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Rotational dynamics of water molecules in a water–short-chain-nonionic-amphiphile mixture: Depolarized light scattering

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Depolarized Rayleigh-wing light scattering experiments on aqueous solutions of 2-butoxyethanol (C_4E_1) as a function of temperature and concentration are reported. The measured spectra give information on the rotational dynamics of water molecules. Their analysis confirms the findings of surface-tension data performed in the same experimental conditions, namely, that the ethoxylated alcohol molecules have an amphiphilic character that can give rise to micellar structures. The water rotational motion is dominated by the presence of such aggregates and by the hydration of the oxyethylene groups of the alcohol molecules.

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I. INTRODUCTION

Interest in the physical properties of aqueous solutions of nonionic amphiphile molecules has grown in recent years because these systems represent a class of the large interdisciplinary research area known as complex liquids [1,2]. In particular, the most studied amphiphiles are the long-chain polyoxyethylene monoalkyl esters which, in aqueous solution at room temperature, form well-defined supramolecular structures as micelles via a self-aggregation process; microemulsions can be formed by adding an oil [3]. As is well known, such structures are obtained above a certain amphiphile concentration known as the critical micellar concentration (CMC). The chemical formula of these amphiphiles is $C_mH_{2m+1}(OCH_2CH_2)_nOH$ (or C_mE_n for short) and they are made of a linear saturated hydrocarbon chain (hydrophobic moiety) linked to a polyoxyethylene chain (hydrophilic moiety).

Usually these solutions have a stable one-phase region in a large range of temperature and concentration where the diameter of the micelles (or microemulsions) remains fixed for a range of amphiphile concentrations. Furthermore, there is a weak short range attractive interaction between the micelles. Although the origin of this interaction is unclear, it is probably entropic, resulting from the entanglement of the hydrocarbon tail groups of two micelles [4].

These systems are used as model systems to study many fundamental dynamical and structural phenomena related to the liquid state (i.e., fractal aggregation, percolation, polymerization, glass transitions, and disorder to order transitions [5]) and to test theoretical models. For example, in some amphiphile water solutions the packing fraction of the micellar droplets can be easily changed while keeping their size constant, therefore giving the possibility to study the behavior of highly packed systems (such as the glass-forming ones) [6]. It has been shown that these systems, in this stable micellar phase, are able to build up large percolating structures.

An additional important feature of many nonionic amphiphile water solutions is that, in the phase diagram, a consolution curve is present which separates a one-phase micellar region from a two-phase one. The minimum of the consolution curve behaves as the critical point [3]. More precisely, the tendency of C_mE_n water solutions to demix increases with temperature, and separation occurs at a lower critical solution temperature (LCST) for critical concentrations lying in the water-rich region of composition [3]. The LCST is usually located above the room temperature [3]. Almost all aqueous nonionic surfactant solutions have been found to have three-dimensional Ising-like values for critical exponents, indicating they are in the three-dimensional Ising universality class, similar to many simple binary liquid mixtures [3]. On the other hand, such aqueous micellar solutions are able to form a larger variety of phases than simple binary mixtures [3]. At high concentration the phase diagrams of these systems may become more complex and present regions of anisotropic phases, as for example lamellar, cubic, hexagonal, and solid. Aqueous solutions of nonionic amphiphiles are well-studied systems both with respect to their behavior near their critical point and in connection with the different structural phases showed as functions of concentration and temperature.

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In these nonionic C_mE_n systems, the whole phase behavior is strongly dependent on the length of both the hydrophobic saturated hydrocarbon chain (alkyl chain) and the length of the hydrophilic polyoxyethylene chain. It is, therefore, interesting to study the behavior of the short-chain normal alcohols (C_mE_0) and alkoxyethanols (C_mE_1) that can be considered as low n and m members of the C_mE_n series. Depending on the length (hydrophobicity) of the alkyl chain, they exhibit different phase behaviors: in fact, normal alcohols with $m \leq 3$ are completely miscible in water and for $m > 3$ they become immiscible, displaying a closed loop of solubility. Shorter alkoxyethanols also display similar trends: up to C_3E_1 they are miscible with water in all proportions and temperatures, while C_4E_1 (2-butoxyethanol or BE) aqueous solutions demix at a LCST $T_c = 42.9\,^{\circ}\mathrm{C}$ and $X_c = 0.052$ (X represents the BE mole fraction) [7]. The phase diagram of this BE-water mixture is shown in Fig. 1(a). It is quite similar to that observed in long-chain C_mE_n amphiphile solutions [3]. Such a behavior indicates that some self-aggregation phenomenon among alcohol molecules may take place, giving rise to micellarlike structures.

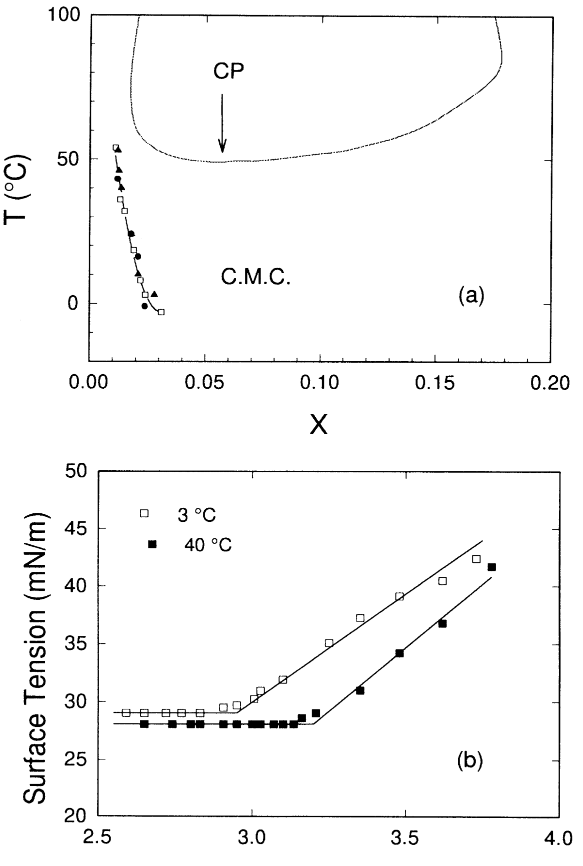

FIG. 1. (a) The phase diagram of the BE-water solution (Ref. [3]). The dashed line is the CMC curve corresponding to partial molar specific heat (triangles) and sound velocity (dots) maxima and surface tension (open squares). (b) Surface tension γ as a function of the concentration C (mol. l^{-1}) of BE in water, at $T = 4$ and 40°C.

Other physical properties of BE-water solutions support the idea that micelles are present in the system. For example, the presence of definite maxima in the partial molar heat capacity [8] at a characteristic concentration makes the BE solution seem quite similar to the other C_mE_n's, suggesting that, among the C_mE_1's, BE has the minimal length required to form micellar aggregates. In addition, a surfactantlike behavior of the simplest ethoxylated alcohols C_4E_1 and C_6E_2 has been found by measurements of density [9], refractive index, and NMR performed on water solutions (and on water solutions with the addition of NaCl salt) [8,9].

There is an indication that some kind of micellar structure is present in these mixtures only above an amphiphile mole fraction X of about 0.018. This behavior is similar to that of known surfactants (e.g., sodium octanoate and sodium dodecyl sulfonate) at their critical micellar concentrations [10,11]. The existence of such a characteristic concentration above which aggregation processes are present has also been found by ultrasonic and hypersonic experiments [12–14]. In particular, the sound velocity data show well-defined peaks for $X = 0.018$ [14]. Furthermore, the relative sound absorption is characterized by two well-defined relaxation processes, one connected to the amphiphilic association (the lower relaxation frequency $f < 5$ MHz), and the other to the amphiphile-water hydrogen bonding (the higher relaxation frequency $f \sim 40$ MHz). Such a low relaxation frequency (< 5 MHz) was observed only in alkoxy ethanols of hydrophobic tail length C_4 or longer. The above experimental findings suggest that these amphiphilic alcohols remain monomolecularly dispersed in water for very low concentrations (lower than 0.018), while for higher concentrations the amphiphilic molecules form micellarlike structures that become more definite when temperature decreases. In addition, viscosity data studied as functions of temperature and concentration, above the CMC, show a behavior that can be explained only by assuming this structural picture. Furthermore, a comparison of recent small-angle neutron scattering (SANS) [15] and light scattering data (elastic and quasielastic) [16] carried out on water-butoxyethanol (C_4E_1) mixtures as a function of temperature, $-10 \leq T \leq 45\,^{\circ}\mathrm{C}$, in the concentration range $0.015 \leq X \leq 0.09$, where ultrasonic attenuation exhibits peak values, seems to support this point of view, indicating the presence in solution of dispersed micellarlike structures whose dimension increases slowly with temperature. The critical behavior of the mixture as a function of temperature, studied by means of shear viscosity and dynamic light scattering, also agrees with this structural picture [17]. More precisely, the analysis of viscosity data and of diffusional relaxation rates in terms of the mode-coupling theory (including background effects of the transport coefficients) gives two characteristic lengths: the short range correlation amplitude ξ_0 and the Debye cutoff length q_D^{-1}. Both these lengths assume values compatible with a micellarlike structure.

No definitive structural models yet exist for the nature of such aggregates. For example, it is not clear if they are composed of molecules of the same species or a mixture of species. In connection with Rayleigh and Raman scattering experiments, a model was suggested for the internal molecular structure of the mixture which seems also to explain the critical phase separation [18–20]. In this model, the simultaneous presence of two local structures of the type $g[(H_2O)_{50}BE]$ and $h[(H_2O)_4BE]$ was proposed, the numbers g and h increasing with temperature from ten to several hundreds. Phase separation was then explained in terms of these two structures with the increase in h and g up to the critical temperature; in particular, it was suggested that demixing occurs at the end of the growth of the local structures, already existing at low temperatures.

A definitive confirmation that micelles are present in the water-BE system comes from two recent SANS studies [21] and from measurements of the surface tension γ [22] performed at different concentrations and temperatures. Indeed, it is well known that surface tension is strongly sensitive to the presence of self-aggregation phenomena in solutions. Measurements of γ for the two temperature values 4 and 40 °C are reported in Fig. 1(b) as a function of the BE concentration C (m 1^{-1}). The surface tension behavior is typical of aqueous surfactant solutions forming micelles [23]. In fact, increasing the BE concentration (that plays the role of the surfactant), γ decreases up to a critical value after which it remains constant. For amphiphilic solutions, this concentration is the CMC. This is the point where micelles start to form in the bulk. Figure 1(a) shows the corresponding CMC data as a function of temperature determined from surface tension, partial molar specific heat, and sound velocity maxima [9,14]. The agreement among the different types of measurements is quite good. It is quite reasonable that BE molecules in water are associated in micelles, as suggested by different experiments (hypersound, density, viscosity, NMR, and specific heat).

A further confirmation of this is given by the data of a recent SANS experiment [21], performed on water solutions of two different C_mE_n amphiphiles, BE(C_4E_1) and C_6E_3 (a nonionic surfactant), at different temperatures and concentrations. The corresponding spectra show clearly the existence of micellar aggregates in BE solutions above the CMC. The corresponding data analysis shows that the size of micelles is constant, with a spherical shape, and its radius corresponds to the length of the surfactant. In addition, the presence of concentration fluctuations that contribute strongly to the scattered intensity is observed for all temperatures. Such fluctuations increase with temperature and are dominant near the demixing line. The micelle stability therefore seems to decrease with increasing temperature, which could be related to the exchange of alcohol molecules between micelles.

The properties of such structures can be analyzed from a molecular point of view by performing anisotropic Rayleigh light scattering measurements, which give fundamental information on the translational and rotational motion as well as on the viscoelastic properties of the solution [24]. Polarized and depolarized spectra are used in these studies. Depolarized Rayleigh scattering, which is sensitive to the molecular rotational motion, can be used to probe the dynamics of water in complex liquids, giving local information about the water properties in the neighborhood of micellar aggregates.

At the present time, great attention is given to the characterization of structure and dynamics of water in complex supramolecular fluids and in confined geometries because of their fundamental and technological importance [25]. In fact, water plays a determining role in the physical properties of such systems.

II. EXPERIMENTAL RESULTS

Water of liquid chromatographic quality, and butoxyethanol of high purity grade (99.99%) obtained from Jannsen Chemicals, were employed in this work. The butoxyethanol was used without further purification. Great care was taken to avoid contamination, and the sample solutions were prepared under nitrogen gas in a dry box. All samples were filtered before measurements. Solutions were prepared by weight at the concentrations $X=0.015$, 0.035, 0.048, 0.052, 0.07, and 0.09. Immediately after preparation, the samples where put into an optical cell. To avoid unwanted stray-light contributions at small forward angles, a 27-mm-diameter, high precision, round optical glass cell was used. A refractive index matching bath ensured flare-free measurements. In these conditions, the measured optical background in the scattered light was negligible. The scattering cell was thermostated, within ±5 mK, by using a proportional temperature controller monitored by a calibrated platinum resistor connected to a resistance bridge.

The depolarized Rayleigh scattering was performed using a fully computerized double pass double monochromator (DMDP), SOPRA model DMDP 2000, with a half width at half maximum (HWHM) resolution of 700 MHz. All spectra were measured in the frequency range from -100 to $+100$ cm^{-1}. The scattering depolarized geometry (VH) was the usual 90° arrangement, with the incident beam vertically polarized with respect to the horizontal scattering plane. The scattered light was collected through a Glan-Thompson polarizer with an extinction coefficient better than 10^{-7}. The exciting source was the 5145-Å line from an Ar^+ laser (Spectra Physics 2020) operating at an average power of 1 W.

The nonshifted depolarized Rayleigh light scattering is caused by the fluctuations of the traceless part of the polarizability tensor [24]. The corresponding time correlation function $G^{\text{anis}}(t)$ and its Fourier transform $I_{VH}(\omega)$ can be characterized by various contributions, which depend on the different mechanisms involved in the scattering processes. Usually the corresponding intensity is written in the form

$$I_{VH}(\omega)=\int_{-\infty}^{\infty} dt\, e^{-i\omega t} \times\{\langle \delta\alpha^*_{xy}(\vec{k},0)\delta\alpha_{xy}(\vec{k},t)\rangle \sin^2(\theta/2) + \langle \delta\alpha^*_{yz}(\vec{k},0)\delta\alpha_{yz}(\vec{k},t)\rangle \cos^2(\theta/2)\} , \tag{1}$$

where $\langle\ \rangle$ denotes the thermodynamic averaging, $\delta\alpha_{ij}(\vec{k},t)$ indicates the traceless part of the polarizability tensor, and θ is the scattering angle in the usual scattering geometry. In the $I_{VH}(\omega)$ spectrum, contributions due to the coupling between rotational motion and collective hydrodynamic transport modes, if present, are also taken into account.

Figure 2 reports the measured spectra of pure BE, for $-10<\omega<20$ cm^{-1} [Fig. 2(a)], and for a water-BE solution, for $-20<\omega<100$ cm^{-1} [Fig. 2(b)]. The spectra contain mainly two contributions: the far contribution ($\omega \geq 30$ cm^{-1}) and the narrow one ($\omega \leq 7$ cm^{-1}) caused by molecular rotational motion. Such contributions are Lorentzian lines related to the exponential time decay of the local molecular order. On this basis, our data were fitted to either a single or a double Lorentzian, plus the instrumental response function. As a result of such a procedure, the pure BE spectrum is found to be properly described by a single Lorentzian line, while all other spectra can be fitted only in terms of two significant contributions. The HWHM and the relative intensity of each Lorentzian line are obtained directly by the fitting. The continuous lines in Fig. 2 are the results of the fitting procedure. Pure alcohol exhibits a HWHM of about 1 cm^{-1} with a weak temperature dependence ($\sim$0.93 cm^{-1} for $T=0$ °C, and $\sim$1.1 cm^{-1} for $T=45$ °C). Solutions, instead, show two contributions having respective HWHM's of about 3 and 40 cm^{-1} which are strongly temperature dependent. They can be related to bulk water in normal and supercooled regions. In fact, bulk water is known to have two Lorentzian lines [26,27]; a fast one, with a HWHM at about 40 cm^{-1} (nearly independent of T), and a slow one with a HWHM ranging from about 1.7 ($T=-20$ °C) to about 8 cm^{-1} ($T=50$ °C). The relaxation times of the slow and fast modes are reported as functions of temperature in Figs. 3 and 4. For comparison, the results for pure water (coming from different experiments) [26,27] and for pure BE (Fig. 3) are also shown.

Another quantity obtained from the spectra is the integrated area of the two different Lorentzian contributions that represents the number of scatterers for the respective modes. Figure 5 reports the ratio of the area of the fast contribution to the total area for various concentrations versus temperature; as a result, it can be observed that the relative number of scatterers of the two distinct modes is independent of concentration and temperature. This means that both modes have the same molecular origin.

III. DISCUSSION

Figures 3 and 4 clearly indicate that the two fast and slow contributions of the measured spectra are due to the dynamics of water within the solutions. The alcohol ro-

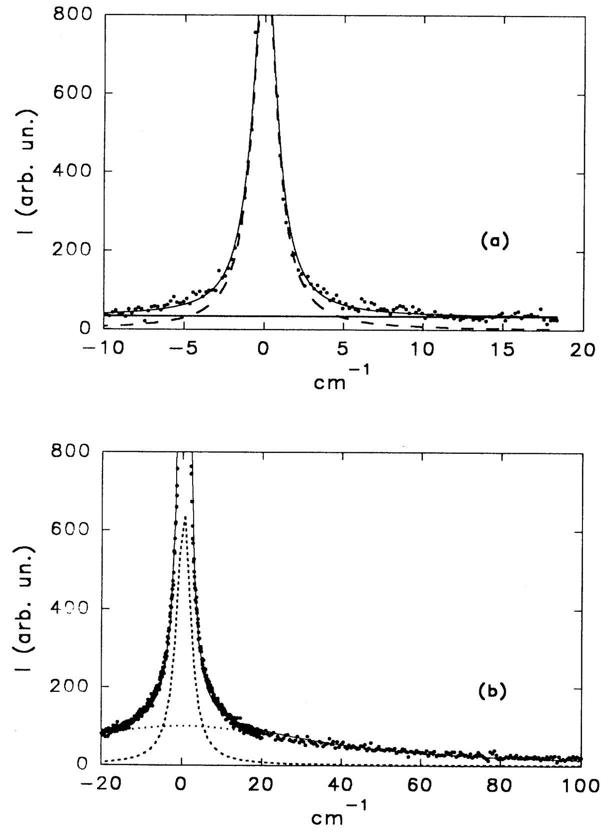

FIG. 2. Anisotropic spectra for pure BE (a) and for a water-BE solution (b). Continuous lines represent the results of the fitting procedure with one (pure BE) or two Lorentzian contributions (water-BE solutions). The dotted line indicates the Lorentzian contributions.

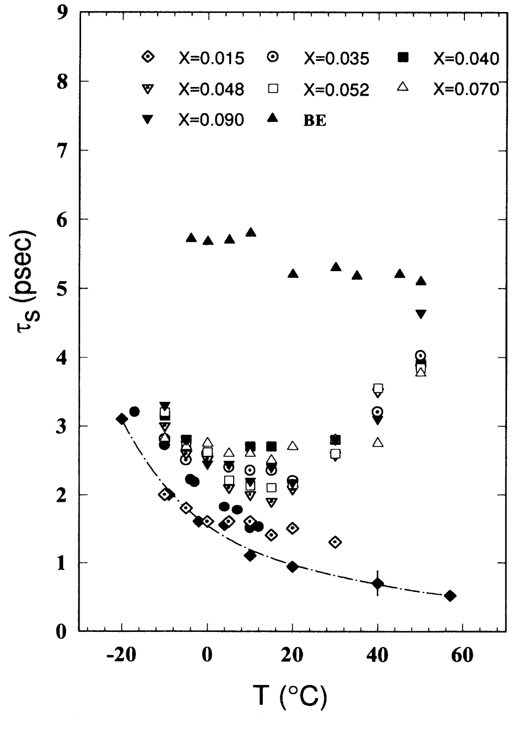

FIG. 3. Temperature behavior of the slow relaxation time τ_s for the various BE solutions. Data for water come from Refs. [26] (full dots) and [27] (full rhombs).

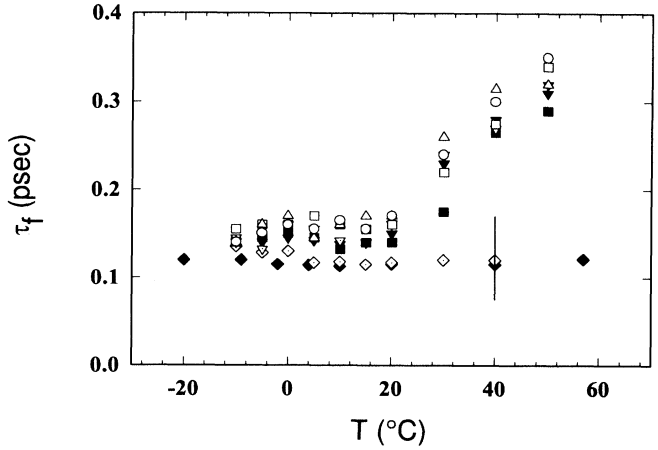

FIG. 4. Temperature behavior of the fast relaxation time τ_f for the various BE solutions. Data for water come from Ref. [27] (full rhombs).

tational dynamics is slower than that of water. The slow contribution (1.7–8 cm^{-1}) is known to be related to the rotational motion of water molecules and to the hydrogen bond. In fact, the measured time follows an Arrhenius temperature dependence with an activation energy that corresponds to the hydrogen-bond energy [28]. The physical origin of the fast contribution ($\sim$40 cm^{-1}), reported for the first time in Ref. [27], is not clear. However, it can be related to the correlations of reorientational modes of water molecules [29], and the results of Fig. 5, as discussed in the following, seem to agree with such an interpretation. In the present case the behavior of this fast mode is independent of temperature in the range from -10 to $+20$ °C within the experimental error (Fig. 4), and is about the same as for pure water, whereas a noticeable difference can be observed for $T > 20$ °C.

The relaxation time τ_S, due to the slow Lorentzian contribution, shows two different behaviors for the two temperature intervals $T < 20$ °C and $T > 20$ °C. For $T < 20$ °C, τ_S at the various water-BE concentrations shows the same Arrhenius temperature dependence as pure water (dotted lines in Fig. 3). However, except for $X = 0.015$ the relaxation times of the BE aqueous solutions are higher ($\sim$25%) than for bulk water. In contrast, in the low temperature region τ_f is nearly the same as in bulk water for all concentrations. For $T > 20$ °C, this mode shows a remarkable difference from water: a sharp increase of τ_s with temperature.

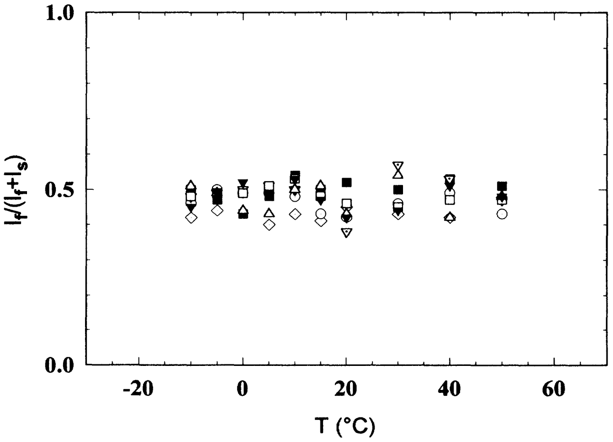

FIG. 5. Ratio of the area of the fast Lorentzian mode with the total area at the various water-BE concentrations vs the temperature.

The above results can be rationalized as follows. First, it is interesting to note that $X = 0.015$ is the only concentration studied here that is lower than the CMC, as shown by the surface-tension data. All other concentrations are above the CMC, where well-defined micellar structures, with a gyration radius corresponding to the length of the alcohol molecule, are present in the system, as verified by SANS [21].

The behavior of τ_s can be understood by taking into account the results of recent studies (x-ray [30] and Raman [31] scattering measurements) on a well known micellar system composed by an aqueous solution of an amphiphile that belongs to the same family as BE, i.e., the long-chain amphiphile polyoxyethylene monoalkyl ester $C_{10}E_5$. These measurements were performed at amphiphile concentrations and temperatures corresponding to the stable micellar phase; more precisely, along an isothermal path crossing the isotropic one-phase region from 0 to 1 amphiphile volume fraction ϕ. From the corresponding data analysis, it was shown that water molecules interact with the hydrophilic groups of the amphiphile. Part of the water is partially bound, via hydrogen bonding, to the oxyethylene groups of the amphiphile, and forms a layer that surrounds the micellar structure. The average number of bound water molecules per group is $n_w \simeq 1.5$ for amphiphile molecules aggregated in micelles and $n_w > 2$ for free amphiphile molecules. In addition, the structure of such bound water presents a local, low density, four-coordinated environment typical of the supercooled water. This behavior has been verified in different experiments concerning transport properties of water in confined geometries [25] (water in confined geometries at room temperature has a behavior similar to supercooled bulk water). The presence of this four-coordinated water layer around the amphiphile is reflected in the corresponding OH stretching vibrational mode with a behavior that corresponds to water at a temperature lower than the actual one in which the measurement is performed [31].

The same effect is observed for τ_s. In addition, the temperature behavior (Arrhenius) of this rotational relaxation time is the same as the corresponding one in bulk water. Therefore, the present data of water dynamics seem to confirm that micellar structures are present in water-BE suspensions.

Further confirmation is given by the results for the relaxation time at the $X = 0.015$ concentration (below the CMC). In fact, the system being unable to buildup alcohol structures at this concentration value (as also verified from SANS data [15]), the observed dynamics corresponds to the hydrogen bonds dynamics in bulk water.

A recent light scattering study [32] of water dynamics in aqueous solutions of $C_{10}E_5$ supports the structural picture proposed from BE in water. Depolarized Rayleigh-wing light scattering from $C_{10}E_5$ solutions showed a well-defined slowing down in the water rotational dynamics just above the CMC; an increase in the amphiphile volume fraction was followed by a further increase in the corresponding rotational relaxation times. The amphiphile volume fractions were comparable with ones studied in the present experiments.

For $T > 20\,^{\circ}\mathrm{C}$ the two relaxation times increase with temperature, showing a water dynamics in the BE solutions drastically different from that of pure bulk water. This behavior in both τ_s and τ_f may be related to the critical demixing which takes place in the system. Light and neutron scattering data [15,16,21] show that the fluctuation correlation length ξ increases in this temperature range. Light scattering data [17] show that the correlation length follows the laws of critical phenomena and diverges upon approaching the critical temperature T_c as $\xi = \xi_0 \epsilon^{-\nu}$, where $\epsilon = |T - T_C| / T_C$ is the reduced temperature and ν is the critical exponent. In addition, whereas in the low temperature region the SANS data are well fitted with a modified Guinier form, for the present temperatures a perfect fit is obtained only with the use of the simple Ornstein-Zernike relation [21]. Both these scattering results give, therefore, the information that the onset of the critical phenomenon can be detectable at temperatures far from the critical one (near 20 °C).

The increase with temperature of the correlation length ξ has been ascribed [21] to concentration fluctuations in the presence of spherical micelles. These fluctuations increase with temperature and are dominant when approaching the demixing curve. One explanation of this phenomenon is that micelle stability decreases with increasing temperature. This can be partly due to a possible exchange of alcohol molecules between micelles. In such a case, the hydration of the amphiphile molecules can play a role.

Another possible explanation of this water dynamics at high temperature is the clustering of micelles in the critical region. The increase in ξ approaching T_c can be connected to some kind of aggregation between micelles. This phenomenon is similar to the percolationlike transitions observed in microemulsions and micellar systems of nonionic amphiphiles [32,33] with a lower critical consolution temperature, where the aggregation (that increases with temperature) is due to the attractive interaction between micelles [4]. The percolation transition has been observed in amphiphiles of the C_mE_n class and in particular in a water solution of $C_{10}E_5$, where percolation takes place in the same range of volume fraction as with the present BE mixture. Due to the relative weakness of the attractive interaction between micelles [33], these clusters could live only on short time scales. For this reason, such clusters and their effects will be observable only by the use of high frequency measurements (when the time scale of the experiment is faster than the dynamics of this interaction). Under these conditions the system can be viewed by the probe as an instantaneous connected network. In contrast, at low frequencies (long times) the dynamics of the system reflects a collection of noninteracting particles undergoing Brownian motion [33,34].

Amphiphilic hydration in the BE system can be considered to be responsible for this intermicellar attractive interaction, which may originate clustering. In particular, such water molecules bound to oxyethylene groups (head groups of the amphiphile) may give rise to strong head-head amphiphiles correlations that increase the existing attractive interactions between the hydrophilic head groups of the surfactant molecules belonging to different micelles. It is also possible that such correlations can have an ordering effect on the structure of the water around the micelles, increasing the amount of tetrabound molecules. It has been observed that such correlations are able to support viscoelastic effects such as those observed in dense polymeric or polyelectrolyte solutions and in nonionic amphiphile-water mixtures [1,34]. Such effects are reflected in the corresponding longitudinal moduli measured via sound dispersion of these suspensions [33].

The temperature behavior of the fast contribution also seems to agree with this second structural interpretation of the BE system. This phenomenon can also be related to this increase in head-head correlations in the amphiphile molecules.

In addition, by means of this droplet model, it is possible to give an accurate explanation of the critical behavior of the shear viscosity and relaxation rate in the density-density correlation function measured by dynamic light scattering in the BE mixture. In fact such data can be analyzed in terms of the mode-coupling theory only if background effects (due to a persisting presence of micellar aggregates) on the transport coefficient are taken into account [17]. This second possibility is also consistent with results for the surface tension γ: the data of Fig. 1(b) show only a small decrease in γ with a strong increase in the temperature. The first explanation, which requires eventual melting of the micellar structure, would give a remarkable increase in γ.

However, both possible explanations of the physical origin of the observed increase of rotational times are accounted for by the results represented in Fig. 5, which shows the ratio of scatterers involved in both relaxational processes.

IV. CONCLUSIONS

This paper presents depolarized Rayleigh light scattering measurements on a water suspension of the C_4E_1 short-chain nonionic amphiphile at various concentrations as a function of the temperature. The comparison with pure water data suggests that the BE spectra refers to the molecular rotational motion of water molecules. In fact, the Rayleigh spectra of the mixture show two characteristic contributions of the water spectra. Two different behaviors for water dynamics are also observed as a function of the temperature, above and below $T \sim 20\,^{\circ}\mathrm{C}$.

Such results are therefore discussed in terms of the existing structural models. The data analysis confirms the amphiphilic character of the ethoxylated alcohol molecules which form micellar structures, indicating that the water rotational motion is dominated by the presence of such aggregates and by the hydration of the oxyethylene groups of the alcohol molecules.

The spectral results at $T < 20\,^{\circ}\mathrm{C}$ indicate that the system is a suspension of stable micelles built up by a self-aggregation of the alcohol molecules, in agreement with recent neutron scattering data. The water dynamics corresponding to spectra observed for $T > 20\,^{\circ}\mathrm{C}$ (when the system evolves toward the phase separation) can be explained by either of two structural models that involve water and alcohol molecules in different ways. The first model indicates the simultaneous presence of micellar aggregates and concentration fluctuations. Such fluctuations increase with temperature and become dominant near the demixing line. As a consequence, the micellar stability decreases with temperature and can be related to the exchange of alcohol molecules between micelles. The other model assumes that the micellar structure is stable in this temperature range and that the observed water dynamics can be due to a micellar clustering in the critical region. In summary, the micellar structure of butoxyethanol in water seems unquestionable, as shown by surface tension and light scattering measurements, especially at higher temperatures where the system evolves toward the phase separation.

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