Raman scattering and water structure in nonionic amphiphile solutions

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The structure of water in aqueous solutions of polyoxyethylene monionic amphiphiles $C_{10}E_5$, where E_5 denotes $H_{21}(OCH_2CH_2)_5OH$, is studied by Raman scattering along an isothermal path crossing the isotropic one-phase region from 0 to 1 amphiphile volume fraction ϕ. The isotropic OH stretching-vibration spectrum points out a water behavior that depends on the amphiphile concentration. The data analysis is performed using the bond-percolation model developed for water. The interpretation of scattering data leads to the following structural picture for the water in the systems: for ϕ lower than 0.75, water is partially bound to the oxyethylene groups of the amphiphile; above $\phi=0.75$ all water present in the system is bound. Analogously to the behavior of water in confined geometries, the structure of bound water presents a local fourfold-coordinated environment.

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INTRODUCTION

Aqueous solutions of the well-known nonionic polyoxyethylene amphiphile have been the subject of many studies [1] in order to clarify the structural and dynamical properties of the supramolecular aggregates formed above the critical micelle concentration (CMC). Their chemical formula is $C_mH_{2m+1}(OCH_2CH_2)_nOH$ or C_mE_n for short. They are made of a linear saturated hydrocarbon chain (hydrophobic moiety) linked to a polyoxyethylene chain (hydrophilic moiety). An important feature of many nonionic amphiphile solutions in water is that, changing temperature and concentrations, the solution behaves as a critical system, with a well-defined consolute curve, which separates the one-phase region from the two-phase region, with a lower critical point. On the other hand, contrary to the simple binary mixtures, such aqueous micellar solutions are able to form various structural phases. At high concentrations the phase diagram of these systems may become rather complex, presenting regions of anisotropic phases as, for example, lamellar, cubic, hexagonal, and solid. Nonionic micellar solutions can be used in physics of condensed matter as model systems in order to study fundamental dynamical and structural properties (i.e., fractal aggregation, percolation phenomena, polymers, glass transition, disorder to order transition [2]) and to test the theoretical models.

In some amphiphile water solutions the packing fraction of the micellar droplets, keeping their size constant, can be easily changed therefore giving the possibility of studying the behavior of highly packed systems [3]. For instance, for the $C_{10}E_5$ water solution in which it is possible to follow a continuous isothermal path which crosses the isotropic one-phase region from the 0% to 100%

volume fraction ϕ of amphiphile, above the mesophase regions and below the cloud-point curve, at around $T=30\,°C$. It is well known that above the CMC $C_{10}E_5$ forms globular micelles, whereas it is not known up to what amphiphile concentration the solution can still be described as a water continuous dispersion of amphiphile aggregates, and how the system evolves towards the pure liquid amphiphile phase. The systems $C_{12}E_8$, $C_{10}E_5$, and C_8E_4 have been recently subjected to careful studies with neutron and x-ray scattering in order to explain its structural properties along such isothermal paths [4]. In particular, it has been shown that the solution is structured for all concentrations ranging from the micellar region to the pure liquid amphiphile. As the volume fraction ϕ increases, the micellar structure becomes less and less sharp, but some orientational correlations between neighboring amphiphile molecules are preserved even at high concentrations. From the small-angle neutron-scattering data (SANS) [4] a structure peak is clearly observable up to $\phi=0.95$, whereas the pure $C_{10}E_5$ neutron spectra are absolutely flat. More precisely, the interpretation of scattering data [SANS and small-angle x-ray scattering (SAXS)] leads to 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 [5].

In the frame of the picture proposed by SANS and SAXS it is interesting to understand the role played by water at high-volume fractions of the nonionic amphiphile. In fact, water is known to be hydrogen bounded to the polyoxyethylene head groups of the amphiphile in the range of 1.5–2 water molecules, on the average, per oxyethylene group [1,4]. Therefore, at high volume frac-

tions, all water molecules are expected to be bounded via the hydrogen bond to the oxyethylene chains.

The study of the vibrational stretching mode of water by Raman scattering can be quite effectively used to give an independent experimental confirmation of the structural model proposed for the nonionic amphiphile solutions by the analysis of SANS and SAXS data. This idea is to investigate te structural properties of water in nonionic amphiphile solutions through the analysis of the spectral region of O—H stretching vibrations [6]. The results of this study may find interesting correlations with the important subject of water physics in confined systems [7,8]. Here, results obtained at 35 °C with $C_{10}E_5$ solutions are presented. The data confirm the model proposed for SANS and SAXS experiments [4], giving detailed information about the dynamics of water molecules that are hydrogen bonded with the polyoxyethylene head groups. In particular, at least for the highest amphiphile concentrations, the O—H stretching vibrations of such bounded water are shown to be analogous to the ones already observed for glassy water [9].

EXPERIMENT

The nonionic amphiphile used in this experiment, of high-purity grade, was provided by Nikko Chemical, Japan, and was used without further purification. Triple-distilled deionized gas-free water was used and the samples were prepared by weight in the proper quantity. All the samples were filtered before the measurements. Immediately after preparation, the samples were put into an optical fused silica cell. Great care was taken, in the sample preparation, to avoid dust contamination. The phase diagram of $C_{10}E_5$ in H_2O [1] gives lower critical points at about 45 °C and at the liquid-crystalline region in the range of amphiphile volume fraction between 0.5 and 0.85 with the temperature between 0 °C and 20 °C; therefore the isothermal path at $T=35$ °C, which does not cross the mesophase regions, was chosen for the measurements. The studied concentrations are $\phi=0.3$, 0.5, 0.6, 0.7, 0.75, 0.87, 0.91, and pure amphiphile.

Raman-scattering measurements were performed in the usual scattering geometry of 90 °C, with the incident beam vertically polarized with respect to the scattering plane, using a fully computerized high-resolution triple monochromator (Spex Ramalog V), together with a Ar^+ laser (Spectra Physics 2020) operating in single-mode TM at a 5145-Å wavelength with a mean power of 300 mW. The scattered light was collected through a Glan-Thompson polarizer with an extinction coefficient better than 10^{-7}. The sample was thermostated in a Harney-Miller cell within ±0.02 °C. A refractive-index-matching bath, continuously filtered, was also used for flare-free measurements. In these conditions the measured optical background in the scattered light was negligible. The power of the laser beam is continuously monitored both before and after the sample in order to take into account small fluctuations in the incident intensity as well as any variation in the transparency of both the sample and the thermostated fluid. The measurements were performed in thermodynamic equilibrium. The measured spectra

were taken in the range 2900–3800 cm^{-1}, with a resolution of 4 cm^{-1}, both in the polarization parallel (VV) and perpendicular (VH) to the polarization vector of the incident light, which was fixed perpendicular to the optical axis of the spectrometer. The spectra were recorded at different times and remained constant to within the statistical counting errors. The obtained spectra were first corrected using a program which (i) corrects the measured intensity for the density ρ and the refractive index, (ii) subtracts the dark count, and (iii) normalizes for the incident beam intensity. No further processing of the data was applied before their analysis and no smoothing or other treating to eliminate noise was performed in particular. Figure 1 shows the obtained spectra of the OH stretching vibration in both the polarization geometries [Figs. 1(a) and 1(b) refer to the VV and VH contributions, respectively] at the different concentrations, and for pure $C_{10}E_5$, the latter showing a stretching contribution due to the OH terminal groups of the amphiphile. It is interesting to observe that a good experimental detection of the OH stretching vibrational contribution is possible, because the CH's stretching contribution to the spectra of the amphiphile molecule falls in a spectral region different from the OH's one. In the frequency region 3000–3070 cm^{-1}, where overlap between the OH and CH stretching modes occurs, a standard deconvolution program has been used to give the OH stretching spectrum (in any case the CH contribution is lower than OH in this spectral region).

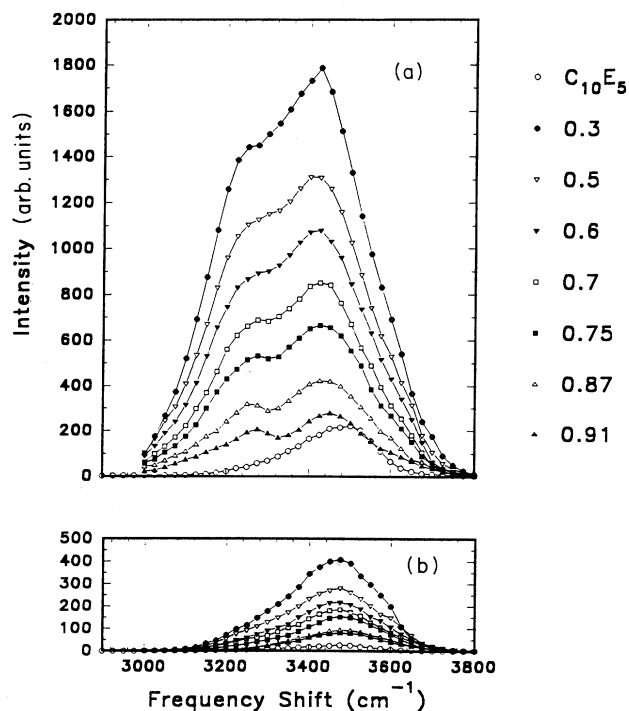According to the theory of Raman scattering the ob-

FIG. 1. Raman spectra of the OH stretching of water at different amphiphile volume fractions. (a) represents the parallel and (b) the anisotropic contribution.
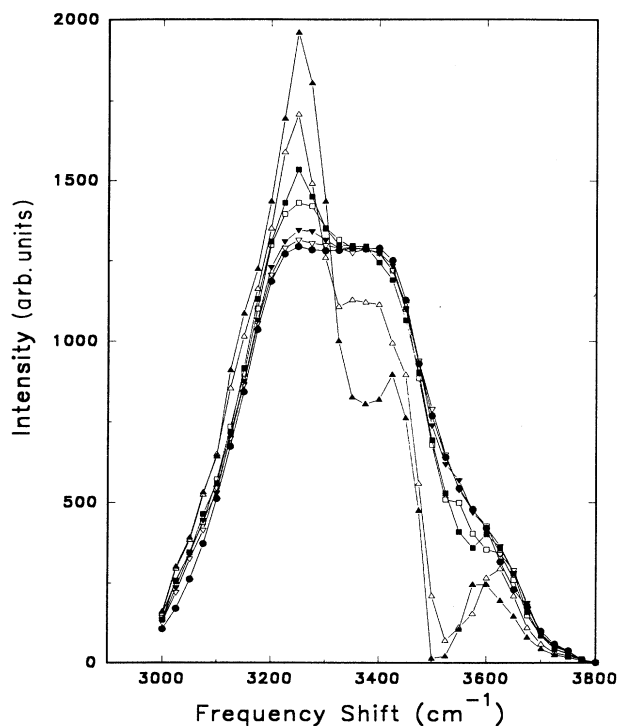
FIG. 2. Isotropic OH stretching contributions of water, $I_{is}^{\phi,wat}(\omega)$, at all the different amphiphile concentrations normalized for ϕ. Symbols for the different $C_{10}E_5$ volume fractions are the same as Fig. 1.

tained spectra were analyzed taking into account the isotropic part of the Raman intensity $I_{is}(\omega)$ which depends only on the molecular vibrations [10] and is written as

$$I_{is}(\omega) = I_{VV}(\omega) - \tfrac{4}{3}I_{VH}(\omega) .$$

In order to study the true dynamic of water in the solution, the isotropic OH stretching spectrum measured for the sample with a volume fraction ϕ, $I_{is}^{\phi}(\omega)$, was considered as the sum of two contributions: one due to the water $I_{is}^{\phi,wat}(\omega)$, and the second to the pure amphiphile $I_{is}^{amorph}(\omega)$, both weighted by the corresponding concentrations. Therefore, the OH stretching spectrum of water in the amphiphile solution was calculated with the following relation:

$$I_{is}^{\phi}(\omega) = I_{is}^{\phi,wat}(\omega)(1-\phi) + I_{is}^{amph}(\omega)\phi .$$

Figure 2 shows the OH stretching spectra obtained with such a procedure for all the solutions studied. As it can be observed, the spectra for $\phi > 0.75$ point out a strong difference in comparison with the others giving the indication of a very different water behavior in the two concentration regions.

RESULTS AND DISCUSSION

Due to the intermolecular hydrogen bond formation, water is considered a particularly "complex" molecular liquid characterized by a local tetrahedral symmetry and

a short hydrogen bond lifetime [11]. Therefore a better understanding of the physics of water mixtures implies consequently a good knowledge of the physics of hydrogen bond. Historically, two main classes of models have been proposed for the water structure [11], i.e., the "continuous model," where water is pictured as a continuous network of tetrahedrally bounded molecules, and the "discrete model," according to which a discrete number of species exist, differing from one another according to the specific structural arrangement.

Recently, a new model has been proposed, which can be considered intermediate between the above-mentioned ones [12]. In this model, by using percolation concepts it is shown that tetrabounded molecules tend to clusterize, giving rise to finite regions, *patches,* whose structural properties are different from those of the remainder. In particular, water is described as "a dynamic gel" (random network of hydrogen bonds) continuously modifying its structural configuration through the breaking and reforming of the hydrogen bonds. Therefore, water appears as myriad of tiny patches of four bounded molecules embedded in a highly connected network or gel. These patches have a local density and a local entropy lower than the global density and the global entropy of the network; in particular they are characterized by highly ramified shapes, just as in the random site percolation. As the temperature is lowered the patches increase in number and size. This theory successfully explains many structural and dynamical properties of the bulk water and, in particular, gives a qualitative explanation of most thermodynamical anomalies observed at low temperatures, and agrees with light, neutrons, x-ray scattering, and molecular dynamics experiments.

On the basis of this model, the OH stretching vibrational contribution can be ascribed at two contributions: "open" water in which a regular tetrahedral structure exists (directly related to the clusters of tetrabounded molecules), and "closed" water, which behaves like a continuum, it being the mixing of all the remaining molecules [13]. Open and closed contributions fall into two different regions of frequency of the OH stretching spectrum [13]; while the open contribution has a mean peak centered at about 3150 cm^{-1}, the corresponding peak for closed structures is centered at about 3500 cm^{-1}.

Figure 3 shows the isotropic OH stretching contributions of the present mixture, $I_{is}^{\phi,wat}(\omega)$, for the amphiphile volume fractions $\phi=0.3$, 0.5, 0.6, 0.7, and 0.75, where the system behaves as a true micellar suspension, as observed from SAXS and SANS experiments. In this concentration interval, the packing fraction of the micelles, considered as spherical particles, increases. For comparison, the OH stretching of pure water at the same temperature of the amphiphile solutions ($T=35$ °C) is also reported in the same figure. As can be observed, the spectrum of pure water differs from the spectrum of water in the mixture also for the less concentrated solution ($\phi=0.3$). In particular, the comparison of the pure water spectrum with the spectrum for $\phi=0.3$, is evidences that in the amphiphile solution a larger amount of water molecules are bounded in structures of low density. This can be seen from the enhancement of the peak at the lower-
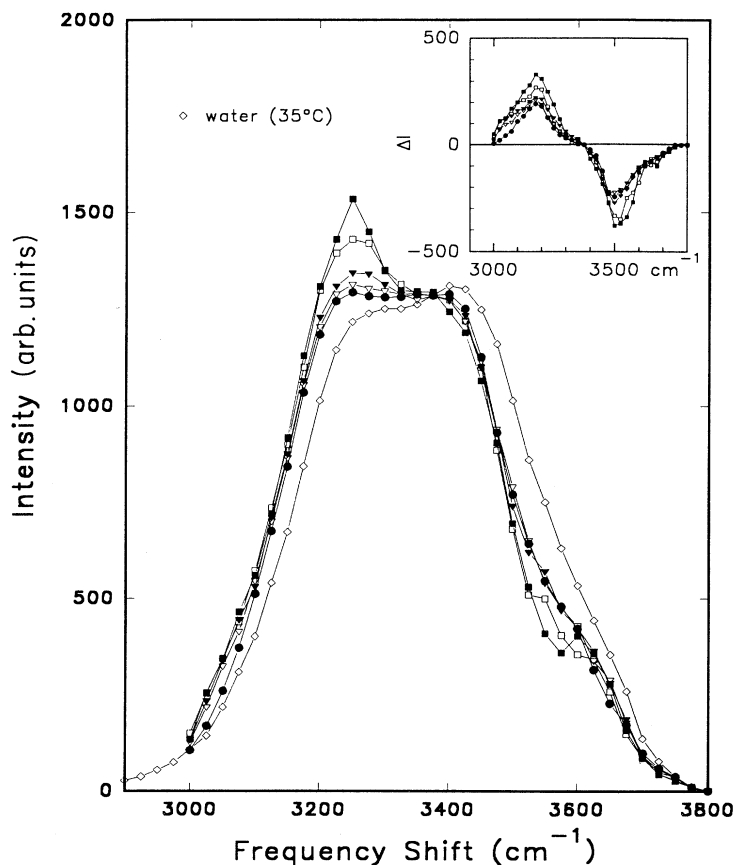
FIG. 3. The OH stretching spectra for the amphiphile volume fractions $\phi \leq 0.75$. The spectrum of pure water at the same temperature (35 °C) is shown for comparison. The differences between the spectra of the different solutions and the spectrum of pure water are shown in the inset.

frequency shift, which corresponds to open low-density structures [13]. An increase of the amphiphile content results in a further increase of the open water contribution to the spectrum, as can be observed in the inset of Fig. 3, where the differences between the intensity of the OH stretching spectra of water in the amphiphile solutions and the corresponding intensity in the spectra of pure water are reported.

Such a behavior is similar to that observed for water in confined geometries, in particular for water protein suspensions [8]. A certain quantity of water molecules is attached to a protein molecule forming a shell of water molecules around the macromolecule where the local water structure is arranged in a different way in comparison with the remaining bulk water. In the present case, due to the hydrophilic character of the head group of the amphiphile molecule, it is not surprising that the water structure of this layer is arranged with a more complete tetrahedral coordination, or open structure, in comparison with the bulk water at the same temperature. More precisely, the interaction of water between the hydrophilic group of the amphiphile at the surface of the micelles partially increases the tetrahedral structure of water, giving rise to a low, dense, more ordered phase.

The above results can be rationalized considering the suggestions of SANS and SAXS [4] which indicate that a certain quantity of water is bounded to the polyoxyethylene head groups, and the remainder water is com-

pletely free, for all values of ϕ below a saturation value ϕ_S ($\phi_S \sim 0.75$). This ϕ range is the concentration interval for which well-defined micellar structures are present in the system. More specifically, in the concentration region where stable micelles are present, SANS and SAXS data can be properly described considering a three-component model: the hydrocarbon region hydrophobic chain of the amphiphile), the hydrophilic region (polyoxyethylene head groups together with bound water, with an average number of water molecules bounded per oxyethylene group $n_w = 1.5$), and a region of free water. The value of n_w can be roughly calculated by evaluating the open water contribution to the area of the OH stretching spectrum, once the latter has been normalized so as to cover a unit area. The obtained values, ranging between 1.4 and 1.7, agree with the SANS value to within experimental uncertainty.

At high surfactant concentration, $\phi > \phi_S$, obtained data give a qualitative confirmation of the main results of the structural model proposed for the small-angle scattering data [4]. All the water present in the system is bound to the oxyethylene groups. The spectra of Fig. 2 show the significant difference between the spectra with ϕ above and below the saturation value ($\phi \sim 0.75$), and the spectrum corresponding to pure water. This is a further suggestion that for $\phi > \phi_S$, the water molecules are arranged in the amphiphile solution in a different way in comparison with the concentrations where the surfactant mole-
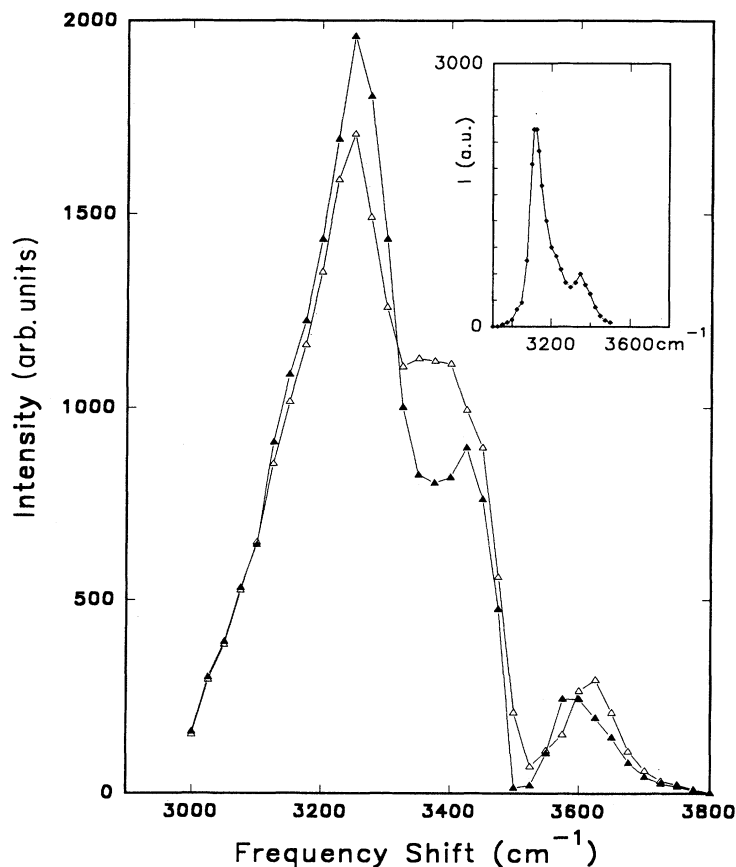
FIG. 4. The OH stretching spectra for solutions with $\phi=0.87$ and 0.91. The isotropic OH stretching contribution for glassy water evaluated from the data of Li and Devlin Ref. [9], is shown in the inset.

cules are aggregated in micellar structures. In particular, Fig. 4, reporting the OH stretching spectra for solutions with $\phi=0.87$ and 0.91, is evidence that the mean intensity is entirely located in the region of open low-density bound water. The percentage of closed water, that is the free water that is very small, is seen from the large reduction of the peak corresponding to the larger frequency shifts. In this situation the number of water monomers, dimers, and trimers is completely reduced; all the water present in the systems is bounded to amphiphile molecules or around them. The corresponding structural arrangement for the water molecules, as shown by the dominant spectral contribution, which is located at the frequency of about 320 cm^{-1}, is the tetrahedral one. Such a result, in agreement with the above considerations about the nature of the interactions between water and the hydrophilic head groups of the nonionic surfactant, is an indication that a very large amount of water molecules is bounded with the amphiphile, and the corresponding structure reflects a local environment with low density in comparison to the bulk water. As proof of this result on the structure of water bounded to the oxyethylene groups of the amphiphile, the inset of Fig. 4 shows the isotropic OH stretching spectrum of amorphous solid water in a film with a thickness of ~ 1 μm, prepared by vapor deposition, at $T=100$ K [9]. As can be observed, the spectra of solutions at high volume fractions are similar to those of glassy water, the relevant difference being only the frequency value of the mean peak, which nevertheless is

known to be a temperature effect (in glassy water this frequency is temperature dependent; it increases with increasing T [9]).

CONCLUSIONS

Raman light-scattering measurements, in the frequency region of OH stretching, are shown to be a valid experimental tool in understanding the behavior of water in concentrated nonionic amphiphile solutions. The analysis of the OH stretching data, performed in the frame of the bond percolation model, gives a clear, independent confirmation of the previous structural picture obtained-with small-angle neutron- and x-ray-scattering data. Water molecules are partially bounded 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 presents a local, low dense, fourfold-coordinated environment typical of supercooled water: a behavior verified in many experiments for transport properties of water in confined geometries.

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[1] See, for instance, M. Corti and V. Degiorgio, Phys. Rev. Lett. **45**, 1045 (1980); J. Phys. Chem. **85**, 1442 (1981); M. Corti, V. Degiorgio, and M. Zulauf, Phys. Rev. Lett. **48**, 1617 (1982); M. Corti, C. Minero, and V. Degiorgio, J. Chem. Phys. **88**, 309 (1984); M. Zulauf and J. P. Rosenbusch, *ibid.* **87**, 856 (1983); J. B. Hayter and M. Zulauf, Colloid. Polym. Sci. **260**, 1023 (1982); R. Tiolo, L. J. Magid, J. S. Johnson, and H. R. Child, J. Phys. Chem. **86**, 3689 (1982); D. J. Cebula and R. H. Ottewill, Colloid. Polym. Sci. **260**, 260 (1982); J. C. Ravey, J. Colloid Interface Sci. **94**, 289 (1983); P. G. Nilsson, H. Wennerstrom, and B. Lindman, J. Phys. Chem. **87**, 1377 (1983); D. J. Mitchell, G. J. T. Tiddy, L. Waring, T. Bostoch, and M. P. McDonald, J. Chem. Soc. Faraday Trans. 1 **79**, 975 (1983); P. G. Neeson, B. R. Jennings, and G. J. T. Tiddy, Chem. Phys. Lett. **95**, 533 (1983); M. Zulauf, K. Weckstrom, J. B. Hayter, V. Degiorgio, and M. Corti, J. Phys. Chem. **89**, 3411 (1985); R. Strey, R. Schomacker, D. Roux, F. Nallet, and U. Olsson, J. Chem. Soc. Faraday Trans. **86**, 2253 (1990); S. Puvvada and D. Blankschtein, J. Phys. Chem. **96**, 5575 (1992) and the reviews: V. Degiorgio, in *Physics of Amphiphilies, Micelles, Vesicles and Microemulsions,* edited by V. Degiorgio and M. Corti (North-Holland, Amsterdam, 1985), p. 303, and references cited therein; and L. J. Magid, in *Nonionic Surfactants: Physical Chemistry,* edited by M. J. Schick (Dekker, New York, 1987).

[2] See, e.g., *Structure and Dynamics of Strongly Interacting Colloids and Supramolecular Aggregates in Solutions,* Vol. 369 of *NATO Advanced Study Institute, Series B: Physics,* edited by S. H. Chen, J. S. Huang, and P. Tartaglia (Kluwer Academic, Dordrecht, 1992).

[3] S. H. Chen, F. Mallamace, J. Rouch, and P. Tartaglia, in *Slow Dynamics in Condensed Matter,* edited by K. Kawasaki, T. Kawakatsu, and M. Tokuyama, AIP Conf. Proc. No. 256 (AIP, New York, 1992), p. 301.

[4] V. Degiorgio, M. Corti, and L. Cantu', Chem. Phys. Lett. **151**, 349 (1988); V. Degiorgio, M. Corti, R. Piazza, L. Cantu', and A. R. Rennie, Colloid Polym. Sci. **269**, 501 (1991); I. S. Barnes, M. Corti, V. Degiorgio, T. Zemb, Prog. Colloid and Colym. Sci. (to be published).

[5] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1969), p. 65.

[6] G. Walrafen, in *Water: A Comprehensive Treatise,* edited by F. Franks (Plenum, New York, 1971), Vol. 1, p. 161.

[7] F. Mallamace, P. Migliardo, C. Vasi, and F. Wanderlingh, Phys. Chem. Liq. **11**, 47 (1981).

[8] M. C. Bellissent-Funel, J. Teixeira, S. H. Chen, B. Dorner, H. D. Middendorf, and H. L. Crespi, Biophys. J. **56**, 713 (1989).

[9] P. C. Li and J. P. Devlin, J. Chem. Phys. **59**, 547 (1973); T. C. Sivakumar, A. S. Rice, and M. G. Sceats, *ibid.* **69**, 3468 (1978).

[10] B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976).

[11] See, e.g., D. E. Eisemberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford University Press, Oxford, 1969); C. A. Angell, in *Water: A Comprehensive Treatise* (Ref. 6), Vol. 7, pp. 1–81, and references therein; C. A. Angell, Annu. Rev. Phys. Chem. **34**, 593 (1983).

[12] H. E. Stanley and J. Teixeira, J. Chem. Phys. **73**, 3404 (1980).

[13] G. D'Ariggo, G. Maisano, F. Mallamace, P. Migliardo, and F. Wanderlingh, J. Chem. Phys. **75**, 4264 (1981).