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Light-scattering study of phase transitions in aqueous solutions of nonionic amphiphiles

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The dynamical behavior of water in aqueous solutions of the nonionic polyoxyethylene surfactant $C_{10}H_{21}(OCH_2CH_2)_5OH$ has been studied using Raman and depolarized Rayleigh-wing scattering, with particular attention to changes due to the structural phase transitions apparent at relatively large amphiphile concentrations. The frequencies and intensities of the two principal components evident in Raman spectra of the water O—H stretching band change at the hexagonal to isotropic phase transition. The width and intensity of the single resolvable line in the depolarized Rayleigh spectra similarly change at this transition: the relaxation time of the rotational water mode increases in the hexagonal phase. The changes are all consistent with an increase in the hexagonal phase of the proportion of water bound to the oxyethylene head groups: the environment of water in the system differs significantly from that in bulk water. At the lamellar to isotropic phase transition very much smaller changes were apparent, but only in the Raman scattering data. This lesser sensitivity suggests that in the lamellar phase almost all of the water is bound to the amphiphile head groups, as in the isotropic phase at such volume fractions. The changes in water dynamics reflect the structural changes in the solutions at the phase transitions, in particular the differing packing constraints in the various phases.

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I. INTRODUCTION

Complex fluid systems represent a class of novel materials of considerable interest both scientifically and technologically [1]. Such complex systems contain extended polyatomic structures of sizes from tens of Å to micrometers. Aqueous solutions of the well-known nonionic polyoxyethylene amphiphiles with chemical formula $C_mH_{2m+1}(OCH_2CH_2)_nOH$ (C_mE_n for short) provide good examples of such systems [2]. They have been the subject of extensive theoretical and experimental study, most attention being aimed at clarifying the structural and dynamic nature of the supramolecular aggregates formed above the critical micelle concentration (CMC). These surfactants comprise a linear saturated hydrocarbon chain linked to a polyoxyethylene head group. While aqueous solutions of many such amphiphiles exhibit behavior like that of a critical system in response to changing temperature or concentration, unlike simple binary fluid mixtures they can form various structural phases [2]. At high concentrations the phase diagram of such systems may become rather complex, exhibiting regions of anisotropic phases such as lamellar, cubic, hexagonal, and solid [3]. Such solutions have been used to model fundamental dynamical and structural properties of condensed matter (e.g., fractal aggregation, percolation phenomena, glass transition, disorder-order transition, etc. [1]) and to test theoretical models.

These systems comprise two components, surfactants and water. While previous studies have tended to concentrate upon the structure and dynamics of the aggregates formed by the amphiphiles, changes in the state of water in the different phases are no less interesting. From small angle x-ray (SAXS) and neutron scattering (SANS) [4] and light-scattering [5,6] studies it appears that the water molecules play an important role in these systems. Part of the water is hydrogen bonded (H bonded) to the polyoxyethylene head groups of the amphiphiles. As the surfactant structures in the various phases are quite different, the structure of the water component would also be expected to change, especially in the more concentrated solutions when water molecules are confined in limited spaces between the organized amphiphile struc-

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tures. For these solutions the nonionic nature of the surfactant permits water to be studied in confined geometries without the effects of charge confusing the situation.

In the present work light scattering, both Raman and depolarized Rayleigh, is used to study changes in water structure at the phase transitions. Whereas Raman scattering provides information on the intramolecular vibrational dynamics and intermolecular interactions, Rayleigh scattering relates to collective molecular motions. Specifically, depolarized Rayleigh scattering allows the study of rotational molecular dynamics [7]. Both sets of dynamics will be influenced by structural arrangements in the solutions. The study of the vibrational stretching mode of water by Raman scattering in the spectral region of O—H stretching vibrations reflects structural properties of water in the nonionic amphiphile solutions as these vibrations are strongly influenced by intermolecular (H bond) interactions, while depolarized Rayleigh-wing observations provide further direct information about the local properties of the water adjacent to the polyoxyethylene surfactants.

We concentrate upon the $C_{10}E_5$-water system, which exhibits two well-defined anisotropic phases: hexagonal (H_1) and lamellar (L_α) [3]. Above the CMC $C_{10}E_5$ forms an isotropic phase (L_1) of spherical micelles over a large part of its phase diagram (Fig. 1), the anisotropic phases being restricted to relatively low temperatures. In recent Raman and elastic light-scattering studies [5] of water structure along a continuous isothermal path at around 30 °C in the isotropic one-phase region, above the mesophase regions and below the cloud-point curve, it was demonstrated that for volume fractions of amphiphile $\phi < 0.75$ the water in the solution is partially bound to the oxyethylene hydrophilic moieties of the amphiphiles, whereas above this concentration all the water molecules present are H bonded to the oxyethylene chains. Raman and depolarized Rayleigh-wing scattering both show that in the latter regime the O—H stretching vibrations of the water bound to the head groups are analogous to those observed for glassy water [8]. This suggests that the solution continues to comprise a water continuous dispersion of amphiphile aggregates only up to $\phi \sim 0.75$. There do not seem to have been any investigations of the changes in water structure at the isotropic-anisotropic phase transitions of this and similar amphiphile systems.

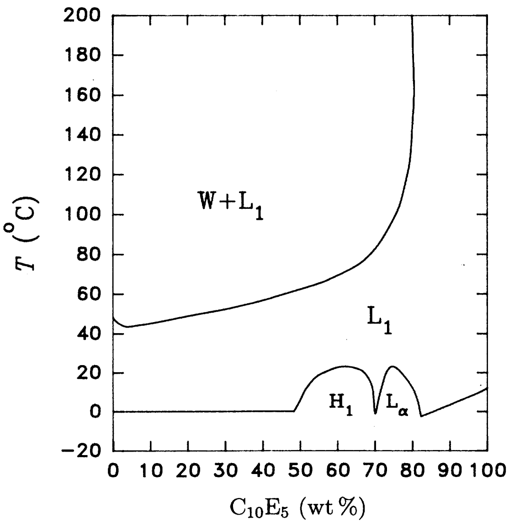

FIG. 1. A portion of the phase diagram of $C_{10}E_5$, adapted from [3]. The present experiments were performed for constant composition paths through the H_1-L_1 and L_α-L_1 transitions, for concentrations of about 55% and 75%, respectively.

There have been some previous Raman spectroscopic observations of changes in the structure and conformation of surfactants in aqueous solutions at phase transitions [9–12], but not all workers have considered problems arising from the depolarization of light in the anisotropic phases. These phases consist of very small oriented domains of lyotropic liquid crystals, at the boundaries of which the incident and scattered light will experience multiple reflections, leading to partial or complete depolarization. A solution to this problem has been proposed [13,12], and is adopted here (see below).

The above background led to the present work, which is devoted to an examination of water dynamics in these complex solutions by means of both Raman and depolarized Rayleigh-wing scattering. Particular attention is paid to investigating the effects of structural transitions on the water behavior. The variation of the spectra with temperature has been studied for various amphiphile volume fractions within the ranges of the transitions from the H_1 and L_α phases to the isotropic one-phase region (Fig. 1).

II. EXPERIMENT

The nonionic amphiphile $C_{10}E_5$, obtained from the Nikko Chemicals Co. (Japan), was used without further purification. Samples were prepared using triple distilled deionized gas-free water, using great care to avoid contamination, and were filtered before measurement. Before spectroscopic investigation the samples were homogenized in a centrifuge for 90 min at 1000 rpm. The system was studied as a function of temperature for various weight fractions of amphiphile: 0.54, 0.57, 0.58, and 0.75. Solutions were prepared by weight, allowing the use of the published phase diagram [3] (in practice weight and volume fractions are almost equal). The concentrations chosen fall in the H_1 and L_α regions of the phase diagram (Fig. 1), allowing the transitions from these phases to the L_1 phase to be studied. The temperature was varied over the range 55–10 °C, increments of 2 °C or smaller being used close to the phase transitions; the samples were thermostatted to within 0.1 °C. The measurements were performed at thermodynamic equilibrium, at least 10 min being allowed for temperature stabilization between successive spectral recordings.

A. Raman spectroscopy

In order to obtain reproducible results for the Raman spectra of the water O—H stretching band in the anisotropic phases and to permit them to be compared with the corresponding spectra in the isotropic phases, we recorded spectra which are linear combinations of parallel and perpendicular contributions [13]:

$$I_{60} = \tfrac{1}{4}I_{\parallel} + \tfrac{3}{4}I_{\perp}, \qquad (1)$$

where I_{60} is the intensity of the spectrum recorded with an analyzer oriented at 60 ° with respect to the polarization of the exciting Ar^+ ion laser beam. As mentioned above, this procedure eliminates errors introduced by depolarization of light due to microcrystallinity of the samples in the anisotropic phases.

Raman scattering measurements were performed in the usual 90 ° geometry using a SPEX 1400 monochromator and charge coupled device detection (ORIEL Instaspec). The 514.5 nm light (mean power 200 mW) was focused into the sample by a 40 cm focal length lens. The spectra of the O—H Raman band of water were not corrected for the contribution of the O—H terminal group of the amphiphile. When studying the transition to the anisotropic phases it was not possible to use the O—H signal of pure $C_{10}O_5$ as a reference (as in [5]) because of transitional changes in the structure of the solution. Spectra of the O—H Raman band of bulk pure water were recorded at the same temperatures for comparison purposes.

The experimental scheme for detection of spectra of the anisotropic phases, allowing for depolarization effects by using an analyzer oriented at 60 ° with respect to the input polarization, was tested for the water O—H band by evaluating the relative difference $\Delta I/I_{60}$. ΔI is the absolute difference between the parallel and perpendicular spectra for the anisotropic phases, integrated over the O—H band (i.e., the one-norm of the difference [14]), after normalization of both spectra to the area of I_{60}. This ratio was less than 5% at all wave numbers in the O—H band. Thus we may assume that depolarization due to microcrystallinity was almost complete in the water Raman spectra studied here.

B. Rayleigh-wing spectroscopy

The depolarized Rayleigh scattering measurements were performed using a double pass double monochromator (SOPRA model DMDP 2000) with a resolution of 700 MHz. We used 1 W of 514.5 nm light for excitation. The scattering geometry was the usual 90 ° arrangement. The scattered light was collected through a Glan-Thompson polarizer with an extinction coefficient better than 10^{-7}. Depolarized spectra were measured in the frequency range -100 to $+100$ cm^{-1}.

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, depending on the different mechanisms involved in the scattering process. Both water and the amphiphile molecules comprise anisotropic units, so that the corresponding spectrum could contain at least two contributions from the different rotating groups. Such contributions are Lorentzian lines related to the exponential decay of local order. In water this order, while it relates to rotational motions, is governed by H-bond dynamics. The free amphiphile molecular rotation apparently fell in a narrower spectral region than the instrumental resolution. In practice, therefore, the spectra could be well fitted with a single Lorentzian line, plus an instrumental response function (Voigt function) and a constant background. This background included the essentially flat central portion of the wide contribution due to the recently observed very fast water dynamics [15]. The physically meaningful parameters of the fit are the half-width at half maximum (HWHM) and the relative intensity of the single Lorentzian line, which corresponds to relatively slow dynamics of water. The intensity relates to the relative contribution of the slow water dynamics to the total signal, including the very fast mode mentioned above.

III. RESULTS

A. Raman spectroscopy

Raman spectroscopic studies were carried out for $\phi = 0.58$ and 0.75. Raman spectra recorded for the water O—H stretching band at various temperatures for an amphiphile weight concentration of 0.58 are shown in Fig. 2. There is a sudden and monotonic change

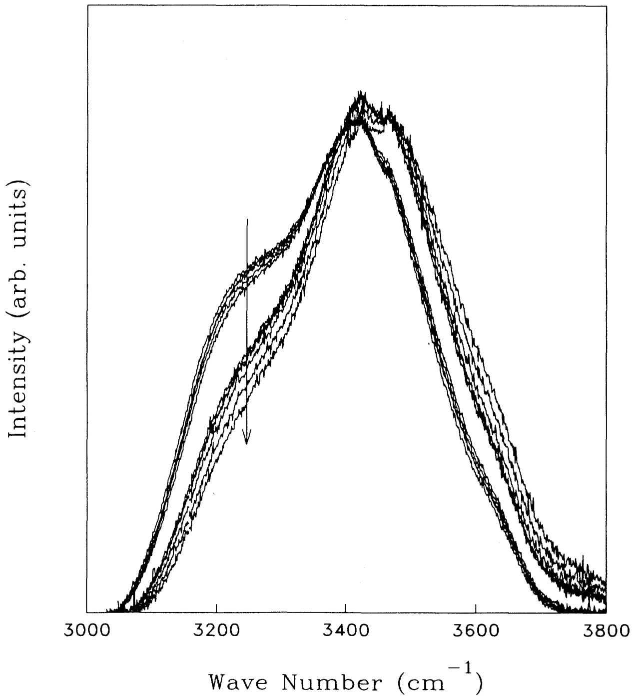

FIG. 2. Raman spectra for the O—H band of a 0.58 weight concentration aqueous solution of $C_{10}E_5$, for temperatures running from 12 to 55 °C (T increasing as shown by the arrow). Spectra are normalized by area. The obvious change in spectral shape occurs between 22 and 24 °C.

in the spectral shape between 22 and 24 °C. As T increases between these two values the spectral feature at about 3250 cm^{-1} falls dramatically in intensity, while that at about 3400 cm^{-1} increases somewhat and shifts to rather higher wave number. These temperatures just bracket the established H_1-L_1 transition at this ϕ, as shown in Fig. 1. Clearly the transition significantly affects the character of water molecules in the solutions. While spectra for concentrations around 0.75 did show some changes on passing through the L_α-L_1 transition, these were much smaller than in the H_1-L_1 case. As noted above, all these Raman spectra contain contributions from the O—H groups of the polyoxyethylene head groups.

The structure of water involves H bonds with a continuous distribution of strengths, but in practice various simplifying models are frequently used [16]. These generally reduce to considering a finite number of populations of water molecules, each being homogeneous with respect to the H bonding.

The Raman spectra were deconvoluted using a Fourier procedure which has been described elsewhere [17]. The Fourier deconvolution yields three components of the O—H band, the first corresponding to water molecules with strong H bonds, the middle one to those with weaker, distorted bonds, and the final one to "free" water. This analysis is particularly well suited to identification of the main components of the water stretching spectra in the present polarization-insensitive mode of comparison of Raman spectra, and agrees in principle with the mixture model for interactions in water [18]. (Because of the method adopted here to compare spectra in the isotropic and anisotropic phases, deconvolution in terms of isotropic and anisotropic Raman spectra is inapplicable, and so direct analysis in terms of the continuous interaction model for water [19,20] is not possible.) The third component, at highest wave number, was of small intensity in all the present spectra, and will be neglected in what follows. We have found that over-deconvolution does permit resolution of the "free" water component, but the results of such fits are not very reliable, and so we prefer to concentrate on the two main features. Deconvoluted spectra for a 0.58 weight concentration sample at 22 and 24 °C are shown in Fig. 3, illustrating the transitional changes in the O—H band.

The effects of phase transitions on water structure in the $C_{10}E_5$-water system can thus be viewed in terms of a particular simplifying model [21], in which the continuous distribution of H bonds between water molecules can be divided into two broad classes: "bound" water (water molecules which are tetra bonded and form clusters connected with strong hydrogen bonds), and all the remaining water molecules, which are connected in a network of higher density by weaker H bonds. The molecules in the first class scatter light in a region centered at around 3230 cm^{-1} in the O—H Raman spectra, while the latter class contributes a peak around 3450 cm^{-1} (Fig. 3).

The results obtained from the deconvolution process include the wave numbers of the two main vibrational components (ν_{3230} and ν_{3450}) and the ratio of their amplitudes, $R = I_{3450}/I_{3230}$, measured from the zero level

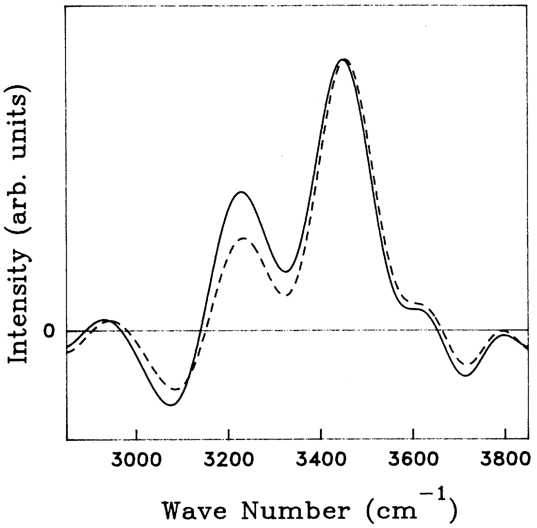

FIG. 3. Raman spectra from Fig. 2 after Fourier deconvolution for 22 (full line) and 24 °C (dashed line). The spectra are normalized so that the lines about 3450 cm^{-1} are of equal height.

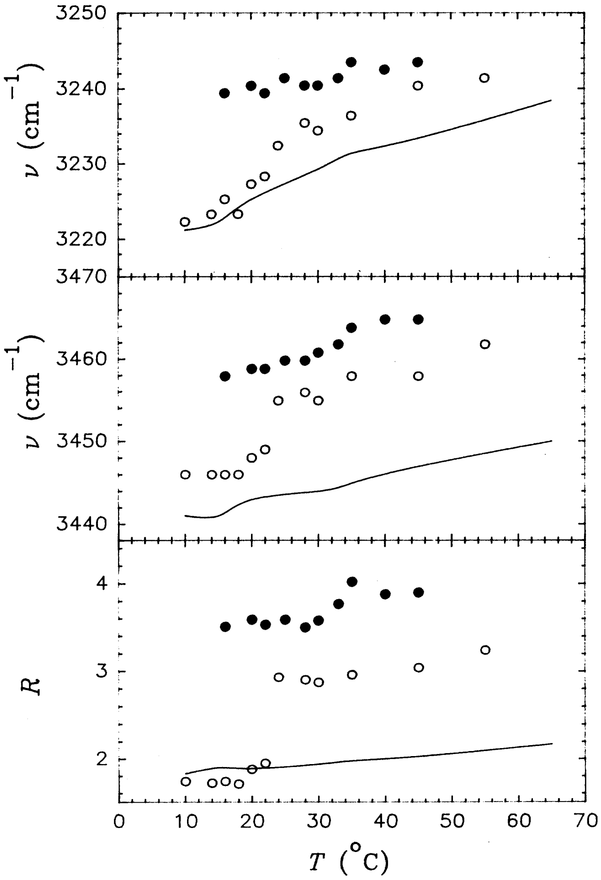

FIG. 4. The T variations of the wave numbers of the two main lines in the O—H band inferred by deconvolution of the Raman spectra, together with the ratio of their amplitudes, for $\phi = 0.58$ (hollow points) and 0.75 (filled points). The lines indicate the behavior found for bulk water for comparison. See text for discussion.

to the peak heights. Equal parameters of deconvolution were used for all spectra analyzed. The wave numbers found are somewhat higher than those for bulk water; their significance is open to interpretation, but they are affected by the transition, as we shall see.

Figure 4 shows the dependence of ν_{3230}, ν_{3450}, and R on temperature for two concentrations. For a concentration of 0.58 the T variations of these parameters differ from those found for bulk water: whereas they are all essentially linear for bulk water, discontinuities are apparent for the present samples in the region of the H_1-L_1 transition. The changes, which occur more or less abruptly between 22 and 24 °C, just at the transition, are similar for ν_{3230} and ν_{3450} but are more abrupt for R. The sudden change in this O—H stretching band, revealed by the stepwise decrease of R for the $C_{10}E_5$ solution on cooling through 23 °C, can be viewed as an increase in the proportion of water molecules assuming a more organized, tetra-bonded structure.

Such changes are not observed in the frequencies of the two vibrational components comprising the O—H band for the 0.75 concentration sample (Fig. 4), but they are apparent in the ratio R, though on a much smaller scale than for $\phi = 0.58$. While the L_α-L_1 transition would be expected to occur at about 23 °C, R seems to be continuous through this temperature but changes in the region 28–35 °C. This accords with the observation of a transition at 28 °C, demonstrated by changes in the shape of the parallel and perpendicular Raman spectra at that T: $I_\parallel$ and $I_\perp$ coincide when the transition to the anisotropic phase is complete, as shown by the ratio $\Delta I/I_{60}$ being $< 5\%$, as already discussed. The temperature of the phase transition likely differs from that expected from the phase diagram (Fig. 1) because of trace impurities or a few dust particles in the sample. We believe that the method of identifying the phase transition used here is more accurate than visual methods, being comparable with polarization methods, as it detects changes in the microscopic characteristics of the sample.

B. Rayleigh-wing spectroscopy

Figure 5 shows a typical spectrum from the depolarized Rayleigh-wing scattering from the isotropic phase of $C_{10}E_5$. The lines indicate the results of the fitting process. It may be seen that an instrumentally broadened single Lorentzian line plus background fits the data rather well.

The results of the depolarized scattering comprise the measured linewidth (HWHM) and the intensity of the only rotational contribution present in the spectra, for the various amphiphile concentrations and temperatures. The relaxation time τ of the exponential decay of the rotational order can be found directly from the HWHM. The measured values of τ are plotted in Fig. 6 as a function of T for three values of ϕ (0.54, 0.57, 0.75). The variation found for pure bulk water [22,15] is shown for comparison; the similarity of the magnitudes of τ for pure

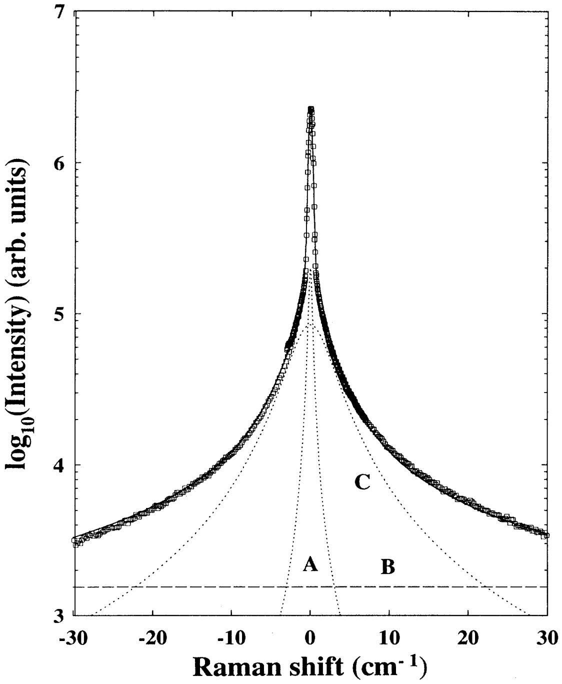

FIG. 5. Depolarized Rayleigh-wing spectrum for a sample of $\phi = 0.54$ at $T = 30$ °C. The continuous line represents the best fit to the data; C is the contribution due to the molecular rotational motion, A the instrumental resolution, and B the constant background.

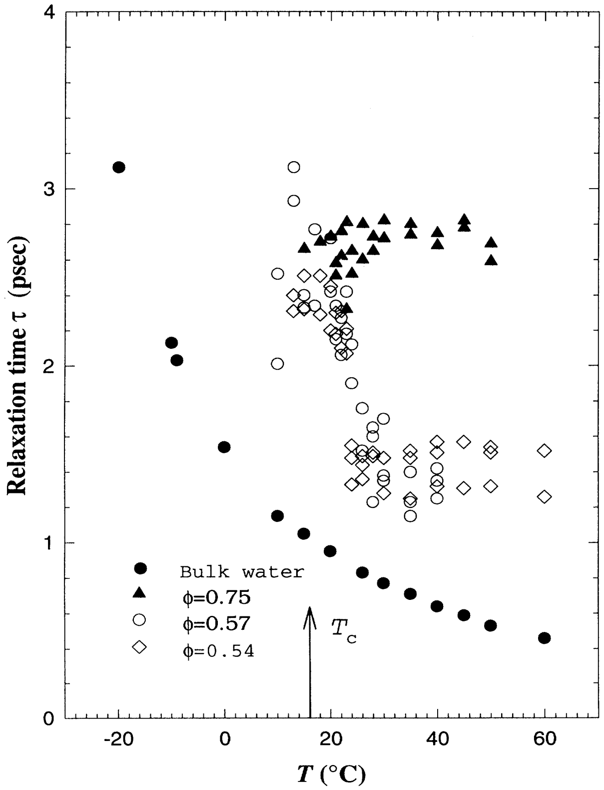

FIG. 6. The relaxation time τ of the water rotational mode as a function of T for three different ϕ values (see legend). The T dependence found for pure bulk water is shown for comparison.

water and the present samples confirms that the spectra recorded for the $C_{10}E_5$ solutions relate to the dynamics of the water component of the system. In contrast, the rotational relaxation time for pure amphiphile would be greater than 8 ps, as the depolarized Rayleigh line is narrower than the instrumental resolution (~ 700 MHz).

It is apparent from Fig. 6 that the rotational dynamics of water in all of these samples are significantly slower than in pure bulk water at the same temperatures. Further, the relaxation time decreases significantly as the solution passes through the H_1 to L_1 phase transition (0.54 and 0.57 concentrations). Similarly, the relative area of the single fitted Lorentzian line, expressed as the ratio $A_l/A_{\rm tot}$ where A_l is the area of the Lorentzian and $A_{\rm tot}$ is the total area of the depolarized Rayleigh-wing spectrum, changes at the H_1-L_1 transition (Fig. 7). No such changes are apparent at the L_α-L_1 transition for the solution having $\phi = 0.75$.

IV. DISCUSSION

The arguments advanced here must be qualitative, rather than quantitative, as for some of the observables our data provide only relative variations. However, our results yield information on transitional changes in the dynamics of water in the nonionic amphiphile solutions, which provides deeper insight into the structural role of water in these complex systems.

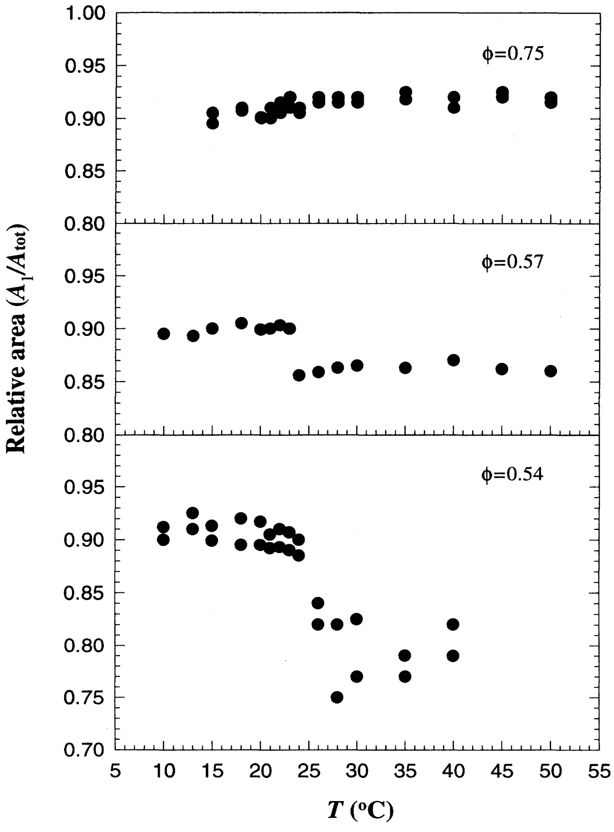

FIG. 7. The T variation of the ratio of the areas of the Lorentzian line, due to the slow water rotational mode, to the total area of the depolarized Rayleigh-wing scattering for various ϕ (see legend).

For both Raman and depolarized Rayleigh scattering, the results for amphiphile concentrations near 0.55 show greater sensitivity to temperature than do the data for a concentration of 0.75, which are nearly independent of T. In contrast, the data for concentrations about 0.55 show significant discontinuities about 23 °C, the temperature of the H_1-L_1 transition. We therefore concentrate upon these latter results in this discussion.

The entire set of data suggests that in the hexagonal H_1 phase a significant fraction of the water molecules changes state compared to the isotropic micellar L_1 phase. In particular, it appears that in the H_1 phase more of the water molecules are bound to the oxyethylene head groups.

We turn first to the details of the results of the Raman spectroscopy of the O—H stretching band, subsequently considering the depolarized Rayleigh-wing data on the rotational dynamics of water molecules in the system.

Figure 4 shows that the frequencies (or, equivalently, the energies) of the O—H stretching vibration, ν_{3230} and ν_{3450}, change at the H_1-L_1 transition, indicating that the state of water in the solution changes. The change $\Delta\nu$, ~ 10 cm^{-1}, is roughly the same for both types of water, tetra bonded (ν_{3230}), and the remainder (ν_{3450}). The similarity of the transitional change $\Delta\nu$ for both populations of water indicates that it is the global environment for water in the system which is affected by the phase transition, rather than just the "bound" water. In bulk water it is conventional to correlate shifts in the frequency of the O—H oscillator (determined from the O—H vibrational band), unperturbed by intermolecular or intramolecular interactions, with changes in the mean distance between the oxygen atoms of nearest neighbor molecules in the H-bonded water network [23]. Such shifts are directly proportional to changes in temperature [20]. The behavior of the frequencies of both types of water in our I_{60} spectra can be understood in these terms. The changes in both ν_{3230} and ν_{3450} at the H_1-L_1 transition indicate that, on average, the separation between the oxygens decreases discontinuously on entering the H_1 phase. The lower energy of the O—H stretching vibrations in this phase thus suggests that the water molecules are more closely packed, and their stretching vibrations are somewhat constrained, compared to the L_1 phase at high T, where the water molecules can move more freely.

The largest transitional effect apparent in the Raman data (Fig. 4) is the change in the ratio R of the relative amplitudes of the two deconvoluted lines for the sample of concentration 0.58. R, as defined above, reflects the inverse of the proportion of tetra-bonded water. R can only be considered as a relative estimate of the fraction of water molecules which are tetra bonded: while the absolute values of R, relating to *amplitudes*, may not express the real ratio of the integrated *intensities* of the various components, it does conveniently express the extent of changes in the shape of the O—H band when the environment of the water molecules is altered in transitions between different phases.

On cooling the 0.58 concentration sample through 23 °C, the fraction of water molecules which are tetra bonded increases sharply—R decreases. In the hexagonal phase the mean diameter of the rod shaped micelles increases relative to that of the spherical micelles in the isotropic phase, and the micelles become more closely packed [2]. The spaces between these close packed micelles, which are filled with water, are narrower than in the L_1 phase, in which comparatively isolated micelles are suspended in "bulk" water, so that the number of water molecules bound to the hydrophilic head groups of $C_{10}E_5$ is significantly higher in the H_1 phase than in the L_1 phase. It is this effect which causes the increase in "bound" water in the H_1 phase. The relatively small degree of binding of water to the amphiphile head groups in the L_1 phase has already been established from SAXS [4] and Raman measurements [5].

Within the different phases for the 0.58 amphiphile sample, and throughout the temperature range studied for the 0.75 sample, the T variations of both R and the wave numbers for the two populations of water molecules basically parallel the corresponding ones for bulk water (Fig. 4). This suggests that within the different aqueous environments in the different phases the effects of temperature upon the Raman band are about the same, as seems appropriate for an intramolecular effect such as O—H stretching.

Turning to the depolarized Rayleigh-wing scattering data, the principal result is the effect of the H_1-L_1 transition on the relaxation time τ, seen in the data for the samples at 0.54 and 0.57 concentration (Fig. 6). The change in τ at this transition indicates that the water molecules are significantly freer to move in the isotropic phase than in the hexagonal phase. This may be emphasized by comparing the data for the present samples with those for pure bulk water. In the L_1 phase, above 23 °C, the relaxation time of water molecules resembles that observed for bulk water cooled to about 5 °C, whereas below 23 °C, in the H_1 phase, τ is of the order of that found for bulk water supercooled to about -15 °C. In the latter situation there would be a considerable increase in the structural organization of the bulk water compared to that at 5 °C, suggesting a comparable increase for the amphiphile solutions in the H_1 phase.

In contrast to bulk water, the amphiphile solutions, within the different phases, all display apparently non-Arrhenius behavior of the rotational relaxation time τ. As is well known [24], for bulk water the T variation of τ reflects a single activation process, which is related to the energy of formation or breaking of the H bond. In the amphiphile solutions this rotational relaxation time is influenced by the presence of oxyethylene groups, to which water is also bound. In contrast to Raman scattering, which is quite incoherent and is due only to intra-molecular dynamics, depolarized Rayleigh scattering probes a collective mode that reflects the relaxation of single molecules influenced by their environment. Whereas in bulk water there is one environment, provided by other water molecules, in the present samples water molecules may be in different environments, adjacent to either water or the amphiphile head groups. In any case, the present results reflect a change in the geometry in which water molecules are more confined than in bulk water. The structural transition changes both the packing of the hydrophilic head groups, which is more open in the micellar phase, and the interaggregate spacing, which is larger in this phase. Both effects reduce the constraints on water molecules in the L_1 phase relative to the H_1 phase.

In the H_1 phase water is constrained by closer packing than in the isotropic micellar phase, leading to a significantly larger relaxation time in the H_1 phase (Fig. 6). This conclusion accords very well with those drawn from the intramolecular vibrational dynamics, in particular with the energies of the two main O—H stretching modes.

The relative amplitude of the depolarized Rayleigh line clearly decreases as T increases through the H_1-L_1 transition (Fig. 7). The number of scatterers responsible for the slow water mode is thus less in the L_1 phase than in the H_1 phase. This is the number of molecules which can reorient due to breaking of H bonds. Interpretation of the data is difficult as, while A_1 depends only on the water molecules, A_{tot} relates to all scatterers, including the amphiphiles, whose rotational contribution is not resolved in the spectra. However, the changes observed accord qualitatively with the effects noted in the amplitudes of the Raman signal from tetra-bonded water.

We briefly comment on the data for the 0.75 amphiphile concentration samples. The Raman spectra differ from those for bulk water (Fig. 4). Similarly, the depolarized Rayleigh-wing data (Figs. 6 and 7) show that the rotational dynamics are significantly slower than those for bulk water. With the exception of the ratio R of the amplitudes of the two deconvoluted components in the present Raman spectra no transitional effects are observable at the L_α-L_1 phase change. R exhibits a small and comparatively smooth discontinuity at the phase transition. However, at this high concentration its magnitude may be influenced by the contribution of the O—H stretching vibrations of the amphiphile. If this contribution could be subtracted, it is possible that the T behavior of the corrected R would not differ from that of the other parameters describing the L_α-L_1 transition. At all events the changes at this transition are very small, and it would be speculative to pursue their interpretation at this stage.

Recent Raman studies [5] suggest that at $\phi \geq 0.75$ in the L_1 phase essentially all water molecules are fully bonded to the oxyethylene head groups of the surfactant: the solution has become predominately a continuous amphiphile structure. It appears that almost the same degree of bonding to the head groups also occurs in the lamellar L_α phase. This might have been expected: in this phase water is "squeezed" in thin layers between the lamellae of surfactant molecules and again essentially all the water molecules are tetra bonded. The similarity of the environments in which the water molecules are situated in the micellar and lamellar phases explains why the light-scattering spectra do not change markedly with temperature at the L_α-L_1 phase transition. The environments are very different from that in bulk water, as shown by the differences of both Raman and Rayleigh spectra from those for bulk water.

Previous depolarized light-scattering studies [6] have shown that for $\phi \geq 0.75$ *all* water molecules in the system are bound to the amphiphile head groups. They can further be regarded as all tetra bonded as the measured τ reaches values typical of deeply supercooled water. For lower ϕ the water molecules, while more significantly bound in low density structures (tetra bonded) than in pure water, are only partially bound to the amphiphile molecules. This overall picture, based on water dynamics in such structured complex fluid systems, confirmed conclusions of earlier SAXS and SANS structural studies [4]. In particular the behavior of the more concentrated solutions confirms the resemblance of these complex fluids to block copolymer melts with all the water bound to the amphiphiles. The present work has demonstrated conclusively the effects upon the water properties, in somewhat more dilute solutions, of structural phase transitions. More precisely, the results show the effects upon the water dynamics of increased packing constraints.

V. CONCLUSIONS

The dynamics of water in confined geometry is a challenging problem of current interest in the physics of complex systems. We have studied such dynamics in a particular system, which affords the possibility of modifying the geometrical constraints upon water. The particular system studied is an aqueous nonionic surfactant solution, in which the confusing effects of charge upon the water molecules are absent. The system, depending upon concentration and temperature, may organize itself into a variety of structural phases, in which the constraints upon water vary. For the particular amphiphile studied, $C_{10}E_5$, it is possible to study transitions between both hexagonal and lamellar phases and the isotropic micellar phase.

Our results show that, on passage from the comparatively open structure of the isotropic phase to the more constrained geometry of the hexagonal phase, there is a considerable change in the dynamics of the water molecules. Both the collective and intramolecular dynamics are affected, as shown by changes in the depolarized Rayleigh wing and Raman scattering, respectively. In the hexagonal phase the proportion of tetra-bonded water increases, and the dynamics slow down, reflecting the greater packing constraints in this phase compared to the isotropic one. In the lamellar to isotropic transition, at higher amphiphile concentrations, very much smaller changes are apparent in the water dynamics as perceived by Raman scattering. This implies that almost all of the water is bound to the oxyethylene head groups in the lamellar phase, as is known to be the case for such concentrations in the isotropic phase [4–6]. The last finding reflects the very confined geometry available to the water molecules in such concentrated solutions.

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