Single-particle dynamics of water molecules confined in a lecithin-based gel

F. Aliotta,[1] M. E. Fontanella,[1] R. E. Lechner,[2] M. Pieruccini,[1] B. Ruffle,[2] and C. Vasi[1]

[1]*Istituto di Tecniche Spettroscopiche, CNR, via La Farina 237, I-98123 Messina, Italy*
[2]*Hahn-Meitner-Institut, Glienicker Strasse 100, D-14109 Berlin, Wansee, Germany*

We present experimental measurements, obtained by a quasielastic neutron scattering experiment, of the self-diffusion coefficient of water confined in the dense structure of lecithin-based gels. The inelastic neutron scattering (INS) technique was also used to monitor the dynamic state of water molecules involved in the gel structure. It is shown that, at least in highly concentrated systems, the diffusional properties of water can be related with the growth process of wormlike aggregates. However, an interpretation of our data consistent with a number of experimental results in the literature and with INS indications requires the adoption of a model in which the gel structure is better described in terms of percolating aggregates rather than the usually described polymerlike entangled (not interconnected) network. In such a way, we are pointing out the existence of an interpretative controversy calling for further investigation to be disentangled. The source of the inconsistencies is found in the commonly accepted basic assumption of the existence of a simple scaling law, relating the average micellar length to the concentration. [S1063-651X(99)04312-3]

I. INTRODUCTION

It is now well known that, when small quantities of water are added to a solution of soybean lecithin in a number of organic solvents, an enormous increase of the shear viscosity is observed, with the formation of a gel phase at high enough values of ϕ, the dispersed phase volume fraction [1]. It was proposed that water induces the linear growth of giant flexible cylindrical micelles, whose mean length, $\langle L \rangle$, should scale as $\phi^{1/2}$ [2]. Following such a picture, these micellar systems closely resemble polymer solutions and one is immediately led to adopt some modified version of the reptation theory [3] to explain the experimentally observed rheological properties. However, several differences are to be taken into account, originated by the finite lifetime of the self-assembled micellar aggregates. The value of $\langle L \rangle$ is determined by the kinetic equilibrium between the breaking and reforming processes and, as a consequence, it will be deeply influenced by any changes of the involved rate constants. As an example, any temperature variation will reflect in a change of the above-described dynamical balance. In addition, the equilibrium can be easily altered by varying the system concentration: any change of ϕ will alter the rate of the intermicellar collisions and, as a consequence, the rate constant for the reforming process. The hypothesized micellar growth upon addition of water can be understood by taking into account that H_2O molecules enter the micellar structure by hydrogen binding to the polar heads of lecithin, thus affecting the value of the scission energy and of the rate constant for the breaking process. The above approach was successfully adopted in the interpretation of data from a number of systems consisting of solutions of surfactants capable of self-assembling in wormlike micelles. Among them, one of the most studied was the ternary system lecithin/water/cyclohexane [4–6]. Furthermore, it is to be stressed that, in order to observe a true curvilinear diffusion (reptation) we need unusually long micellar lifetimes: at least we need that a micelle survives over a time comparable with the reptation time, the time required for the micelle to disengage from its environment. In this respect, from a very recent pulse field gradient NMR experiment [7] in which the surfactant curvilinear diffusion in lecithin/water/cyclohexane was measured at fixed water content $R = 10$ (R denotes the number of water molecules per lecithin molecule), the surfactant molecular lifetime was estimated to be longer than 1.5 s. Such a result, besides furnishing further confirmation of the hypothesized analogy between the system and polymer solutions, calls for additional experimental investigations in order to clarify how the interaction between water and surfactant can induce the formation of such stable structures.

In this paper we present the self-diffusion data, obtained in an incoherent quasielastic neutron scattering experiment (QENS), for water molecules confined within the gel structure of lecithin/water/cyclohexane systems, which will be compared with the result from an inelastic neutron scattering (INS) experiment performed at the Thermal Original Spectrometer with Cylindrical Analysers (TOSCA) spectrometer [Rutherford Appleton Laboratory (RAL)].

II. EXPERIMENTAL SECTION

Soybean lecithin (Epicuron 200) was a gift by Lucas Meyer and was used as received. D_2O (100% D) and d_{12}-cyclohexane (99.5% D) were purchased by Aldrich Chemicals. Water was deionized and bidistilled.

The microemulsions were prepared by weight, first dissolving the lecithin in the d_{12}-cyclohexane and then adding the appropriate amount of water. Then, weight fractions of the dispersed phase were converted to volume fractions (more suitable for comparisons with previous results [7,8] and with theoretical predictions [2]), using for the density of lecithin at 25 °C the value 1.014 g/cm^3.

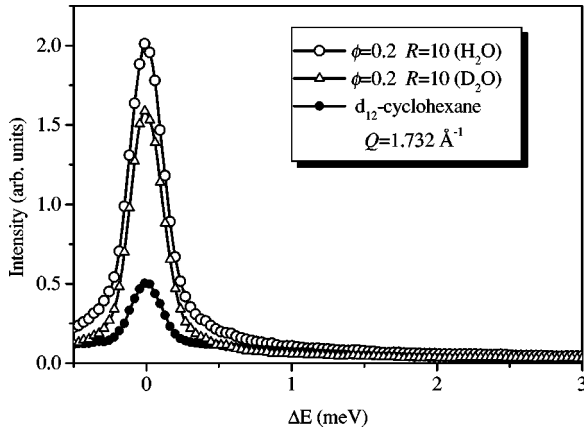The QENS experiment was performed on the NEAT spec-

FIG. 1. QENS spectra of d_{12}-cyclohexane and of systems at $\phi = 0.2$ and $R = 10$, prepared both with light and heavy water. Continuous lines are the fitting results from Eq. (2).

trometer at the Berlin Neutron Scattering Center (BENSC), using an incident wavelength of 5.1 Å and an instrumental resolution $\Delta E = 217 \ \mu$eV (vanadium) at room temperature (25 °C). The covered exchanged wave vector (Q) range was 0.3 Å$^{-1} \leqslant Q \leqslant 2.2$ Å^{-1} (at energy zero transfer). In order to separate the water contributions from those of the other components, the isotopic substitution method was adopted: lecithin/water/d_{12}-cyclohexane systems of different compositions ($\phi = 0.2, R = 10$ and $\phi = 0.1, R = 5$) were prepared both with light and heavy water. Spectra from pure d_{12}-cyclohexane and from a binary system ($\phi = 0.2, R = 0$) were also taken, to check the matching among this experiment and previous QENS results [8] obtained at LLB (MIBEMOL, $\Delta E = 20 \ \mu$eV) and RAL (IRIS, $\Delta E = 8 \ \mu$eV). All time-of-flight spectra were preliminarily translated into energy scale and corrected for the empty cell contribution. In Fig. 1 we report, as an example, the experimental spectra for pure d_{12}-cyclohexane and for two isotopically substituted samples of the same composition.

The INS spectra were taken on the TOSCA spectrometer at RAL, at room temperature, over an energy range 1 meV $\leqslant \Delta E \leqslant 1000$ meV. Samples at $R = 0$ and $R = 10$ (H$_2$O) were investigated at a fixed volume fraction $\phi = 0.2$. Spectra f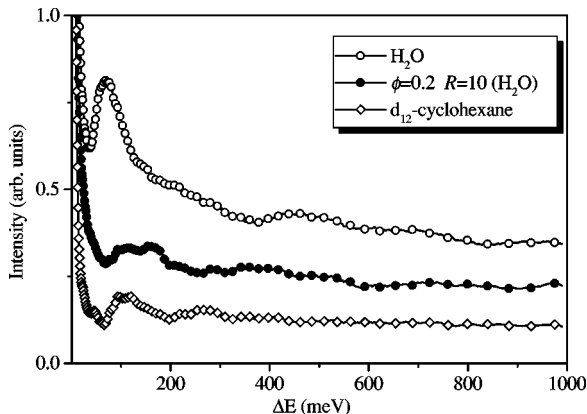rom pure solvent and H$_2$O were also taken in order to separate the contributions from each component. In Fig. 2 the experimental spectra of pure water, d_{12}-cyclohexane, and the solution at $\phi = 0.2$ and $R = 10$ are reported, after subtraction of the empty can contribution, and normalized for the sample thickness.

III. HANDLING OF THE DATA AND RESULTS

A. QENS spectra

The QENS spectra were analyzed under adoption of the Sears [9] formalism, following which the scattering law can be written as

$$S(\mathbf{Q},\omega) \propto J_1^0(Q,\xi) \frac{1}{\pi} \frac{\Gamma_T}{\Gamma_T^2 + \omega^2} + \sum_{l=1}^{\infty} (2l+1)$$

$$\times J_1^2(Q,\omega) \frac{1}{\pi} \frac{\Gamma_T + l(l+1)D_r}{[\Gamma_T + l(l+1)D_r]^2 + \omega^2}, \quad (1)$$

where J_l are the spherical Bessel functions, D_r is the rotational diffusional coefficient, Γ_T is the translational linewidth, ξ is a correlation length characteristic of the system, and the other symbols have the usual meaning. As a consequence, a fitting was adopted, able to resolve, after convolution of the scattering law with the instrumental resolution function $R(\mathbf{Q},\omega)$, the n independent Lorentzian contributions, $L_n(\mathbf{Q},\omega)$, to the experimental QENS spectra:

$$S(\mathbf{Q},\omega) \propto \left[\sum_n L_n(\mathbf{Q},\omega) \right] \otimes R(\mathbf{Q},\omega). \quad (2)$$

In the case of pure d_{12}-cyclohexane, two Lorentzian lines are resolved. The first one is translational in character and exhibits the effect of a coherent structure factor contribution, centered at $Q \simeq 1$ Å^{-1}, with a de Gennes narrowing at the same wave vector (see Ref. [8] for details). The good matching among the different QENS experiments is shown in Fig. 3(a), where the Q dependence of the half-width at half maximum (HWHM) of this line is reported, for the three sets of data. The second contribution turns out to be originated by the convolution of the translational line with a rotation (HWHM approximately equal to 300 μeV). In analyzing the QENS spectrum from the solution of lecithin in d_{12}-cyclohexane at $\phi = 0.2$, we assumed the additivity of solvent and solute contributions, which does not seem too crude an approximation if one looks at the NMR indication for a solvent mobility completely insensitive to the presence of lecithin [10]. The good statistics obtained at NEAT allowed us to well-separate the QENS contributions from solvent and solute: some doubts advanced in Ref. [8] about possible interference effects between d_{12}-cyclohexane and surfactant are now removed (probably, the adopted normalization procedure did not perform very well when applied to low statistics data). In Fig. 3(b), we report one of the QENS spectra of the solute lecithin, after subtraction of the weighted solvent contribution. These spectra can be reproduced by the convolution of the instrumental resolution with two rotational lines (HWHM approximately equal to 100 μeV and 2 meV, respectively) which ultimately coincide, within the experimental uncertainties, with those resolved by depolarized light

FIG. 2. INS spectra of H$_2$O, d_{12}-cyclohexane, and the system lecithin/H$_2$O/d_{12}-cyclohexane at $\phi = 0.2$ and $R = 10$. Only one experimental point for each ten has been represented in the figure.
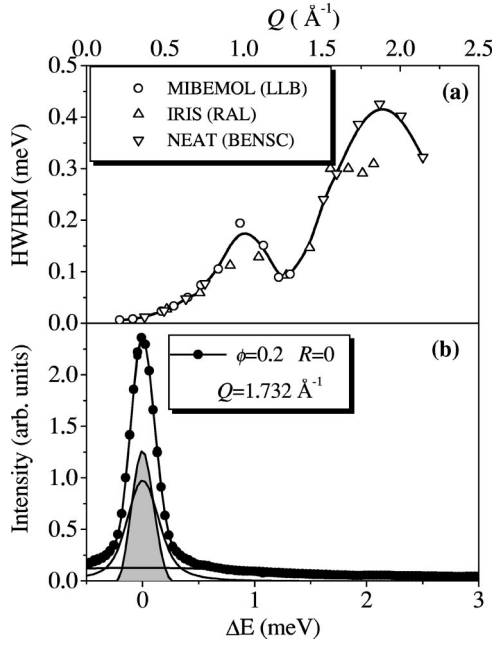
FIG. 3. (a) d_{12}-cyclohexane: Q dependence of the translational component as obtained by the fitting procedure. (b) QENS spectrum of the solution at $\phi=0.2$ and $R=0$. Circles: experimental data; continuous lines: fitting results; shadowed area: elastic contributions.

scattering (DLS) [8]. Since DLS in liquids is to be related both with the *self* and *distinct* contributions to the time correlation function of the traceless part of the polarizability tensor fluctuations, the results obtained through this technique can be directly compared with indications from QENS, when the observed linewidths are appropriately rescaled for the Q values [11]; as a consequence, we are confident that both QENS and DLS are monitoring the same rotational contributions that we can ascribe to reorientational processes of the whole lecithin molecule or, more likely, of its end groups. Moreover, an intense elastic scattering is observed, in which the slow translational contributions from the lecithin protons (resolved in the high-resolution experiments [8]) are collapsed. In Fig. 3(b), the fitting result and each resolved rotational contribution are reported as continuous lines, while the shadowed area represents all the fast translational lines collapsed within the instrumental resolution.

After the above-described checks, we extracted the incoherent QENS contributions from water confined in the micellar core as the difference between spectra of isotopically substituted samples of the same composition (accounting for the sample thickness). In Fig. 4(a), two of the extracted QENS spectra of water, at two different values of the exchanged wave-vector, are reported as an example. When the fitting procedure is applied to the obtained spectra, both a translational and a rotational line are detected. The average HWHM of the latter is about 1.3 meV, close to that of bulk water [12]; unfortunately, there is a large uncertainty ($\simeq 40\%$) about this value, originated by small errors in the normalization procedures which are non-negligible when the wings of this broad contribution are extracted, as described above. Thus, we cannot decide about the possible effects of the sample composition on this relaxational process. However, the translational contributions have been resolved with
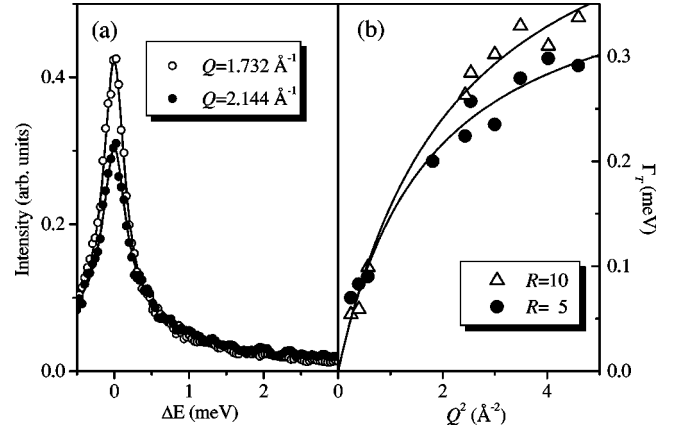

FIG. 4. (a) Extracted QENS spectra of water confined in the system at $\phi=0.2$ and $R=10$. (b) HWHM of the resolved translational contribution of water; continuous lines are the fitting results with a jump diffusion model.

a much better accuracy. Their HWHM, Γ_T, versus Q^2 dependence, reported in Fig. 4(b), shows a typical jump-diffusion behavior [12]

$$\Gamma_T(Q)=\frac{D_T Q^2}{1+D_T Q^2 \tau_0},\qquad(3)$$

where D_T represents the diffusion constant and τ_0 is the residence time before jump. The worked out best-fit parameters [solid lines in Fig. 4(b)] are reported in Table I, together with literature data for bulk water [12] and the estimates for the values of the characteristic jump lengths, $\mathcal{L}=\sqrt{6\tau_0 D_T}$.

Some results from water confined in micropores of a Vycor glass [13] are also reported for a comparison.

B. INS results

In the analysis of the INS contributions from water confined in the micellar core, we will limit ourselves to the analysis of the low-frequency spectra ($\Delta E \le 100$ meV), where the modes more sensitive to the confinement, namely translations and librations, are localized. In order to better evidence these spectral features, we proceeded as follows: (i) from the normalized spectra of the samples at $\phi=0.2$ ($R=10$ and $R=0$), the spectrum of d_{12}-cyclohexane, appropriately normalized for the volume fraction, was subtracted; (ii) the obtained spectral contributions from the dispersed phases

TABLE I. Extracted jump diffusion parameters for water confined in the micellar core. Literature data for bulk water and water confined in a Vycor glass are also reported for a comparison.

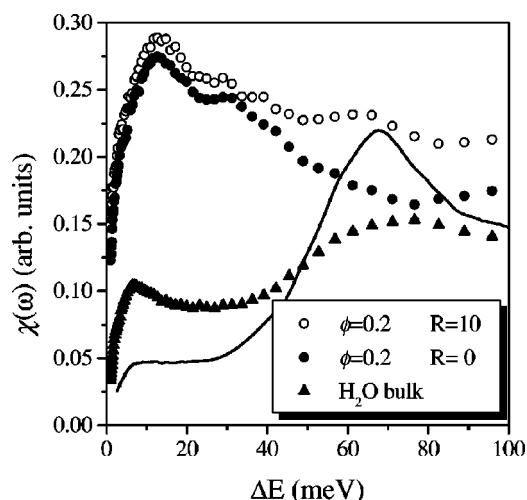| Sample	$D_T(10^{-5}$ cm^2/s$)$	τ_0(ps)	$\mathcal{L}$(Å)
$\phi=0.2;R=10$	3.4±11%	1.28±8%	1.6
$\phi=0.1;R=5$	3.5±13%	1.63±8%	1.9
bulk water [12]	2.3	1.1	1.2
Vycor 100% hydrated [13]	2.43	2.2	1.8
Vycor 52% hydrated [13]	2.61	5.7	3.0
Vycor 25% hydrated [13]	2.45	15	4.7

FIG. 5. $\chi(\omega)$ spectra of the dispersed phases in two systems of different composition and in bulk water. Continuous line represents the estimate for the contribution from water confined into the micellar core. Note that a different normalization factor was used for the dispersed phases and H$_2$O spectra (see text).

of the two samples have been normalized at the same lecithin volume fraction; (iii) the INS contribution from water molecules confined in the micellar core was then obtained by the difference between the two spectra; (iv) finally, the corrected vibrational neutron scattering spectra were divided by the Bose-Einstein population factor, obtaining a generalized dynamic susceptibility, $\chi(\omega)$. Such a function approximately corresponds to a generalized vibrational density of states divided by the frequency ω (when the Q dependence is neglected). In Fig. 5, the above-described $\chi(\omega)$ spectra are reported together with the calculated difference spectrum (continuous line). It should be noticed that in Fig. 5, the above-mentioned difference spectrum is multiplied by a factor 4 (which corresponds to the same fictitious sample thickness of $\phi = 0.2$ and $R = 0$ data, in the same figure). The $\chi(\omega)$ curve for the bulk water, normalized by the same factor, is also reported for a comparison.

IV. DISCUSSION

In the case of bulk water, the value of the jump length, $\mathcal{L}$, is close to that of the intermolecular H-H distance and slightly increases with decreasing temperature. This result was interpreted consistently with the opening of the O-O-O angles (thus allowing for the completion of the local tetrahedral coordination in H$_2$O), as was deduced from the analysis of the x-ray structure factor of water [14]. Table I shows that the water molecules confined in the micellar core are characterized by a residence time very close to that typical of bulk water, exhibiting a higher value at lower R. This would suggest that the fraction of water molecules involved in the formation of the micellar interface slightly increases at lower water contents, with subsequent deformation of the original intermolecular bond angle. It could be interesting to compare the results of Fig. 4(a) with literature data concerning the single-particle dynamics of water confined in the micropores of a Vycor glass [13], the size of which ($\simeq 50$ Å) is comparable with the micellar cross section of lecithin/cyclohexane/water systems obtained by SANS. In Table I,

the data corresponding to 25%, 52%, and 100% hydrated Vycor samples are reported. The tendency of τ_0 to increase upon decreasing of R is revealed both in Vycor and lecithin gels. In particular, the value of τ_0 we found is in between those of bulk water and fully hydrated Vycor. Its variation with the system composition, together with its relatively low values, could be taken as the sign of a structural evolution reflecting in a high mobility of water: both a blowing up of the micelle and a growth process of tubular aggregates upon the addition of water are compatible hypotheses. The INS experiment can be of some help in solving the point. If one compares the $\chi(\omega)$ spectra for water confined in the micellar core and for bulk water, reported in Fig. 5, it becomes clear that the main result of the confinement is a dramatic attenuation of the peak associated with the translational motions, around 6 meV. The same result, interpretable as the reduction of the translational degrees of freedom upon confinement, was obtained for water confined in Vycor glass [13]. This would suggest that, also in our case, almost all the water molecules are involved at the interface with no evidence of bulky properties. In such a way, a noticeable blowing-up of the micelles should be excluded, also at the maximum water content, and the growth process of cylindrical micelles remains a picture able to fit both QENS and INS results. In addition, a sharpening of the librational motion is observed, centered at 70 meV, which may indicate a preferred local coordination for the water molecules, induced by interaction with lecithin polar end groups, which is also reflected in a more localized spectral distribution.

The observed high value of the diffusion coefficient of water could appear consistent with the hypothesis of the existence of giant wormlike micelles (that could be branched or not). However, the picture of a connected network of branched cylindrical micelles better agrees with recent results from depolarized light scattering [8], in which it is shown that, at high values of the micellar volume fraction, the addition of water results in an enlargement of the rotational contribution associated with the lecithin end groups: at a branch point the interface is curved toward the water and, as a consequence, the rotational relaxation time is shifted to lower values. The same indication was given by NMR measurements, both in cyclohexane [15] and in isooctane [16]. Also, the occurrence that the diffusion coefficient of water measured by NMR [15] is smaller than the values reported in Table I is a further observation that is consistent with the hypothesis of an infinite percolated structural model: due to the fact that the diffusion coefficient in confined space is a time-dependent quantity, the NMR probe furnishes a long-time and long-range diffusion coefficient that must be related to a larger confinement volume. The same idea of a percolating extended network of branched wormlike micelles was suggested recently [16] to account for the observed dependence of the conductivity on ϕ at high R.

At low water contents the conductivity decreases and the entangled network could be enough to explain the experimental data, if micelles can stick together at the entanglement points (without formation of a water channel). Of course, from the static point of view the two situations cannot be distinguished if the entanglement points are almost equidistant. This is, in our opinion, a very appealing idea since it is also able to fit previous results from small-angle

neutron scattering (SANS) experiments [17] on the same system, where a well defined interference peak was detected that does not agree with the structural hypothesis of an entangled random network of neutral polymerlike micelles.

The hypothesis of an entangled network of polymerlike micelles also conflicts with the NMR indication that the ^{13}C linewidth did not point out any alkyl chain entanglement, while it was shown that the increase of the macroscopic viscosity is correlated with a strong stiffening of the phosphorus atom of the lecithin and of the adjacent triglyceride moiety [10]. As a last point, we wish to point out that the values of the self-diffusion coefficient for the lecithin protons, D_l (in the range 1.1×10^{-6} cm^2/s $\leqslant D_l \leqslant 3.2 \times 10^{-6}$ cm^2/s, as obtained by the slopes of the data reported in Fig. 6 of Ref. [8]), are not too far from that ($\simeq 10^{-7}$ cm^2/s) required for a good matching of the persistence length, roughly estimated by Angelico and co-workers [7], with literature data [4]; however, the observed dependence of the self-diffusion constant for the lecithin molecules on R and ϕ does not agree with the polymerlike picture. The latter would imply that the lecithin mobility decreases when R increases, contrary to what was observed [8].

V. CONCLUDING REMARKS

Although our discussion above seems to indicate that the percolated structure is better suited to describe the lecithin gel, our conclusions are far from being definitive. In fact, we pointed out a controversy that calls for more data in order to be disentangled. As an example, some results from pulse field gradient NMR [7] seem to indicate that micelles do not form branches, a conclusion that, in agreement with the conventional point of view, conflicts with the results from dielectric spectroscopy [16] and with the picture we have drawn from the analysis of SANS and QENS spectra. An argument against the hypothesis of branch points often reported in the literature is the idea that a branched system should exhibit a low viscosity: branch points, unlike true chemical connections, can slide along the branches [18]. However, we wish to point out that the theory predictions are for only a moderate importance of such an effect. In addition, the establishment of extended networks of interconnected cylindrical micelles was independently evidenced in micellar solutions of lecithin in n-decane [19] and isooctane [16]. One could argue that different behaviors can be induced by different solvents. However, the close similarity among the rheological properties of the different systems (at least until the water content does not exceed the value at which the maximum shear viscosity is observed) would suggest a situation in which where all the systems are described within a unique general framework.

We wish to recall that, very recently, we have shown [17,20] that, in the limit of a mean-field approximation [2] in which the micellar size in highly diluted systems is determined by the kinetic equilibrium between the breaking and the reforming processes of chains, no scaling law exists for the average micellar length, $\langle L \rangle$, this quantity being independent of ϕ and only determined by the value of the rate constants for the involved processes [17,20]. This result was fully confirmed by the analysis of dielectric spectroscopy data from diluted samples [16]. The numerical results obtained from a rough phenomenological model [20] indicate that describing the growth process of the wormlike micelles in dense systems as a process driven by excluded volume effects leads to a concentration-dependent scaling exponent. Once again, an analogous result was found in Ref. [16]. Very recent oscillatory rheology results on n-decane/lecithin/water system [19] pointed out the lack of any correlations between micellar growth and shear viscosity. In order to overcome the interpretative difficulties, the authors hypothesized that the mechanism of the growth process of wormlike micelles should be dependent both on the system density and water content; the possibility of branching of the micelles at high R values was also taken into consideration.

We claim that any interpretation of the experimental data, from any technique whatsoever, based on the *a priori* (not theoretically supported) assumption of any scaling law for the average micellar length, will introduce further confusions and inconsistencies in the literature. At the same time, we wish to point out that our results do not mean that entangled (not interconnected) polymerlike micelles cannot exist in the semidilute regime. From the whole body of the experimental results, we merely obtained indications that at high dilutions the system polydispersity is concentration independent, while in concentrated solutions the close-packing arrangement typical of any conventional micellar solution is retrieved. In the semidiluted region the situation is of course more complicated, since a wide spectrum of different mechanisms can take place, leading to a number of different interpretative models when the system is investigated by different probes.

[1] R. Scartazzini and P. Luisi, J. Phys. Chem. **92**, 829 (1988).

[2] M. E. Cates, Macromolecules **20**, 2289 (1987).

[3] P. G. de Gennes, J. Chem. Phys. **55**, 572 (1972).

[4] P. Schurtenberger, L. J. Magid, S. M. King, and P. Lindner, J. Phys. Chem. **95**, 4173 (1991).

[5] P. Schurtenberger and C. Cavaco, J. Phys. II **3**, 1279 (1991).

[6] P. Schurtenberger, G. Jerke, and C. Cavaco, Langmuir **12**, 2433 (1996).

[7] R. Angelico, U. Olsson, G. Palazzo, and A. Ceglie, Phys. Rev. Lett. **28**, 23 (1998).

[8] F. Aliotta, M. E. Fontanella, M. Pieruccini, and C. Vasi, Phys. Rev. E **59**, 665 (1999).

[9] M. Bée, *Quasielastic Neutron Scattering* (Adam Hilger, Bristol, 1988).

[10] D. Capitani, E. Rossi, A. L. Segre, M. Giustini, and P. L. Luisi, Langmuir **9**, 685 (1993).

[11] P. A. Egelstaff, J. Chem. Phys. **53**, 2590 (1970).

[12] S. H. Chen, in *Hydrogen-Bonded Liquids*, Vol. 329 of *NATO Advanced Study Institute, Series C: Mathematical and Physical Sciences*, edited by J. C. Dore and J. Teixeira (Kluwer Academic, Dordrecht, 1991), and references therein.

[13] M. C. Bellissent-Funel, S. H. Chen, and J. M. Zanotti, Phys. Rev. E **51**, 4558 (1994).

[14] L. Bosio, S. H. Chen, and J. Teixeira, Phys. Rev. A **27**, 1468 (1983).

[15] R. Angelico, G. Palazzo, G. Colafemmina, P. A. Cirkel, M.

Giustini, and A. Ceglie, J. Phys. Chem. B **102**, 2883 (1998).

[16] P. A. Cirkel, J. P. M. van der Ploeg, and G. J. M. Koper, Phys. Rev. E **57**, 6875 (1998).

[17] F. Aliotta and M. Sacchi, Colloid Polym. Sci. **275**, 910 (1997), and references therein.

[18] F. Lequeux, Europhys. Lett. **19**, 675 (1992).

[19] Y. A. Shchipunov and H. Hoffmann, Langmuir **14**, 6350 (1998).

[20] F. Aliotta, M. E. Fontanella, M. Sacchi, and C. Vasi, Physica A **247**, 247 (1997).