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Light-scattering studies on water–nonionic-amphiphile solutions

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The structure of water in aqueous solutions of the polyoxyethylene nonionic amphiphile $C_{10}H_{21}(OCH_2CH_2)_5OH$ is studied by depolarized Rayleigh-wing and Brillouin light scattering along an isothermal path crossing the isotropic one-phase region from 0 to 1 amphiphile volume fraction ϕ. Depolarized Rayleigh-wing light scattering shows a well defined slowing down in the water rotational dynamics just where the structure of the system changes from the micellar structure to a block copolymeric melt. The interpretation of the obtained data gives the following structural picture for water: for ϕ lower than 0.75, water is partially bound to the oxyethylene groups of the amphiphile; above $\phi=0.75$ all the water present in the system is bound. Brillouin scattering, probing thermodynamical quantities as the bulk modulus, gives information about the collective properties of the system. Two distinct behaviors in the bulk compressibility of the system are observed in two different concentration ranges. In the micellar region, measurements of the dispersion of the sound velocity as a function of the droplet volume fraction show an increased rigidity of the system at high frequencies. This increase in the bulk modulus is consistent with a percolation phenomenon. Micelles build up transient networks due to the attractive interaction. Above this region Brillouin scattering probes the evolution of the system towards the pure amphiphile phase for which a decrease of sound dispersion with ϕ is observed. Strong correlations between amphiphile molecules are present at large amphiphile concentrations.

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I. INTRODUCTION

Complex fluid systems represent a class of novel materials that are of large interest in many fields of pure and applied research, as well as in technological applications [1]. As is well known, complex systems contain extended polyatomic structures, of length scales larger than atomic and molecular ones, typically in the range from tens of Å to several microns. Consequently the microscopic properties of these materials are currently studied on length scales ranging from neutrons to light wavelengths. Water solutions of nonionic surfactants are good examples of complex fluids both for their dynamical and structural properties. Aqueous solutions of the polyoxyethylene amphiphiles $C_mH_{2m+1}(OCH_2CH_2)_nOH$ or (C_mE_n for short) have been the subject of extensive theoretical and experimental studies [2,3], mostly above the critical micellar concentration (CMC) where supramolecular aggregates are formed. C_mE_n's are constituted by a linear saturated hydrocarbon chain (hydrophobic moiety) linked to a polyoxyethylene chain (hydrophilic moiety). A characteristic feature of these solutions is that they behave as critical systems, with a well defined consolute curve which separates the one-phase region from the two-phase one, with a lower critical point. On the other hand, in contrast to simple binary mixtures, such systems are able to form various structural phases. At high concentrations the phase diagram of these systems can become rather complex, presenting regions of anisotropic phases, as, for example, lamellar, cubic, hexagonal, and solid [2,3].

Recently it has been proposed that such nonionic micellar solutions can be used as model systems of more fundamental studies in the physics of liquids. In some regions on the phase diagram the spherical micellar structure is kept for a very large range of amphiphile volume fraction ϕ. For example, for $C_{10}E_5$ at a constant temperature, the packing fraction of the spherical droplets simply increases with ϕ up to a concentration value of $\phi\simeq0.75$. The interparticle interaction is generally modeled as a repulsive hard core potential plus an attractive Yukawa tail [4]. It is then interesting to compare the properties of this amphiphile system with the results of hard sphere models developed for liquid systems [5], mostly in connection with cooperative phenomena, i.e., phase transition, fractal aggregation, percolation phenomena, glass transition, and disorder-order transition [1-6], that are typical of a moderately or highly packed hard sphere system.

Whereas many of the physical properties of such aqueous solutions are known for the micellar phase up to now the system behavior has not been well understood at very high amphiphile concentrations. For instance, it is not clear what is the limiting amphiphile concentration at which the solution can still be described as a water con-

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tinuous dispersion of amphiphile aggregates, and how the system evolves toward the pure liquid amphiphile phase. Light scattering can give detailed information about the structural and dynamical behavior of such systems, such as the vibrational, translational, and rotational molecular modes and the viscoelastic properties which are due to the intermicellar interactions [1,2]. More precisely, whereas Raman scattering can furnish details about the intramolecular vibrational dynamics, polarized and depolarized Rayleigh and Brillouin spectra can be used to study collective molecular motion in this class of systems [7]. In the two latter cases the measured spectra give information mainly about the translational motion, as reflected by the density correlation function. More specifically, depolarized scattering allows the study of the rotational motion of the molecules as influenced by the presence of structural arrangements, while Brillouin scattering is useful to characterize the viscoelastic behavior in the high frequency range (GHz).

The present paper reports extensive Brillouin and depolarized Rayleigh-wing scattering measurements aimed at providing insight into the structure and dynamics of a dense amphiphile-water system, namely the $C_{10}E_5$-water solution. The phase diagram [2] of $C_{10}E_5$ in water allows isothermal paths, between 25 and 45°C, which cross all volume fractions from $\phi=0$ to 1, and for which the solution is isotropic. These paths lie above the mesophase regions and below the cloud-point curve. On these paths above the CMC (9×10^2 μmol/l), $C_{10}E_5$ forms globular micelles that are stable and also nearly monodisperse in the high concentration region. Recently, the structural properties of the $C_{10}E_5$ water solution have been carefully studied by means of small angle x-ray (SAXS) and neutron scattering (SANS) experiments [8] along the isothermal path at $T=35$°C. The solution is structured for all concentrations ranging from the micellar region to the pure liquid amphiphile. More precisely, as the volume fraction ϕ increases, the solution presents a structure peak which becomes sharper and sharper. In addition, some orientational correlations between neighboring amphiphile molecules are preserved even at high concentrations. From the SANS data [8] a structure peak is clearly observable up to $\phi=0.95$, but the pure $C_{10}E_5$ neutron spectra were absolutely flat. This is due to the fact that the neutron scattered intensity is mainly determined by the large contrast between the deuterated water and the hydrogenated amphiphile. The data interpretation of SANS and SAXS allow the following conclusions: large orientational correlations exist among neighboring amphiphile molecules and, at high surfactant concentrations ($\phi>0.7$), the system behaves essentially as a block-copolymer melt. The observed structure peak at $\phi=0.95$ for neutrons and $\phi=1$ (pure amphiphile) for x-rays is due to the block structure of the surfactant monomer with attractive head-head and tail-tail interactions and repulsive head-tail interactions, the so called correlation-hole effect [9].

From this structural picture it appears that water molecules play a significant role in these systems. A part of the water is hydrogen bound (HB) to the polyoxyethylene head groups of the amphiphile. The analysis of SANS data gives an average number of water molecules bound to each oxyethylene group as $n_w\simeq1.5$ for $\phi<0.7$, and $n_w\simeq2$ for $\phi>0.7$. Furthermore, for $\phi>0.7$ all water molecules are HB to the oxyethylene chains. The fact that, at high concentrations, there is no free water in the system is consistent with the low values of the electric conductivity measured in the same solution. Raman light-scattering experiments performed on the same system [10] confirm the SANS and SAXS results. In fact Raman scattering, sensitive to the details of the molecular vibrational dynamics [7,11], allows a precise characterization of the local organization of water. In particular it is found that the O-H stretching vibrations of the water bound to polyoxyethylenes are analogous to the ones observed for the glassy water.

Additional information about these water-amphiphiles systems can be obtained from the analysis of the depolarized Rayleigh-wing data. As is well known, the central frequency contribution of the scattered light is sensitive to the molecular rotational motion and can probe the water rotational dynamics in the system. The linewidth, or the corresponding relaxation time, can be related to the hydrogen bond (HB) rotational dynamics [12]. Therefore, depolarized Rayleigh-wing measurements provide further direct information about the local properties of water in the neighborhood of the polyoxyethylene surfactants all along the isothermal path of the phase diagram, both in the micellar region, at low ϕ, and in the region of high ϕ. Furthermore, since the system maintains a well defined micellar structure at high concentrations, acoustic propagation measurements can be of interest. Because absorption and the velocity of sound are directly related to the bulk compressibility of the medium, these measurements probe the collective system properties [13].

II. EXPERIMENT

The phase diagram of $C_{10}E_5$ in H_2O [2] shows a cloud-point curve with a minimum at about 45°C and a liquid crystalline region in the range of amphiphile volume fraction between 0.05 and 0.85 with a temperature between 0 and 20°C, so that the system can be studied along two isothermal paths ($T=25$ and 35°C) that do not cross mesophase regions. The concentrations are those used in SAXS, SANS, and Raman scattering measurements: i.e., $\phi=0.3$, 0.5, 0.6, 0.7, 0.75, 0.87, 0.91, and 1 (pure amphiphile). Triple distilled deionized gas-free water was used. Great care was taken to avoid any contamination, and all the samples were filtered before measurements. The measurements were performed after a suitable time in order to ensure the thermodynamical equilibrium of the samples.

The depolarized Rayleigh and Brillouin scattering measurements were performed using a double pass double monochromator (DMDP), SOPRA model DMDP 2000, with a resolution of 700 MHz. The resolution of the DMDP is comparable to that of a Fabry-Pérot étalon working at a free spectral range of ~50 GHz. For the study of the Brillouin contribution this instrument has several advantages with respect to the Fabry-Pérot interferometer: an optical stability of several days, no problems arising from periodic boundary conditions, and an exceptionally high stray-light rejection. For all the scattering measurements the exciting source is the 5145-Å line from an Ar^+ laser, and the scattering geometry is the usual 90° arrangement. The scattered light is collected through a Glan-Thompson polarizer with an extinction coefficient better than 10^{-7}. The samples are thermostated in an optical cell to within 0.02°C. Depolarized spectra are measured in the frequency range -100 to $+100\ \mathrm{cm}^{-1}$, and Brillouin data in the range -10 to $+10$ GHz.

The nonshifted depolarized light scattering is due to the fluctuations of the traceless part of the polarizability tensor [7]. The measured scattered intensity $I_{VH}(\omega)$ can be characterized by various contributions, which depend on the different mechanisms involved in the scattering processes. Since the information which can be extracted from the measured spectra is related mainly to the rototranslational motion, as reflected by the density correlation function, more precisely to the molecular rotational motion of the molecules, such a scattering technique gives information about the system dynamics on a microscopic length scale. Because both water and amphiphile molecules of the system are composed of anisotropic units, the corresponding spectrum can involve at least two contributions from the different rotating molecular groups. Such contributions are Lorentzian lines related to the exponential time decay of local order [7].

Because the free amphiphile molecular rotation linewidth or the contribution related to the rotational dynamics of polyoxyethylene terminal groups can fall in a spectral region smaller than the present instrumental resolution, the measured spectra were fitted with a single Lorentzian plus an instrumental Gauss-Lorentzian response function and a constant background. This procedure seems appropriate to the present experimental results. As an example, Fig. 1 shows the spectrum of the $C_{10}E_5$ solution at $\phi=0.6$ in the frequency range -30 to $+30\ \mathrm{cm}^{-1}$. The continuous line represents the best fit of the data; in the same figure the contribution caused by molecular rotational motions is indicated as C, the instrumental resolution as A, and the constant background as B. Therefore the HWHM (half width at half maximum) and the relative intensity of the single Lorentzian are obtained directly by the fitting program.

The measured linewidths are of the same order of magnitude as those of pure water for the same temperature. Therefore the observed spectral contributions can be related to the hydrogen bond (HB) dynamics [14] in the neighborhood of the amphiphilic molecules.

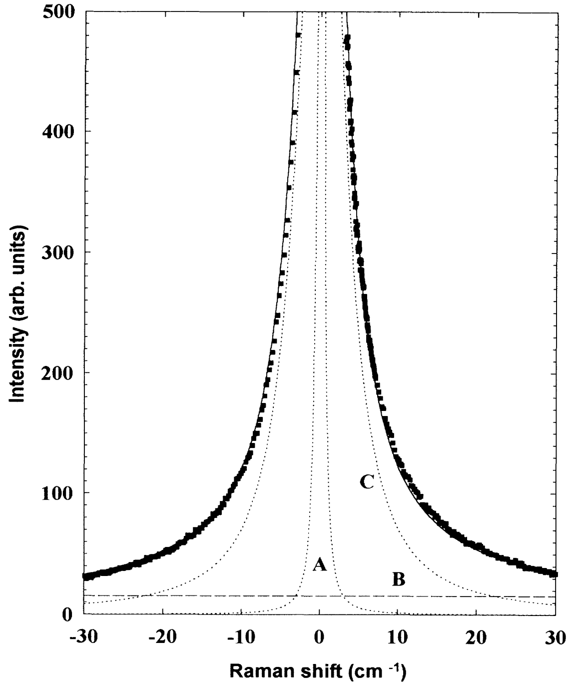

FIG. 1. Anisotropic spectrum for the suspension with $\phi=0.6$ in the frequency range -30 to $+30\ \mathrm{cm}^{-1}$. The continuous line represents the best fit of the data; C is the contribution caused by molecular rotational motions, A the instrumental resolution, and B the constant background.

In both the depolarized and Brillouin scattering measurements the high quality of the data fit implies that it is not necessary to consider other central ($\omega=0$) components due to other relaxation modes [15]. Therefore the observed spectra can be considered to be characterized only by the molecular rotational motion.

The fully polarized scattering intensity vs the frequency ω at a given scattered wave vector k, gives information about the dynamical structure factor $S(k,\omega)$ which is the Fourier transform of the kth component of the density-density correlation function $G_\rho(k,t)=\langle\delta\rho(k,0)\delta\rho(k,t)\rangle$. The dynamic structure factor depends on the viscoelastic behavior of the system under examination and can be written as [16]

$$\begin{aligned}S(k,\omega)=\frac{1}{\pi}V\rho^2k_BT\beta_T\Bigg\{&\left[\frac{\gamma-1}{\gamma}\right]\frac{2D_Tk^2}{\omega^2+(D_Tk^2)^2}\\&+\frac{1}{\gamma}\Bigg[\left[\frac{\Gamma(k)}{[\omega-\Delta\omega(k)]^2+\Gamma^2(k)}+\frac{\Gamma(k)}{[\omega+\Delta\omega(k)]^2+\Gamma^2(k)}\right]\\&+\frac{\Gamma(k)}{\Delta\omega(k)}\left[\frac{\omega+\Delta\omega(k)}{[\omega+\Delta\omega(k)]^2+\Gamma^2(k)}-\frac{\omega-\Delta\omega(k)}{[\omega-\Delta\omega(k)]^2+\Gamma^2(k)}\right]\Bigg]\Bigg\}\ .\end{aligned} \tag{1}$$

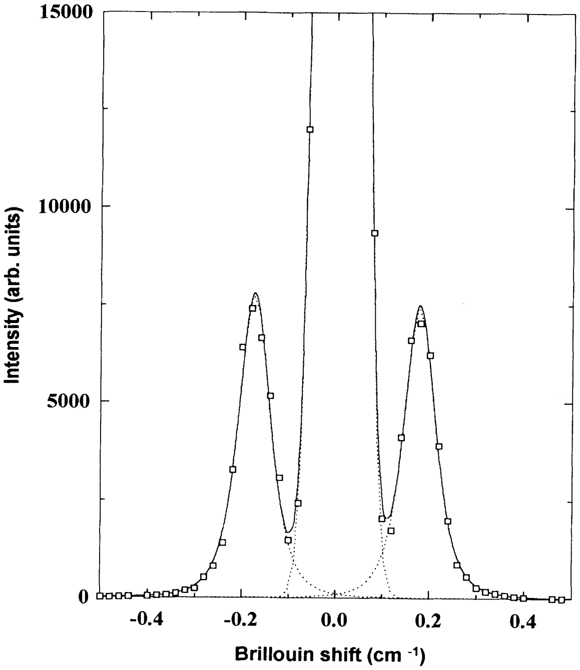

FIG. 2. Typical Brillouin spectrum in the frequency range -0.5 to $+0.5$ cm^{-1} (± 15 GHz). The continuous line represents the best fit of the data with Eq. (2).

Here V is the scattering volume, ρ the system density, k_B the Boltzmann constant, T the temperature, β_T the isothermal compressibility, γ the specific heat ratio, D_T the thermal diffusivity, $\Gamma(k)$ the Brillouin linewidth, and $\Delta\omega(k)$ the Brillouin shift. The first term of Eq. (1) represents the zero-frequency quasielastic component, while the second one is the Brillouin contribution written as the sum of its symmetric and asymmetric parts. We fit our spectra to Eq. (1) in order to derive $\Delta\omega(k)$; the result of such a procedure is shown in Fig. 2. The hypersound velocity V_s can be calculated from the frequency shift $\Delta\omega(k)$.

III. RESULTS AND DISCUSSION

A. Depolarized light scattering

The experimental results of depolarized scattering concern the measured linewidth Γ, obtained as the HWHM of the only rotational contribution present in the spectra for each amphiphile concentration. The related relaxation time τ, measured at the two temperatures 25 and 35°C, is reported as a function of ϕ in Fig. 3. A comparison of the τ values for moderate amphiphile concentrations with the pure water values at the same temperature confirms that these spectra refer to water dynamics around the amphiphile aggregates. Figure 3 also shows the τ value of the pure amphiphile phase.

Many experimental studies of depolarized scattering [14], performed on water both in the stable and the metastable supercooled phases, assign the observed spectral contributions to the hydrogen bond (HB) dynamics. Together with the O—H stretching studies [10], these results can give a precise picture of the water structure and dynamics. The results of Fig. 3 can be discussed in terms of the HB dynamic models commonly used for the interpretation of water properties [17]. The depolarized light-scattering data show that there are two completely different behaviors in the spectra above and below a saturation value ϕ_S that are nearly coincident with the maximum value of the packing fraction of spherical particles ($\phi_S \sim 0.75$). Similarly to SAXS and SANS data [8], this saturation value gives the threshold value of existence of stable micellar aggregates in the system. Above this concentration the system behaves as a polymeric melt.

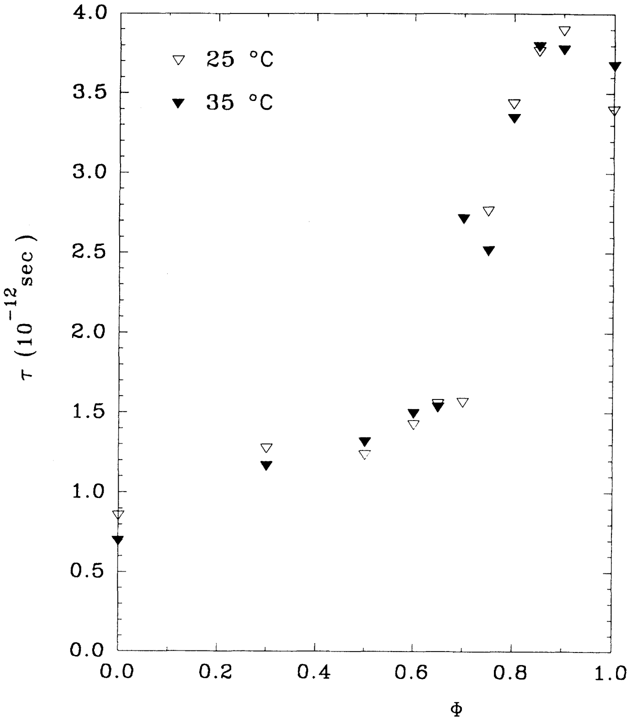

FIG. 3. Relaxation time τ of the water molecular rotational contribution vs the volume fraction ϕ as obtained from the depolarized Rayleigh-wing scattering.

Below ϕ_S the following are known [10,17].

(i) The O—H stretching spectrum of pure water differs from the spectrum of water in the amphiphile solutions even at low concentrations.

(ii) In the amphiphile solution a larger amount of water molecules are bound in low density structures (tetrabound) [17], as compared with pure water.

(iii) An increase in the amphiphile content results in an increase of the contribution of the more connected water.

(iv) Above the saturation value ϕ_S, the observed O—H stretching spectra are entirely located in the spectral region of the contribution of the tetrabound water molecules (about 3200 cm^{-1}); the percentage of partially bound water is irrelevant. The spectral form is similar to that of glassy water.

These results can be explained by considering the suggestions of previous SANS and SAXS studies [8], where it was proposed that, for all concentrations below ϕ_S, a certain quantity of water is bonded to the polyoxyethylene head groups. More specifically, in the concentration region where stable micelles are present, SANS and SAXS data can be well described by considering a three component model: the hydrocarbon region (hydrophobic chains of the amphiphile), the hydrophilic region (polyoxyethylene head groups together with bound water, with an average number $n_w = 1.5$ of water molecules bounded per oxyethylene group), and a region of free water. The values of n_w calculated both from the OH stretching spectra and from the SANS data are nearly coincident within the experimental uncertainty. For high surfactant concentration, $\phi > \phi_S$, Raman and SANS data suggest that all water present is bound to oxyethylene groups, giving $n_w = 2$.

Figure 3 shows a different behavior for the measured relaxation times, above and below a well defined volume fraction value, for the data at both $T = 25$ and 35°C. Also in this case the concentration that separates the two distinct τ behaviors is about the same as the saturation value ($\phi_S \sim 0.75$) observed in previous experiments. For $\phi < \phi_S$, i.e., in the phase region of very stable micellar aggregates, a small increase with concentration of the rotational relaxation time is observed. For very low amphiphile concentrations, the observed τ values are almost coincident with those corresponding to water at the same temperature. This comparison suggests that a rotational dynamics due to water molecules was observed, thus confirming the physical picture proposed by SAXS and Raman data. In this concentration region the slow increase of τ must be related to the presence of a certain amount of water bound around the micelles, the remainder being bulk water. The relative amount of bound and bulk water changes with the amphiphile concentration. Since an exchange of water molecules between the two species is allowed, at low concentrations a relatively low value of the average number of water molecules bound per oxyethylene group is observed, in comparison with samples of higher volume fraction.

For $\phi > \phi_S$ the measured relaxation times gives evidence of a dramatic slowing down in the HB dynamics. In this concentration region all the water present in the system is bound to the amphiphile, and in addition it can be considered all to be tetrabonded because the final τ value (for $\phi = 0.91$) is about the same as the relaxation time of deeply supercooled water at $T = -27$°C [14]. The measured pure amphiphile τ value is related to the rotational dynamics of the $C_{10}E_5$ molecule, and can be due to the presence of an external hydroxylic (O—H) in the hydrophilic head group.

At these very high concentrations, the structural organization of the mixture changes. The micellar structure typical of the previous concentration regime evolves toward a block-copolymer melt. In this case all water is confined around the amphiphile. Such water molecules, with the same tetrabound structure, act as a bridge between the amphiphilic molecules, giving rise to well defined orientational correlations. This allows the observation of well defined structure peaks in this phase by means of SANS and SAXS measurements. Such water molecules bound to the amphiphile head groups enhance the contrast between the hydrophilic and hydrophobic molecular tails and increase the attractive head-head interaction between amphiphiles. The final result is the observation of the correlation-hole effect.

B. Brillouin scattering

Sound propagation in amphiphile suspensions is sensitive to collective phenomena such as self-aggregation that originate from the micellar structure and from the connectivity of such aggregates. The presence of interactions between these colloidal particles in the suspension can result in structures with a length scale larger than the molecular one. These latter structures can be observed by light scattering (elastic) in charged colloidal solutions at moderate concentrations or in dense amphiphile suspensions. Sound propagation measurements as a function of frequency can provide information about the dynamics of these structures. The presence of long range intermicellar aggregates will be reflected in the elastic properties of the medium, giving rise to a viscoelastic behavior. In such a case the system dynamics presents a well defined time behavior with a characteristic frequency dependence. For long times (low frequencies), it reflects a collection of noninteracting spheres for which shear stresses are relaxed. Micelles behave like isolated particles undergoing Brownian motion. Therefore, the observed sound velocity mainly reflects the physical behavior of the suspending fluid. For short times, the solidlike network is able to support shear stresses and exhibits a finite elastic modulus. By increasing concentration, the system rigidity (and therefore the sound velocity) increases at high frequencies, showing a behavior typical of solidlike structures.

Since Brillouin scattering is directly related to the system density-density correlation function, it reflects the system collective properties modulated by the interactions [7]. In this technique, the light scattered at some wave vector k is spectrally resolved, probing the light scattering from the thermally excited sound waves with the same wave vector k. A measure of the linewidth and frequency of these sound waves yields the sound absorption and velocity, respectively. Complementary ultrasonic measurements can provide a measure of the system sound behavior at much lower frequencies and longer wavelengths.

As it is well known, the elastic behavior of a system is well described in terms of the frequency dependence of the complex longitudinal modulus $M(\omega) = M'(\omega) + iM''(\omega)$, which is the inverse of the adiabatic compressibility associated with the longitudinally compressional wave [13]. It is directly connected with the quantities measured in a Brillouin or ultrasound experiment, i.e., the velocity V_s and the absorption coefficient α; more precisely the velocity is associated with the real part of M by $V_s^2 = M'/\rho$ (ρ is the average density) whereas the damping of the sound wave is determined by the imaginary part of M ($\alpha = \omega M''/4\pi V_s^3 \rho$) [13]. Furthermore, since M is related to the compressional modulus K and the shear modulus G ($M=K+4G/3$), the Brillouin data are also sensitive to the shear rigidity of the system, although only longitudinal properties are probed directly. Considering the previous discussion, in a complex fluid at fixed composition and temperature, observed higher sound velocities may be associated with a behavior typical of solidlike or associated structures, and slower sound velocity with a liquidlike behavior.

Water–nonionic-amphiphile $C_{10}E_5$ solutions were investigated by means of hypersound along the same continuous isothermal paths as in depolarized light-scattering experiments. These measurements provide information about the elastic properties of the system in the two volume fraction intervals that characterize the one-phase region; that is, in the dense micellar region as a function of the micelle packing fraction, and in the region where the system evolves from the micellar to the pure amphiphile phase.

As pointed out by the current theoretical models for liquid state [5], an assembly of hard spheres tends to form extended structures by means of percolation, because of the attractive interparticle interactions. More generally, such a system can also perform a transition from a liquid to a crystalline or glassy state depending on temperature and concentration. Also micelles, because of their weak attractive interaction, tend to form extended clusters whose size and concentration increase with ϕ. Therefore Brillouin scattering experiments are useful to study the connectivity properties of such intermicellar aggregates.

Figure 4 shows the hypersonic velocities V_s ($\sim$6 GHz) in the $C_{10}E_5$ water system as a function of ϕ at temperatures of 25 and 35°C (full squares). The dotted line represents the hypothetical velocity of the mixture obtained from a volume-weighted mix of the velocity of each of the constituent phases. Some ultrasound velocity data at 5 MHz (open squares) are also reported in the figure. As can be observed, V_s also shows two different behaviors above and below ϕ_S. In particular the hypersound velocity increases with ϕ in the concentration range 0–0.75, with a maximum value centered around ϕ_S; further increasing ϕ, going toward the pure amphiphile phase, results in an abrupt velocity decrease. A comparison between the hypersound and ultrasound data clearly shows a strong dispersion effect: sound velocities are quite different for the two frequencies, 5 MH and 6 GHz, at the same amphiphile concentration. Dispersion increases with ϕ in the entire concentration region of stable micelles.

Such a velocity dispersion below ϕ_S can easily be connected to the presence of an intermicellar structure. Particle interactions build up cluster aggregates whose size increases with the particle packing fraction This aggregation phenomenon is typical of colloidal suspensions and follows a characteristic kinetics that depends on the particle's properties [1]. In amphiphile solutions above the CMC this is due to the attractive part of the intermicellar interactions, and the resulting structures depend on the relative interaction strength. Also such systems, when in the microemulsion state (obtained by adding an oil to the amphiphile solution), are well described by a potential function having a repulsive hard core plus a Yukawa tail representing the attractive interaction [1,4]. This interaction gives rise to very interesting properties, like a phase diagram with an upper cloud point [5], and a percolationlike transition.

Due to the weakness of the attractive interaction between micelles [18], existing clusters can live only on short time scales. Therefore, at high frequencies (hypersound), the time scale of the measurement will be faster than the dynamics of these interactions, and the system is viewed as an instantaneous connected network. By contrast, at low frequencies (long times) the dynamics of the system reflects a collection of noninteracting particles in which shear stresses are relaxed. Consequently, for short times the solidlike network is able to support shear stresses and exhibits a finite elastic modulus. The data of Fig. 4 confirm the presence of a connected intermicellar network at high ϕ. For micellar systems, as shown by Ye *et al.* [18], this observed elastic behavior can be entirely connected with an aggregation kinetics driven by percolation above a certain threshold. Because the structures are self-similar, the increase in the elastic modulus follows a well defined scaling behavior with concentration. The scaling indexes in the percolating quantity are

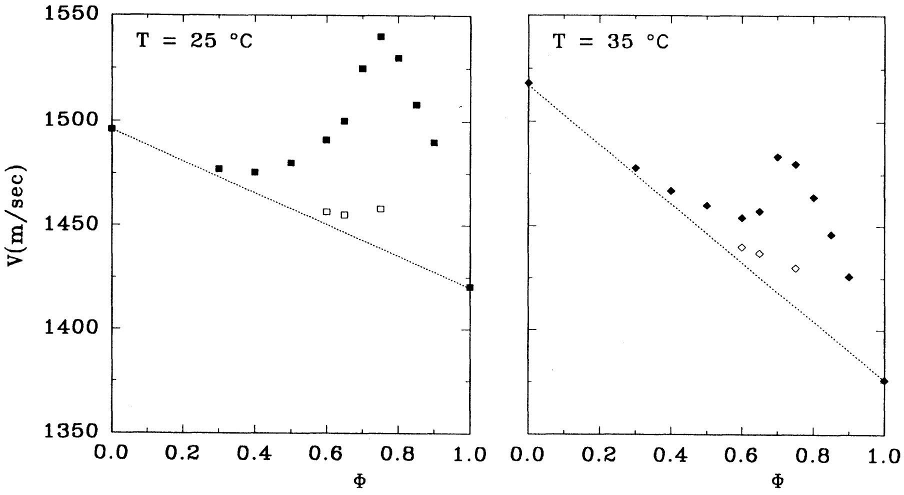

FIG. 4. The measured hypersonic ($\sim$6 GHz) velocities V_s as a function of ϕ at temperatures of 25 and 35°C (full squares); the dotted line represents the hypothetical velocity of the mixture obtained from a volume-weighted mix of the velocity of each of the constituent phases. Also, some ultrasound velocity data measured at 5 MHz are reported (open symbols).

different if the threshold value is approached from above or below [19]. In particular, above the concentration threshold the elastic modulus has to scale as

$$\Delta M' \sim (\phi - \phi_P)^t ,$$

where ϕ_P is the volume fraction corresponding to the percolation threshold, t is the percolation exponent above the percolation, and $\Delta M'$ is the difference between the measured and corresponding values calculated from an effective medium model M'_e, i.e.,

$$\Delta M' = M' - M'_e$$

and

$$M'_e = (1-\phi) M'_{\text{wat}} + \phi M'_{C_{10}E_5} ,$$

where M'_{wat} and $M'_{C_{10}E_5}$ refer to the longitudinal modulus of water and the pure surfactant, respectively. In order to calculate M' for the present suspensions, we have also measured the relative densities.

Figure 5 reports $\Delta M'$ as a function of $(\phi - \phi_P)$ in a log-log scale for the two temperatures 25 and 35°C with best fit values of $\phi_P = 0.16$ and $t = 2.4 \pm 0.2$. This value for ϕ_P is in agreement with the one obtained for different micellar systems in Ref. [18]. The t value is in complete agreement with the one proposed from theoretical studies of percolation [19].

The strong decrease in V_s observed for $\phi > \phi_S$ can be related to a change in the structure of the system. In such a concentration region the micellar structure is gradually destroyed and the system evolves toward pure amphiphile solutions through a more disordered phase. The high values of the longitudinal modulus and the remaining presence of sound dispersion are due to strong correlations between the amphiphile molecules. In particular, water molecules totally bound to the oxyethylene groups increase attractive interactions between the hydrophilic head groups of the surfactant molecules, giving rise to strong head-head amphiphile correlations. Such correlations are able to support viscoelastic effects such as those observed in dense polymeric or polyelectrolyte solutions. This explains the system behavior in such a high ϕ region, and is in agreement with the picture proposed by SAXS and SANS data [8] that propose for the present system a dynamical behavior analogous to a block-copolymer melt, with interactions due to the correlation hole effect [9].

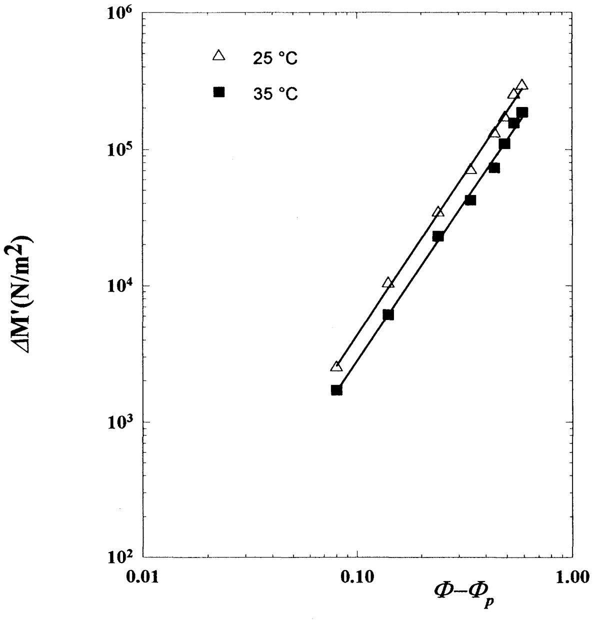

FIG. 5. Scaling behavior of $\Delta M'$ (for $T = 25$ and 35°C) as a function of $(\phi - \phi_P)$. Full lines represent the best fit of data.

IV. CONCLUSIONS

Two different scattering techniques have been used to study the isotropic single-phase region in a water–nonionic-amphiphile solution (water-$C_{10}E_5$). These studies, performed by means of depolarized Rayleigh-wing and Brillouin light scattering, allow a careful analysis of the structure and dynamics of the suspension along an isothermal path that does not cross structured phases in the phase diagram. Although it is well known that above the CMC the system structure is that of a colloidal suspension in which the $C_{10}E_5$ molecules are arranged in globular micelles that are stable and nearly monodisperse in a large concentration range, at present the system properties for very high amphiphile concentration and the role played by water are not completely established. Therefore, the scattering data reported in this paper are meant to elucidate these points.

As a conclusion, Rayleigh-wing and Brillouin scattering measurements confirm the picture proposed for this suspension by SAXS, SANS, and Raman studies, that is that water molecules are partially bound to the oxyethylene head groups of the surfactant for amphiphile volume fractions ϕ lower than 0.75; above such a value all the water present in the system is bound to the oxyethylene groups. In addition, the water structure around the surfactant has a local structure typical of tetrabonded water.

More precisely, the depolarized Rayleigh-wing light scattering, acting as a local probe, shows a well defined slowing down in the water rotational dynamics when the structure of the system changes from the micellar structure to a block copolymeric melt. The measured values of the rotational relaxation times τ of water show a general trend that agrees with the structural picture given by other scattering techniques, and, in addition, have numerical values that furnish a deeper confirmation that the water structure around the amphiphile molecules corresponds to an environment of tetrabound molecules.

The Brillouin scattering shows an increasing dispersion in the sound velocity with concentration in the region of stable micellar structures, whereas this effect decreases in the interval of very high volume fraction. The present data indicate two characteristic dynamical behaviors, i.e., above and below $\phi \sim 0.75$. For the concentration range below $\phi \sim 0.75$ the presence of extended percolating structures originated by the intermicellar interaction is observed. The increase in the longitudinal modulus of the system scales with the increase in volume fraction above a certain critical value, $\phi_P \approx 0.16$, as $\Delta M' \sim (\phi - \phi_P)^t$, with $t \approx 2.5$. This agrees with the model of dynamic rigidity percolation [18]. The attractive interaction between micelles will tend to form clusters of droplets. As the strength of the interaction is weak, such clusters will live for a very short time. This explains the observed sound dispersion; in fact, if the period of the sound wave is smaller than the characteristic time during which the clusters remain intact, the acoustic propagation will be sensitive to properties of this network, otherwise the system appears as a Brownian dispersion. At higher frequencies these networks can support shear and make a contribution to the bulk modulus of the system, resulting in an increase of the sound velocity at higher frequencies volume fractions above ϕ_P.

The different behavior observed for the sound propagation above $\phi_S \sim 0.75$ has been explained qualitatively by considering the change in the structure of the system. Above ϕ_S, the increase of the amphiphile concentration gives rise to a gradual destruction of the micellar structure. The system evolves toward pure amphiphile solutions through a more disordered phase than the micellar one or than the micellar percolating network. In particular, in this phase water molecules totally bound to the oxyethylene groups increase attractive interactions between the hydrophilic head groups of the surfactant molecules, giving rise to strong head-head amphiphile correlations. Such correlations are able to support viscoelastic effects such as those observed in dense polymeric or polyelectrolyte solutions. The large values of the longitudinal modulus and sound dispersion in these nonionic amphiphile-water solutions are due to strong correlations between amphiphiles molecules.

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