; ϕ can be written in terms of the critical index y and ν as $\phi = y/\nu$. Considering the divergence in the correlation length ξ, the measured viscosity can be written as

$$\eta(T) = [\eta_B(T)(Q_0\xi_0)^{\phi}]\epsilon^{-\nu\phi} = [\eta_B(T)(Q_0\xi_0)^{\phi}]\epsilon^{-y} . \tag{4}$$

In this equation the quantity within square brackets includes the fluid-dependent quantities $\eta_B(T)$, Q_0, and ξ_0. This form is useful because it specifies how to treat the noncritical background viscosity contribution. In particular, in this equation the critical divergence is multiplied by η_B; this is confirmed by a previous accurate analysis performed for critical systems [37,38], and represents a well established procedure in order to describe the experimental data [38,27].

It is important to consider, at this point, that near T_C shear can affect the measured viscosity [39,40]. For the present measurements the experimental shear rate of the used viscometer is sufficiently small to avoid this problem. Using the Oxtoby calculation [39], we estimate, for $\epsilon = 6.2 \times 10^{-5}$, a "shear thinning" of about 2%.

The temperature dependence of the background viscosity cannot be ignored in the data analysis. Usually, this contribution can be evaluated by performing an extrapolation of $\eta_B(T)$ from the noncritical region into the critical region, or by fitting the measured viscosity to a product of a simple analytic function and a divergent term [34,20,41,42]. For our data we used a well established procedure based on the consideration that far from the critical region the viscosity is assumed to be entirely due to the background contribution that follows the Arrhenius law [31,27,37,41]:

$$\eta_B(T)=A\,\mathrm{expt}\left[\frac{E}{1-\epsilon}\right]. \tag{5}$$

After the evaluation of A and E, by means of Eq. (5) ($A=1.421\pm0.05\times10^{-3}$ cP and $E=6.7934\pm0.04$), the scaling index y and $(q_D\xi_0)$ will be obtained using Eq. (4). The result of such an analysis for the critical concentration $X_C=0.052$ is shown in Fig. 1. In particular, using $\phi=0.054$, we obtained $y=0.0414\pm0.001$ (a part of the uncertainty in y is due to the effect of the "shear thinning" in η) and $Q_0\xi_0=(9.2\pm0.06)\times10^{-2}$. The difference in the present value of the critical index y and the previous one, reported in Ref. [14], is due to an incorrect evaluation of the background contribution. The A and E values are in good agreement with previous experimental studies [33–35] in the same samples. As far as the critical index y is concerned, we have a good agreement with other studies which use Eq. (4) [33,35], while y is larger than the result of Ref. [34] ($y=0.036$), where ϕ is 0.063. As pointed out by Berg and Moldover [35] the value $y=0.0414$ can be considered a universal one for the viscosity exponent in pure fluids and binary liquid mixtures. For $Q_0\xi_0$ we obtain a value that is in agreement with Ref. [34]. The differences obtained in these quantities from the different studies can be related to a difference in the BE samples (i.e., purity, chemical degree, preparation, etc.); in fact, the measured X_C and T_C lie in the intervals 0.05–0.062 and 47.3–49.25 °C, respectively.

As far as background effects (the temperature behavior of $Q_0\xi$) are concerned, and in particular for the calculated values, it is important to consider the structural picture suggested above for our system by several investigations. The obtained viscosity data obeys an Arrhenius law [Eq. (5)] in the temperature range 20–40 °C ($9.061\times10^{-2}\le\epsilon\le2.8569\times10^{-2}$). As discussed in a previous paper [14], this is due to the presence of micellar structures. In fact, we can explain the shear viscosity of a water-butoxyethanol mixture as a function of concentration and temperature (in particular, in the region $-10\le T\le40$ °C) by only taking into account the physical picture proposed to explain the data of different experimental techniques, such as SANS and quasielastic and elastic light scattering that give confirmation of the amphiphilic character of the alcohol molecules (C_4E_1) and show how the butoxyethanol molecules give rise to a well defined micellar structure. The presence of such supramolecular aggregates affects the physical properties of the solution. In particular, using these concepts we can explain why critical effects emerge in the system only at a few degrees from the critical temperature, while far from T_C the viscosity behavior is the same for a micellar solution. In fact, for ultrasound the dimensions of such structures (large if compared with those of binary critical molecular systems) determine a short-range correlation length ξ_0, which in turn reduces the characteristic relaxation frequency and the amplitude of critical ultrasound attenuation. Usually, in pure fluids or in binary molecular mixtures the short-range correlation length ξ_0 and the Debye cutoff length q_D^{-1} are of the same order of magnitude—a few angstroms—comparable to the range of the intermolecular potential [26]. In a micellar solution the short-range correlation length can be fairly large ($\xi_0\sim10$ Å) and, as shown by Fisher [30], q_D^{-1} should be of the order of the size of the micelles (in our case, around some tens of angstroms). Therefore, in a critical micellar or microemulsion system, when ξ is such that $\xi q_D\gg1$, the system should behave like an ordinary liquid mixture, with $q_D\xi$ the relevant scaling variable, and q_D the wave number of the order-parameter fluctuations. For the system far from T_C, ξ and q_D^{-1} can be of the same order of magnitude, and the critical phenomenon ceases to exist. In this latter regime, identifiable as a crossover from the critical to the single-particle regime, the behavior of the system is the same as the nonideal solution of interacting micelles whose dynamics is dominated by the Brownian motion of the dispersed particles. For a temperature regime around and below the crossover temperature $T_x\,[q_D\xi(T_x)\simeq1]$ the equilibrium and the dynamic behavior of the dispersion are completely modified and $q_D\xi$ no longer plays the role of a scaling variable. The $q_D\xi(T)$ values obtained in the present experiment seem to indicate that, for our system, $q_D\xi\simeq1$ for $T_x\simeq43$ °C ($\epsilon=1.87\times10^{-2}$), therefore, for temperatures higher than this, the critical phenomenon could be observable. In particular we obtain that $q_D\xi$, upon increasing T, increases up to a value of about 80 for $T=49.19$ ($\epsilon=6.2\times10^{-5}$). This result is in agreement with the findings of previous works performed on microemulsions [28] and for analogous micellar systems [29] and reflects the suggestions of Fisher's theory [30] for which such a quantity should be of the order of the size of the supramolecular structures. In any case, this picture will be explained in more detail in the forthcoming section, where the results of the dynamic light-scattering measurements will be discussed in terms of the mode-coupling theory [18], and the effects of the background contribution on the transport coefficients will be pointed out. This structural point of view has supported several experimental results and in particular studies of viscosity behavior [14], sound velocity and absorption [10,11], and SANS data [12] in a temperature range well below the critical region.

B. Dynamic light scattering

Using the same assumptions for the mode-coupling equations as for the analysis of critical microemulsions [31] [a simplified Ornstein-Zernike form for the nonlocal susceptibility $\chi_T(k,T)$ with Fisher exponent η put equal to zero] the decay rate of the order-parameter fluctuations can be written as the sum of two terms:

$$\Gamma(k,T)=\Gamma_C(k,T)+\Gamma_B(k,T). \tag{6}$$

This quantity, proportional to D, can be directly measured by photon correlation spectroscopy. The critical part can be written in terms of the solution of the mode-coupling equations (using the OG formalism) [16,18] as

$$\Gamma_C(k,T)=k^2\frac{Rk_BT}{6\pi\eta(T)\xi}\,\frac{K(k\xi,T)}{k^2\xi^2}=k^2D_C\frac{K(x)}{x^2}, \tag{7}$$

where $D_C = Rk_BT/6\pi\eta\xi$, $x = k\xi$, and $K(x) = (3/4)[1+x^2+(x^3-1/x)\tan^{-1}x]$ is the Kawasaki universal scaling function for the decay rate and k_B is the Boltzmann constant. R is a universal amplitude equal to 1.027, which in the mode-coupling theory represents the amplitude correction to the Stokes-Einstein diffusion law. To the same order of approximation the background contribution on the decay rate is [31]

$$\Gamma_B(k,T) = k^2 D_C \frac{3}{4} \frac{C}{q_D'\xi}(1+x^2)\frac{\eta}{\eta_B} , \tag{8}$$

where, for the comparison with the viscosity data, $q_D' = 2RCq_C/\pi$. The theoretical predictions for the decay rate of the order parameter accounted for in Eqs. (6), (7), and (8) can be more easily compared with the experimental data if these equations are written in a reduced form involving only universal quantities. In this respect it is customary to define a reduced critical relaxation rate:

$$\Gamma_C^*(k,T) = \Gamma_C(k,T)\frac{6\pi\eta}{Rk_BTk^3} = \frac{K(x)}{x^3} , \tag{9}$$

which is a universal function of the scaling variable x. Similarly, the scaled background relaxation rate is defined as

$$\Gamma_B^*(k,T) = \Gamma_B(k,T)\frac{6\pi\eta}{Rk_BTk^3}$$

$$= \frac{3C}{4}\left[\frac{k}{q_D'}\right]^{(1-\phi)}\left[1+\frac{1}{x^2}\right]x^{\phi} . \tag{10}$$

This contribution, being the product of a universal function of x and a nonuniversal term involving the ratio k/q_D', depends on both the geometry of the experimental setup and the physical nature of the system through the Debye wave vector. By reducing, in the same way, the experimental relaxation rate $\Gamma_{\text{expt}}(k,T)$, the inverse of the experimental order-parameter fluctuations correlation time,

$$\Gamma_{\text{expt}}^*(k,T) = \Gamma_{\text{expt}}(k,T)\frac{6\pi\eta}{Rk_BTk^3} , \tag{11}$$

it is then possible to make a direct comparison between the theory and the dynamic light-scattering experiment. In fact, the difference of the reduced linewidth, $\Gamma_{\text{expt}}^*(k,T) - \Gamma_B^*(k,T)$, computed from the previous two equations, can be compared with the universal function $\Gamma_C^*(k,T)$ given by Eq. (9). This comparison is performed in our case from the data obtained at the critical concentration X_C for several relaxation rates measured at the experimental wave vectors ($k = 1.979$, 1.183, 0.7247, and 0.606×10^5 cm^{-1}) where the long-range correlation length ξ diverges according to the well established criti-

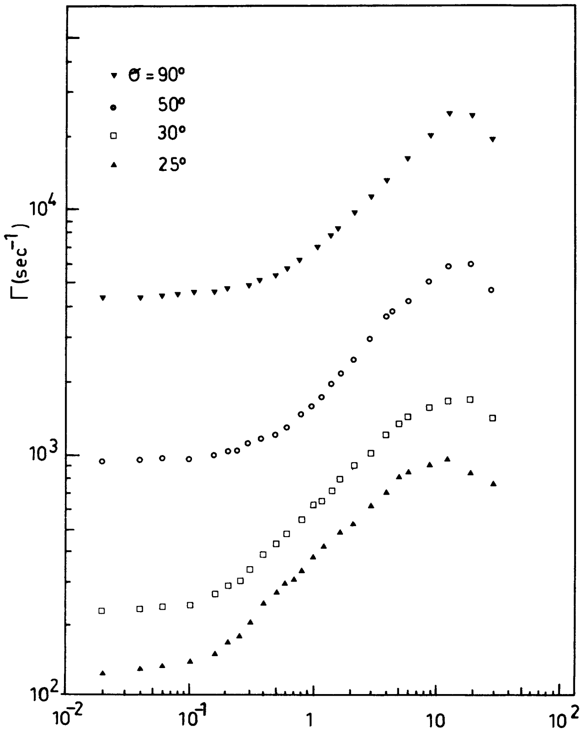

FIG. 2. Log-log plot of the obtained relaxation rate Γ_{expt} vs $T_C - T$, for different scattering wave vectors. Inverted open triangles, $\theta = 90°$; open circles, $\theta = 50°$; squares, $\theta = 30°$; and full triangles, $\theta = 25°$. Temperature is measured in degrees Kelvin.

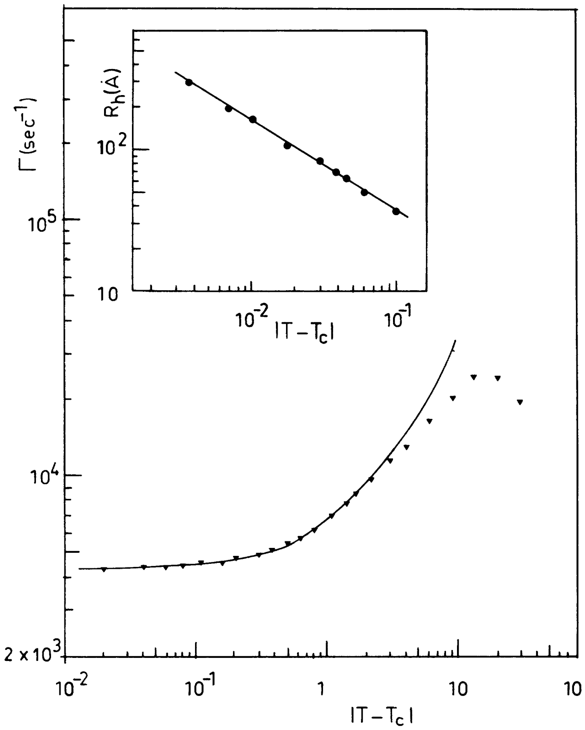

FIG. 3. Log-log plot of the relaxation rate of the critical concentration ($\theta = 90°$) vs $T_C - T$; the dots are the experimental results, whereas the solid line is the calculation in terms of the prediction of mode coupling including background effects. In the inset is reported the power-law divergence of the hydrodynamic radius R_h. Temperature is measured in degrees Kelvin.

cal law. Figure 2 shows in a log-log plot the obtained relaxation rate Γ_{expt} vs $T_C - T$. As can be observed far below the phase-separation temperature, for $T_C - T$ ranging from 20 to 43 °C, and for all the samples, the decay rate increases and reaches a maximum around 32 °C and then decreases again. This is consistent with the structural picture proposed by elastic light-scattering and neutron-scattering data that our mixture behaves like a macromolecular solution [12,13].

Let us discuss now the experimental results for the dynamical behavior of the system. Since, close to the critical temperature, the shear viscosity diverges with a critical index $y = 0.0414 \pm 0.001$, we believe that mode-coupling equations can be applied to our critical mixtures. The experimental values of the relaxation rate Γ_{expt} are first reduced according to Eq. (11). In order to calculate the background contribution to the relaxation rate Γ_B^*, the Debye cutoff must be known. Since from the actual treatment of viscosity data, based on Eq. (2), we are able to calculate the quantity $q_D'\xi(T)$, we use for Γ_B^* the following modified expression of Eq. (10):

$$\Gamma_B^*(k,T) = \frac{3C}{4}(q_D'\xi)^{(\phi-1)}\left[\frac{1+x^2}{x}\right]. \qquad (12)$$

The difference between Eqs. (10) and (12) is that Eq. (12) uses the quantity $(q_D'\xi)$ obtained from the viscosity data; Eq. (10) instead is written in terms of the ratio k/q_D'. A direct evaluation of the scaling variable $x = k\xi$, and therefore of the diverging fluctuation correlation length ξ can be calculated, with $\phi = 0.054$ and $\nu = 0.63$, using the value (obtained from the viscosity data) for $q_D'\xi_0 = (Q_0/0.26)\xi_0 2RC/\pi$ and the experimental linewidth background values; in this manner Eq. (12) gives us $\xi_0 \sim 5$ Å and $Q_0^{-1} \sim 57$ Å. This evaluation has been performed in a temperature range not too far from T_C (35–47 °C). For comparison a direct measurement of ξ_0 can be obtained from intensity data or the linewidth data by using the Stokes-Einstein relation. In the latter case, using the actual mixture viscosity, we can calculate the hydrodynamic radius of the dispersed particles R_H. The use of such a procedure, as shown in the inset of Fig. 3, gives as a result that the hydrodynamic radius (measured from both light and SANS), corresponding to the critical concentration, and reported in a separate work [25], diverges according to the law $R_H = R_{H0}\epsilon^{-\nu}$, with $\nu = 0.63 \pm 0.004$ and $R_{H0} = 8.9 \pm 1$ Å that correspond to $\xi_0 \simeq 4.5 \pm 0.5$ Å (in accordance with the well-known relation $R_H = \sqrt{5}\xi$ [12]). The so-obtained ξ_0 agrees, within the experimental error, to the value obtained in other experiments [33,34].

This value of ξ_0 is significantly larger than those usually obtained for pure fluids or binary liquid solutions [26,27], but it is of the same order of the values found for critical nonionic micellar suspensions [29] and water in oil microemulsions [28]. Having obtained $Q_0^{-1} \sim 50$ Å we can evaluate the Debye cutoff q_D^{-1} in all the explored temperature ranges far and near T_C. In fact, working under the assumption $q_C \simeq q_D$, we obtain $q_D^{-1} \sim 16$ Å, a value in agreement with Fisher's prediction; in fact, q_D^{-1} is of the order of the size of the dispersed particles, confirming again the structural picture proposed by other experimental observations. Furthermore, the comparison with the same parameter obtained for a binary critical mixture (n-hexane and nitrobenzene [27]), i.e., $q_D^{-1} \approx 5$ Å, implies that the background contribution to the relaxation rate Γ_B^* given by Eqs. (10) or (12) is very large in our system. With this value of the Debye cutoff length we fit our linewidth data in the critical regime. Figure 3 shows in a log-log plot the relaxation rate of the critical concentration ($\theta = 90°$) vs $T_C - T$; the dots are the experimental results, whereas the solid line is the calculation in terms of the prediction of mode coupling, including background effects. Finally in Fig. 4 we plot, against x, the reduced critical decay rate $\Gamma_C^*(k,T)$ obtained by computing the difference $\Gamma_{\text{expt}}^*(k,T) - \Gamma_B^*(k,T)$ for all the k values used. The solid line represents the theoretical mode-coupling result $K(x)/x^3$. It can be seen that the agreement between the theory and the experiment is good, for x ranging from 0.28 to 12, when background effects are taken into account.

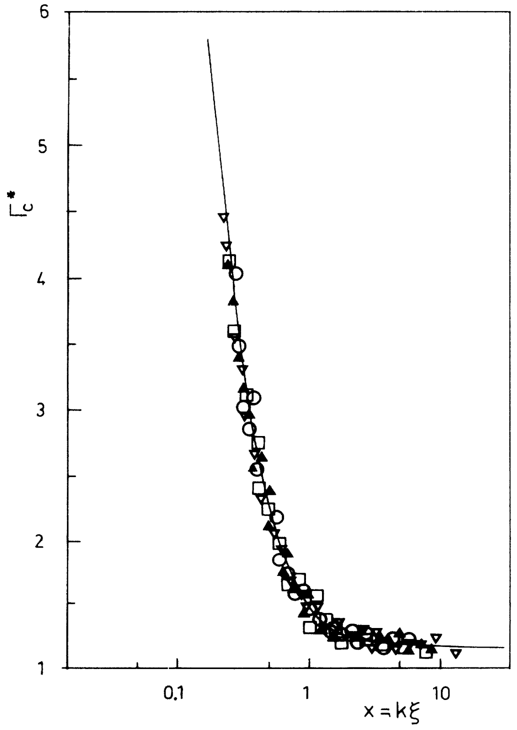

FIG. 4. Log-log plot of the reduced relaxation rate $\Gamma_C^*(k,T)$ as a function of $x = k\xi$. The solid line represents the theoretical mode-coupling result $K(x)/x^3$. The symbols are the same as in Fig. 1.

Let us go back now to the low-temperature domain. With the above numerical values for ξ_0 and q_D, and the critical indices y, ϕ and ν, we obtain $Q_0\xi(T_x) \simeq 1$ for $\Delta T = 6$ °C below T_C, i.e., around 43 °C which corresponds to the crossover temperature T_x. If we increase the temperature, the sample obeys the usual critical laws, whereas moving below it the previous divergent quantities (e.g., correlation time of the order-parameter fluctuations) remain roughly constant.

IV. CONCLUSIONS

We studied both the shear viscosity and the relaxation rate of a water-butoxyethanol mixture as a function of the temperature at the critical concentration. The obtained results confirm the physical picture proposed by the data of different experimental techniques (ultrasound velocity and absorption, SANS, quasielastic and elastic light scattering) giving confirmation of the amphiphilic character of the alcohol molecules (C_4E_1). These properties in the butoxyethanol molecules give rise to a well-defined micellar structure. The presence of such supramolecular aggregates is reflected in the physical properties of the solution. In particular, with the present study we confirm that the critical properties of the mixture can be described within the framework of the mode-coupling theories for critical systems, taking into account dynamic background effects. In our case, such effects come from the noncritical contribution to the transport coefficient entering in the mode-coupling dynamics. Using these theoretical concepts we can explain why critical effects emerge in the system only at a few degrees from the critical temperature, while far from T_C the viscosity behavior is the same as a micellar solution. In our data analysis the main role is played by the Debye cutoff length q_D^{-1}, which is of the same order of the size of the micelles. Depending on the value of the correlation length ξ, and in particular on the quantity $\xi q_D(T)$ as shown by the analysis of dynamic light-scattering data, the system ranges through a crossover from a critical to a single-particle behavior. More precisely, the analysis of the shear viscosity in terms of a multiplicative law for the background and the critical contribution gives a value for the critical index y which agrees with recent measurements in simpler fluids and also allows the direct evaluation of the quantities $q_D\xi(T)$ and the crossover temperature T_x $[q_D\xi(T)=1]$. Combining these results with those derived from the Stokes-Einstein law for the diffusion coefficient, we can calculate the short-range correlation length ξ_0 and the parameter q_D^{-1}; both the obtained values are consistent with the above exposed structural picture. In particular, the measured $q_D^{-1}\sim 16$ Å, in agreement with Fisher's prediction for critical scattering from analogous supramolecular aggregates such as micellar structures and microemulsions.

Finally, using the mode-coupling theory for the decay rate of the order-parameter fluctuations, including the dynamic background effect for the transport coefficient, we make a quantitative analysis of the linewidth results. More properly, in addition to the background contribution to the experimentally obtained rate relaxation data, we obtain excellent agreement between the critical contribution with the dynamic scaling of Kawasaki in the whole range of the scaling variable $k\xi$ (from 0.28 to 12). In conclusion, the performed analysis gives evidence for the overall determining role of the quantity q_D in controlling the critical dynamics for both the divergence of the viscosity and the order-parameter correlation time.

ACKNOWLEDGMENTS

We acknowledge financial support from the Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, Italy, and from the Centro Interuniversitario di Stuttura della Materia del Ministero della Publica Istruzione, Italy.

---

[1] See, for instance, V. Degiorgio, in *Physics of Amphiphiles; Micelles, Vehicles and Microemulsions,* edited by V. Degiorgio and M. Corti (North-Holland, Amsterdam, 1985), p. 303 and references therein.

[2] B. L. Halfpap and C. M. Sorensen, J. Chem. Phys. **83**, 1385 (1985).

[3] G. Roux, D. Roberts, G. Perron, and J. E. Desnoyers, J. Solution Chem. **9**, 29 (1980).

[4] T. Kato and T. Seimiya, J. Phys. Chem. **90**, 3159 (1986).

[5] G. D'Arrigo and A. Paparelli, J. Chem. Phys. **88**, 7687 (1988).

[6] S. Nishikawa, T. Tanaka, and M. Mashima, J. Phys. Chem. **85**, 686 (1981).

[7] P. K. Kilpatrick, H. T. Davis, L. E. Scriven, and W. G. Miller, J. Colloid Interface Sci. **118**, 270 (1987).

[8] S. Puvvada and D. Blankschtein, J. Chem. Phys. **92**, 3710 (1990).

[9] G. M. Musbally, G. Perron, and J. E. Desnoyers, J. Colloid Interface Sci. **48**, 494 (1974).

[10] S. Kate, D. Jobe, N. P. Rao, C. H. Ho, and R. E. Verrall, J. Phys. Chem. **90**, 4167 (1986).

[11] G. D'Arrigo and A. Paparelli, J. Chem. Phys. **88**, 405 (1988).

[12] G. D'Arrigo and J. Teixeira, J. Chem. Soc. Faraday Trans. **86**, 1503 (1990); G. D'Arrigo, J. Teixeira, R. Giordano, and F. Mallamace, J. Chem. Phys. **95**, 2732 (1991).

[13] F. Mallamace, N. Micali, C. Vasi, and G. D'Arrigo, Nuovo Cimento D **14**, 333 (1992).

[14] F. Mallamace, N. Micali, and G. D'Arrigo, Phys. Rev. A **44**, 6652 (1991).

[15] G. D'Arrigo, F. Mallamace, N. Micali, A. Paparelli, and C. Vasi, Phys. Rev. A **44**, 2578 (1991).

[16] D. W. Oxtoby and W. M. Gelbart, J. Chem. Phys. **61**, 2957 (1974).

[17] L. Kadanoff and J. Swift, Phys. Rev. **166**, 80 (1967).

[18] K. Kawasaki, in *Phase Transition and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 5A, p. 165.

[19] E. D. Siggia, B. I. Halperin, and P. C. Hohenberg, Phys. Rev. B **13**, 2119 (1976); P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).

[20] R. Perl and R. A. Ferrell, Phys. Rev. Lett. **29**, 51 (1972); Phys. Rev. A **6**, 2358 (1972).

[21] D. W. Oxtoby and W. M. Gelbart, J. Chem. Phys. **61**, 2957 (1974).

[22] T. Ohta and K. Kawasaki, Prog. Theor. Phys. **55**, 1384

(1976); T. Ohta, J. Phys. C **10**, 791 (1977).

[23] J. K. Bhattacharjee, R. A. Ferrell, R. S. Basu, and J. V. Sengers, Phys. Rev. A **24**, 1469 (1981); J. K. Bhattacharjee and R. A. Ferrell, *ibid.* **28**, 2363 (1983); H. C. Burstyn, J. V. Sengers, J. K. Bhattacharjee, and R. A. Ferrell, *ibid.* **28**, 1567 (1983); R. S. Basu and J. V. Sengers, in *Proceedings Eighth Symposium of Thermophysical Properties,* edited by J. V. Sengers (American Society of Mechanical Engineers, New York, 1982), p. 434.

[24] J. V. Sengers, Int. J. Thermophys. **6**, 203 (1985); M. L. S. Matos Lopes, C. A. Nieto de Castro, and J V Sengers, Int. J. Thermophys. **13**, 283 (1992).

[25] G. D'Arrigo, F. Mallamace, N. Micali, A. Paparelli, J. Teixeira, and C. Vasi, Progr. Coll. Polymer Sci. **84**, 177 (1991).

[26] H. C. Burstyn, J. V. Sengers, and P. Esfandiari, Phys. Rev. A **22**, 282 (1980).

[27] S. H. Chen, C. C. Lai, J. Rouch, and P. Tartaglia, Phys. Rev. A **27**, 1086 (1983).

[28] M. Kotlarchyk, S. H. Chen, J. S. Huang, and M. W. Kim, Phys. Rev. A **28**, 508 (1983); **29**, 2054 (1984).

[29] M. Corti and V. Degiorgio, Phys. Rev. Lett. **55**, 2005 (1985), and references therein.

[30] M. E. Fisher, Phys. Rev. Lett. **57**, 1911 (1986).

[31] J. Rouch, A. Safouane, P. Tartaglia, and S. H. Chen, J. Chem. Phys. **90**, 3756 (1989).

[32] N. Ito, T. Fujiama, and Y. Udagawa, Bull. Chem. Soc. Jpn. **56**, 379 (1983).

[33] I. L. Pegg and I. A. McLure, Mol. Phys. **53**, 897 (1984).

[34] K. Hamano, T. Kawazura, T. Koyama, and N. Kuwahara, J. Chem. Phys. **82**, 2718 (1985).

[35] R. F. Berg and M. R. Moldover, Phys. Rev. A **42**, 7183 (1990).

[36] R. F. Berg and M. R. Moldover, J. Chem. Phys. **93**, 1926 (1990).

[37] G. D'Arrigo, L. Mistura, and P. Tartaglia, J. Chem. Phys. **66**, 80 (1977); in *Proceedings of the Seventh Symposium on Thermophysical Properties,* edited by A. Cezairliyan (American Society of Mechanical Engineers, New York, 1977), p. 831.

[38] P. Calmettes, Phys. Rev. Lett. **39**, 1151 (1977).

[39] D. W. Oxtoby, J. Chem. Phys. **62**, 1463 (1975).

[40] A. Onuki and K. Kawasaki, Phys. Lett. A **75**, 485 (1980).

[41] D. Beysens, S. H. Chen, P. Chabrat, L. Latamendia, J. Rouch, and C. Vaucamps, J. Phys. (Paris) Lett. **38**, L203 (1977).

[42] R. F. Berg and M. R. Moldover, J. Chem. Phys. **89**, 3694 (1988).