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Aggregation phenomena in a lecithin-based gel: Transient networks and diffusional dynamics

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The diffusional properties in the cyclohexane/lecithin/water gel are investigated by means of quasielastic neutron scattering and depolarized light scattering. Also the pure organic solvent and sol phases of different compositions are investigated for a comparison. It is found that both translational and rotational diffusion of water and lecithin are strongly correlated, and become faster in the gel phase. This does not fit the current point of view, where the rheological properties of the system are supposed to result from the entanglement of giant linear micelles which grow up under addition of water. As a further investigation, the aggregative phenomena occurring in the system at the sol-gel transition are observed by means of a calorimeter too. Also in this case, the interpretation of the experimental data in terms of the growth of linear giant aggregates leads to some inconsistencies. It is suggested that the macroscopic shear viscosity behavior can be thought of as originated by a transient network determined by cooperative intermicellar interactions, where the role played by water is not as simple as assumed up to now. [S1063-651X(99)03401-7]

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I. INTRODUCTION

The formation of a gel phase in lecithin-in-oil microemulsions after addition of water is currently interpreted in terms of an entanglement of wormlike micelles, the mean length L of which scales with the volume fraction ϕ of the dispersed phase as $L \propto \phi^{1/2}$ [1,2]: The idea underlying such a polymerlike approach is that when lecithin molecules are dissolved in an organic solvent they self-arrange in spherical aggregates the shapes of which change to rods and then to giant flexible aggregates upon progressive addition of water, at least until a maximum water content is reached, which is characteristic of the solvent under consideration. The average micellar length, at a given concentration, should be determined by the kinetic equilibrium between the breaking and reforming processes. There are two ways by which such a dynamic equilibrium can be altered: (i) a change of the rate constant for the reforming process (i.e., the rate of the intermicellar collisions) through the variation of ϕ; (ii) a change in the rate constant for the breaking process through the variation of the water content R (the number of water molecules per lecithin molecule). In fact, water enters the micellar structure by hydrogen binding to the polar heads of lecithin, thus affecting the value of the scission energy.

The appeal of such a picture lies in its capability of explaining the viscoelastic properties of the system by means of analogies with semidilute polymer solutions, for which the well-known reptation theory [3] is able to furnish good predictions. Such a description of a monotonous unlimited growth process with the concentration is the result of a mean-field approximation. When one is interested in describing dense systems, excluded volume effects are to be taken into account. In effect, small angle neutron scattering (SANS) and static and dynamic light scattering experiments on diluted water-in-oil lecithin micelles have furnished results that have been easily interpreted within the above framework [4,5], indicating that the average micellar length scales with concentration as predicted by the model, at least at high enough dilution (more pronounced growth laws are found when concentration increases [5]). However, a gel structure consisting of an entangled random network of wormlike micelles should be confirmed by a SANS scattering profile characterized by a Lorentzian structure factor [6,7]. On the other hand, the experiments have shown that at high enough concentration, intermicellar interactions determine the existence of a well-defined correlation length, resulting in a pronounced interference maximum [8–10]. After a revision of the current ideas, we realized that the dependence of the mean micellar length on the concentration actually results from a complex phenomenon on which excluded volume effects play a major role, and that cannot be described at all in a mean-field approximation [10–12]. A rough phenomenological model [12] was developed, based on the above considerations, that is able to describe, at least qualitatively, the experimentally observed dependence of the micellar size on the concentration. The occurrence that SANS experiments have shown that at high ϕ values almost the same local arrangement exists in both samples at $R=0$ and $R=10$ (where viscosity exhibits its maximum value) means that mechanisms other than the hypothesized entanglement are the source of the observed sol-gel transition. In particular the investigation of the role played by the water molecules on the macroscopic viscosity of the system becomes of paramount relevance.

The statics is not able to solve the puzzle, and deeper insight can be obtained looking also at the diffusional dynamics of the system. Elsewhere it will be shown by diffusional data obtained from quasielastic neutron scattering (QENS) and depolarized light scattering (DLS) that the sol-gel transition is not monitored by local structural changes (SANS), but rather by a marked increase of the water mobility (as also confirmed by NMR studies [13]). On the one hand, the interpretation of the rheological properties of the system as originated from a transient hydrogen bonding network, where water plays a major role, is not consistent with the observed high mobility of the water itself. On the other hand, the existence of an entangled network of wormlike micelles is not consistent with the SANS results and with the lack of evidence of entanglement points from NMR data. It will be also shown how the results from the calorimetric probe, which directly *sees* the intermicellar aggregation phenomena, lead to the same inconsistencies when interpreted in terms of growth processes of polymerlike chains.

II. MATERIALS AND METHODS

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

The microemulsions were prepared by weight, first dissolving the lecithin in the cyclohexane and then adding the appropriate amount of water. Weight fractions of lecithin were converted to volume fractions, using for the density of lecithin, at 25 °C, 1.014 g/cm^3.

Two QENS experiments were performed. The first one was performed on the MIBEMOL time-of-flight spectrometer at the Laboratoire Leon Brillouin (LLB), Saclay. Neutrons with $\lambda_0 = 9$ Å were used as a probe and the exchanged wave vector was spanned in the range $0.2 \leqslant Q \leqslant 1.3$ Å^{-1}. The energy resolution (vanadium sample) was better than 20 μeV [half-width at half-maximum (HWHM)] and the explored energy range was $-3 \leqslant E \leqslant 0.5$ meV. Two series of samples were prepared at fixed water content $R = 10$ and at different ϕ values (deuterated cyclohexane was used as the solvent). In the first H_2O was used ($\phi = 0.002, 0.022, 0.104, 0.223$), the other was prepared with D_2O (ϕ=0.002,0.021,0.121,0.233). Also the pure solvent was investigated. All the measurements were performed at fixed temperature ($T = 25$ °C) with the exception of the sample with H_2O at $R = 10$ and $\phi = 0.223$ for which spectra were collected at the temperatures of 15, 25, and 35 °C.

The second QENS experiment was performed on the IRIS spectrometer at the Rutherford Appleton Laboratory (RAL). The energy resolution was about 8 μeV (HWHM) and the explored energy range was $-0.4 \leqslant E \leqslant 0.4$ meV. Spectra were collected within the exchanged wave-vector range $0.5 \leqslant Q \leqslant 1.8$ Å^{-1}. All the samples were prepared with deuterated cyclohexane. Two series of samples were prepared at $R = 0$ ($\phi = 0.003, 0.01, 0.2$) and with D_2O at $R = 10$ (ϕ=0.01 and 0.2), respectively. Also in this experiment the spectrum of the pure solvent was collected. All the measurements were performed at fixed temperature, $T = 25$ °C. In both experiments, the time of flight spectra, transformed to the energy scale, were corrected for the empty-cell contribution and symmetrized for the detailed balance.

The DLS measurements were performed on a double-monochromator double-pass (DMDP 2000, SOPRA). The experiment was performed in a 90° geometry using the 5145-Å vertically polarized line of a unimode Ar$^+$ laser, Spectra Physics model 2020, working at a mean power of 700 mW. Spectra were collected on the energy range $-50 \leqslant \Delta\omega \leqslant 50$ cm^{-1}. For each sample three spectra were collected at different resolutions, ΔE, on the energy range $-3 \leqslant \Delta\omega \leqslant 3$ cm^{-1} ($\Delta E = 0.05$ cm^{-1}), $-10 \leqslant \Delta\omega \leqslant 10$ cm^{-1} ($\Delta E = 0.5$ cm^{-1}) and $-50 \leqslant \Delta\omega \leqslant 50$ cm^{-1} ($\Delta E = 2$ cm^{-1}), respectively. The spectra at different resolutions were subsequently numerically matched and corrected for the detailed balance. The DLS measurements were performed, at $T = 25$ °C, on pure cyclohexane, on a solution of soybean lecithin in cyclohexane at $\phi = 0.2$, and on the ternary system lecithin/cyclohexane/water at $\phi = 0.2$ and $R = 10$.

The calorimetric measurements were carried out at 25 °C with a LKB thermal activity monitor equipped with a mix-flow cylinder. For the measurements of the enthalpies of solution, a fixed amount of cyclohexane (about 2.6 cm^3) was placed in the compartment of the perfusion cell. Then, the cell was introduced into the calorimeter and, after thermal equilibration, small amounts of sample at a fixed initial volume fraction $\phi_i = 0.123$ were added into the sample compartment by an injection cannula connected to a Hamilton syringe. The final volume fraction ϕ_f was in the range $0.5 \times 10^{-3} \leqslant \phi_f \leqslant 8.7 \times 10^{-3}$. Samples were investigated at different water contents: $R = 5.1$, $R = 10.1$, and $R = 15.3$. The calorimetric signal, appropriately amplified, was used to calculate the thermal effect (estimated uncertainty approximately 0.5%).

The same procedure was followed for the measurement of the enthalpy of solution of water, when 2.6 cm^3 of a solution of lecithin in cyclohexane at $\phi = 0.135$ was put in the cell and then small quantities of water were added (the final R values were ranging from 0.8 to 15.4).

III. SOLVENT DYNAMICS

In performing our incoherent quasielastic neutron scattering experiment we used deuterated cyclohexane, with the aim of separating the solvent and the lecithin contributions (the latter being almost incoherent) to the overall scattered intensity. However, it should be stressed that the d_{12}-cyclohexane is far from being just a pure coherent scatterer, as for deuterium nucleus coherent and incoherent cross sections are comparable (σ^{coh}=5.6 b and σ^{inc}=2 b, respectively). The measured dynamic structure factor $S(\mathbf{Q},\omega)$ represents the double Fourier transform of the van Hove space-time correlation function, $G(\mathbf{r},t)$. It is clear that $G(\mathbf{r},t)$ includes both the *self* and the *distinct* dynamic correlation functions, which would mean that

$$G(\mathbf{r},t) = G_s(\mathbf{r},t) + G_d(\mathbf{r},t). \tag{1}$$

Of course, $G_s(\mathbf{r},t)$ is identical to $G_{\text{inc}}(\mathbf{r},t)$. In our case the problem of separating the two contributions can be at least partially solved by observing the pronounced increase of the total integrated scattered intensity at around $Q = 1.3$ Å^{-1}, as shown in Fig. 1, where both data from MIBEMOL and IRIS experiments are reported. This is indicative of the prevalence of $G_d(\mathbf{r},t)$ over $G_s(\mathbf{r},t)$ in that range, which, implying the existence of a characteristic correlation length in the system, is also accompanied by a narrowing of the translational diffusion line [14] (see below). On the other hand, the scattered intensity turns out to be almost constant for exchanged wave-vector values below 1 Å^{-1}, showing that the incoherent contribution dominates. The difference in the apparent backgrounds of the diffraction patterns reported in Fig. 1 are due to the different normalization procedures used and to the different resolutions and explored energy ranges chosen for the two experiments. Once the main character of the scat-

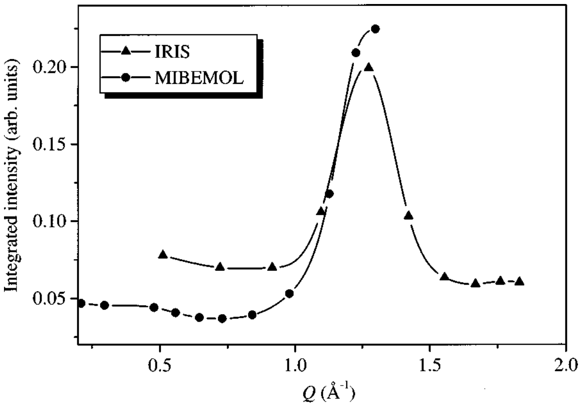

FIG. 1. Diffraction pattern of d_{12}-cyclohexane.

tered spectrum in the various Q ranges is identified, and the existence of a coherent contribution assessed, we remain with the question of the number of components of the observed intensity. In the absence of a generally accepted model, we adopted the choice of estimating the minimum number of Lorentzians required to reproduce the spectrum. In conformity with the Sears formalism [15–17], which assumes that molecular reorientation takes place through small-angle random rotations (angular diffusion), decoupled from the translational motion, the scattering law can be written as

$$S(\mathbf{Q},\omega)\propto J_0^2(Q\xi)\,\frac{1}{\pi}\,\frac{\Gamma_T}{\Gamma_T^2+\omega^2}+\sum_{l=1}^{\infty}(2l+1)J_l^2(Q\xi)\,\frac{1}{\pi}\,\frac{\Gamma_T+l(l+1)D_r}{[\Gamma_T+l(l+1)D_r]^2+\omega^2},\tag{2}$$

where J_l are the spherical Bessel functions, D_r is the rotational diffusion coefficient, Γ_T is the translational linewidth, ξ is a correlation length characteristic of the system, and the other symbols have the usual meaning.

Our fitting procedure was able to resolve just two independent Lorentzian lines, after convolution of the scattering law with the instrumental resolution function $R(\mathbf{Q},\omega)$:

$$S(\mathbf{Q},\omega)\propto[L_1(\mathbf{Q},\omega)+L_2(\mathbf{Q},\omega)]\otimes R(\mathbf{Q},\omega).\tag{3}$$

The first Lorentzian shows a markedly Q-dependent linewidth the value of which scales as Q^2 at low Q values. Such a behavior is typical of the translational line associated with a centre-of-mass motion. However, as asserted above, at wave-vector values $Q>1$ Å^{-1} the coherent scattering contribution becomes of main relevance, as it is stressed by a maximum of the intensity of the translational line to which a de Gennes narrowing of the linewidth corresponds [14] (see Fig. 2).

The second Lorentzian line can be unambiguously detected only in the MIBEMOL experiment (it can be, at least partially, confused with a constant background in the high-resolution spectra of IRIS). From the analysis of the MIBEMOL spectra it turns out that the second Lorentzian line is rotational in character: it appears as the convolution of a translational line with a Q-independent rotational contribution with HWHM of about 260 μeV. Due to the not very good statistics obtained on the wings of the quasielastic spectra, at the moment, we are not able of going into the details of the rotational diffusion of the solvent. Further measurements are actually in planning on this subject that, however, falls outside of the aim of this paper.

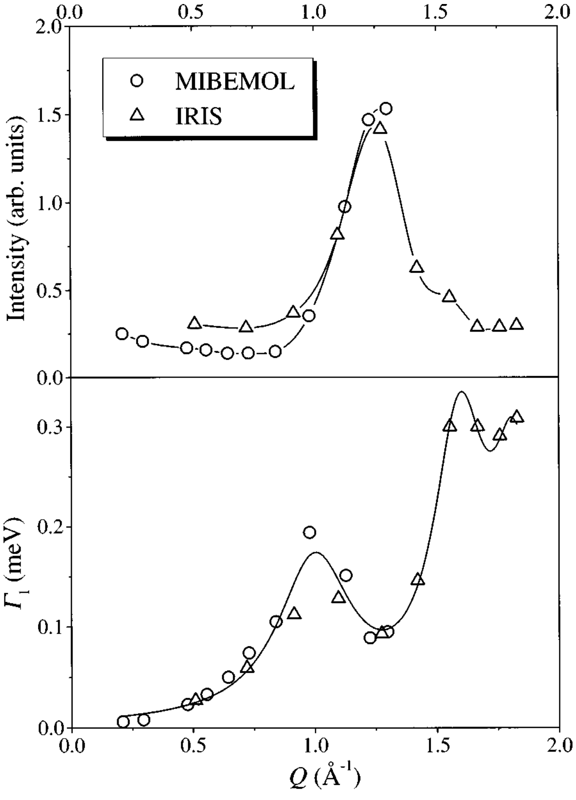

FIG. 2. d_{12}-cyclohexane: Q dependence of the integrated area (up) and of the half-width (down) of the translational component as obtained through the fitting procedure [see Eqs. (2) and (3)].

The comparison with results from depolarized light scattering technique should be of some interest in this respect. Depolarized Rayleigh scattering in liquids is originated by the time correlation function $C_\beta^{\text{anis}}(\mathbf{Q},t)$ of the traceless part of the polarizability tensor fluctuations $\delta\beta_{ij}(\mathbf{Q},t)$ [18]. The scattering profile I_{VH} is given by the Fourier transform of the time correlation function $C_\beta^{\text{anis}}(\mathbf{Q},t)$,

$$I_{\text{VH}}(\mathbf{Q},\omega)=\int_{-\infty}^{+\infty}dt\,\exp(-i\omega t)\times\left\{\langle\delta\beta_{xy}^{*}(\mathbf{Q},0)\,\delta\beta_{xy}(\mathbf{Q},t)\rangle\sin^2\frac{\theta}{2}+\langle\delta\beta_{yz}^{*}(\mathbf{Q},0)\,\delta\beta_{yz}(\mathbf{Q},t)\rangle\cos^2\frac{\theta}{2}\right\},\tag{4}$$

where $\langle\,\rangle$ denotes the thermodynamical averaging, θ is the scattering angle, and the subscripts VH refer to the polarization directions of the incident (*vertical*) and scattered (*horizontal*) fields with respect to the scattering plane.$I_{\text{VH}}(\mathbf{Q},\omega)$ contains both the self-contributions and the distinct contributions of the correlation functions $C_\beta^{\text{anis}}(\mathbf{Q},t)$. This means that depolarized Rayleigh spectra depend on both self-particle

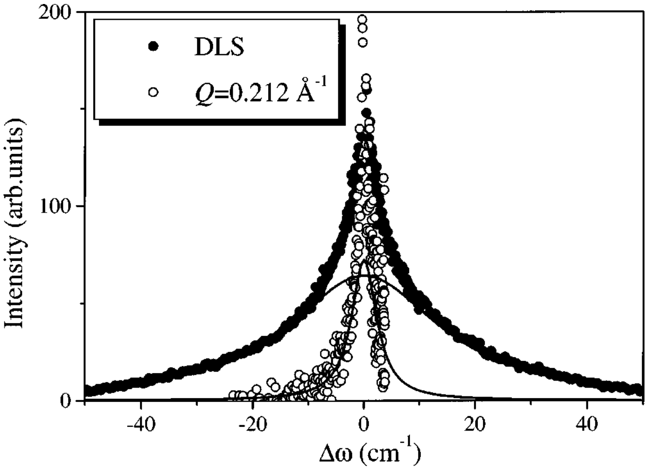

FIG. 3. The DLS spectrum of cyclohexane. The two rotational contributions obtained through the fitting procedure (see text) are reported as continuous lines. The QENS spectrum (open circles) is reported for a comparison.

motions and correlated motions of different molecules and, as a consequence, can be directly compared with results from quasielastic neutron scattering, once the observed linewidths are appropriately rescaled for the Q values.

In Fig. 3, the results from depolarized light scattering measurements, in a 90° scattering geometry, are reported, together with the neutron spectrum from d_{12}-cyclohexane obtained at the minimum Q value we explored at the MIBEMOL time-of-flight diffractometer. The experimental spectrum was analyzed in terms of a superposition of Lorentzian contributions. Two Lorentzian lines were detected and in Fig. 3 the result of the fitting procedure is reported together with each resolved component. It should be stressed that in a light-scattering experiment, due to the large value of the incident wavelength ($\lambda_0 = 5145$ Å in the actual case), the exchanged wave vector is virtually zero ($Q = 0.0017$ Å^{-1}). As a consequence, any translational contribution revealed in the quasielastic neutron scattering experiment will be collapsed within the experimental resolution and only the Q-independent rotational lines will be comparable. In effect, the narrower contribution detected in the light-scattering experiment seems to be coincident (see Fig. 3) with the faster motion observed in the neutron scattering experiment, thus supporting its interpretation as a rotational line. However, a further larger contribution is observed in the DLS spectrum, which could be originated by a faster relaxation process and that, in addition, cannot be detected within the limited Q range spanned in the neutron scattering measurement. Furthermore, the investigation of the far wing should be of interest, to detect probable collisional contributions. As asserted, the investigation of the above-mentioned fast relaxation process in cyclohexane will require further measurements and we will limit ourselves here to the study of the translational line revealed in the quasielastic neutron scattering spectra.

IV. DIFFUSIONAL PROCESSES IN LECITHIN-IN-OIL MICROEMULSIONS

In Fig. 4 we report the Q dependence of the integrated scattered intensity for solutions of lecithin in d_{12}-cyclohexane at different values of the volume fraction. From an inspection of the figure it appears that, when the concentration increases, the solvent contribution remains almost unaltered (at least as far as the coherent dynamical structure factor is concerned) while a new, partially coherent, component from lecithin is detected, centered at very low Q values. In the inset of the same figure, the diffraction pattern from the lecithin/d_{12}-cyclohexane/water system at $\phi = 0.2$ and at a water content $R = 10$ is reported. The data are obtained both at the MIBEMOL and the IRIS instruments; the very good agreement between the two experiments is quite evident. It is to be stressed that the above reported indications for a solvent dynamics essentially not influenced by the presence of the dispersed phase agrees with NMR experiments in which it was found that the linewidths for ^{13}C and ^{1}H of cyclohexane are completely insensitive to the composition of the system (and then to the macroscopic viscosity) [13]. Taking into account the above considerations, we analyzed the quasielastic neutron scattering spectra from our samples by fitting them with Eq. (2), where the linewidths of the solvent contributions were held fixed (while the intensities should be scaled by the concentration), and looking for the presence of further Lorentzian lines or of purely elastic scattering. However, as will be shown elsewhere, such an approach is only a rough approximation, and it is not appropriate for the analysis of the broad rotational lines. Besides the cyclohexane components and an additional translational line connected with the dispersed system, a purely elastic component is detected, at low-Q values, for samples at $\phi \geqslant 0.1$ and $R = 10$. One could be misled in interpreting such a component as an elastic incoherent structure factor contribution. Actually, such an event can be excluded, as after the scattered intensities from samples containing D_2O and H_2O are compared one is allowed to consider the water contribution as essentially coherent too, at least at very low Q values and at high enough concentrations (in the inset of Fig. 4, note that scattering from D_2O turned out to be more intense than from H_2O). The existence of an intense coherent contribution at low values of the exchanged wave vector is consistent with small-angle neutron scattering experiments [8–11], in which we detected the existence of a maximum in the intermicellar

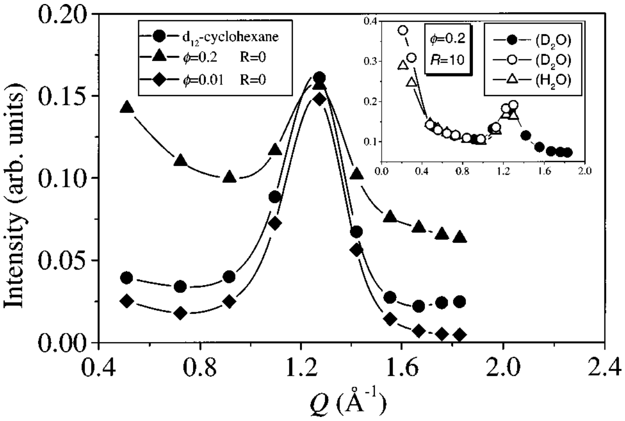

FIG. 4. Diffraction patterns of solution of lecithin in d_{12}-cyclohexane at different values of the volume fraction. In the inset the diffraction pattern of the gel phase is reported. Full symbols, IRIS data; open symbols, MIBEMOL data.

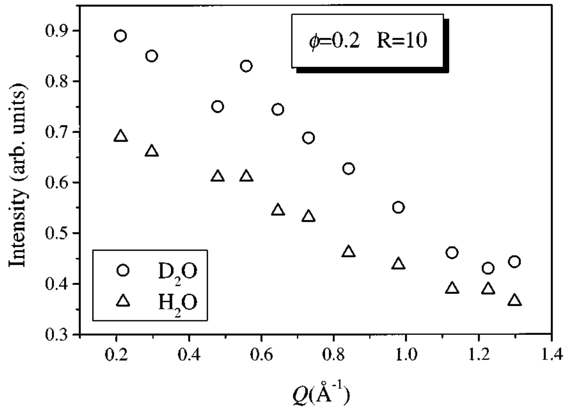

FIG. 5. Q dependence of the integrated area of the resolved translational component in the gel phase.

structure factor, centered at $Q \cong 0.1$ Å^{-1} at $R=0$ and moving towards lower values after the addition of water (note that the analysis of the elastic structure factor, detected by our fitting procedure for samples at $\phi \geqslant 0.1$, furnishes a value of the correlation length that is in good agreement with SANS results). The establishment of a preferred correlation length, at high enough concentration, is also suggested by a phenomenological model [12], describing the micellar growth process as a complex behavior that emerges from intermicellar excluded volume interactions. The coherent nature of the scattering from the dispersed phase is further confirmed by the Q dependence of the integrated area of the resolved translational line (see Fig. 5).

The translational character of the observed component can be easily deduced by the DQ^2 behavior of the linewidth (see Fig. 6). The slowing down of the diffusive motion at higher concentrations is also evident and agrees with the observed increasing of the macroscopic viscosity. On the contrary, a higher mobility is detected after addition of water and such a result may appear inconsistent with the observed sol-gel transition. The same indication comes from DLS measurements (see Fig. 7): when lecithin is dissolved in cyclohexane, the rotational line narrows but, when water is added, a broadening is unambiguously observed. The broadening of the linewidth with increasing R agrees with NMR [13] indications for a high water mobility at high R values. On this basis, the measured Lorentzian contribution could be considered as a superposition of reorientational motions of lecithin molecules (which do not appear to be related with the macroscopic viscosity, as reported in [13]) and of water.

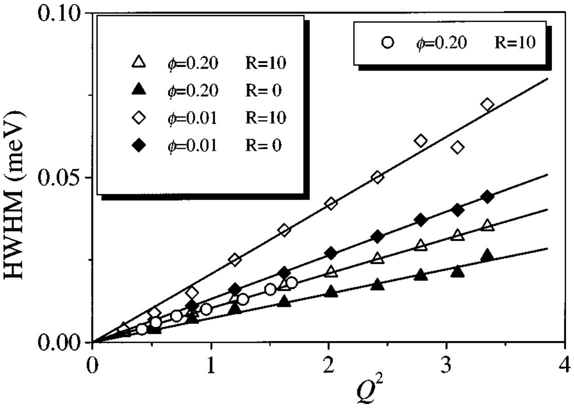

FIG. 6. Q^2 dependence of the resolved translational line connected with the dispersed phase. Data are reported for system of different composition. Open circles refer to MIBEMOL data; all the other points come from the IRIS experiment.

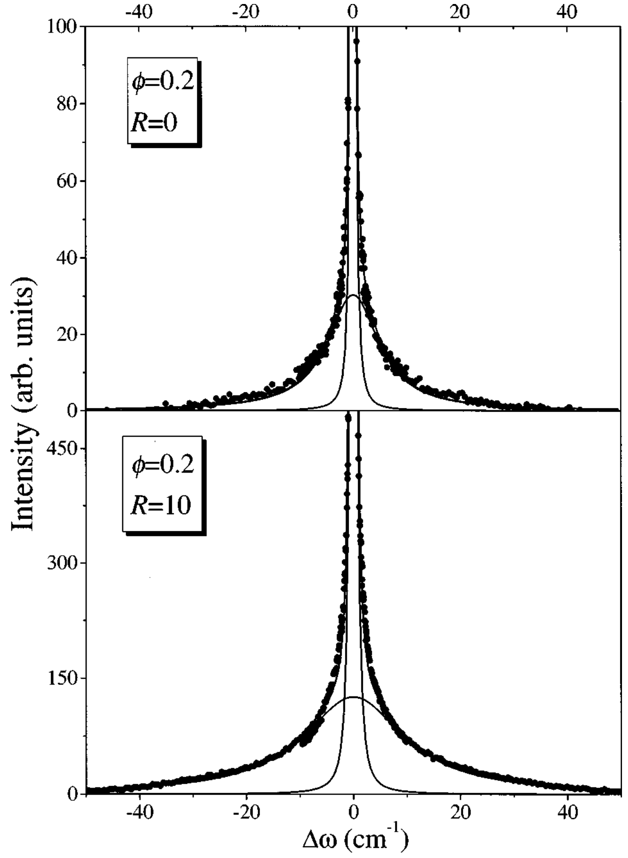

FIG. 7. The DLS spectra of a solution of lecithin in cyclohexane (up) and of the gel (down). The two rotational contributions obtained through the fitting procedure (see text) are reported as continuous lines.

The above interpretation of the translational diffusive process detected in the quasielastic neutron scattering experiment is supported by the observed T dependence of the HWHM, which is consistent with an activation energy of about 30 kJ mol^{-1}. Such a value, the order of magnitude of which is typical of hydrogen-bonded systems, enforces the hypothesis that the observed diffusive processes are, at least partially, triggered by the breaking of the hydrogen bond between water and the polar head of lecithin.

In conclusion, the working hypothesis for a solvent dynamics not influenced by the presence of the dispersed phase can be taken just as a first approximation, which is useful when one is only interested in the analysis of the intense translational contribution. In fact, from an inspection of Fig. 8, where the normalized cyclohexane and gel spectra are compared, it becomes immediate to realize that the cyclohexane contribution cannot be simply considered as additive. The rotational diffusion detected in the gel phase turns out to be slower than the corresponding motion for pure solvent, suggesting for stronger solvent-surfactant interactions than up to now hypothesized.

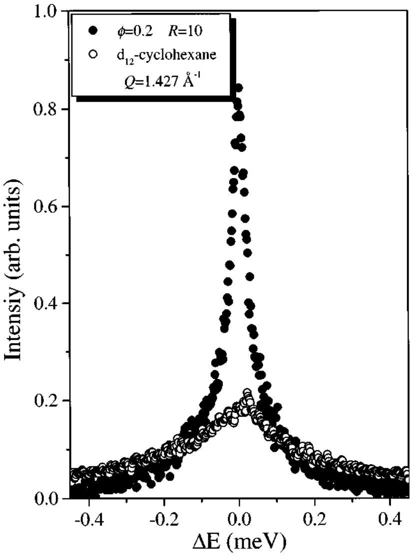

FIG. 8. QENS spectra from the gel and pure d_{12}-cyclohexane. The intensity of the two spectra are normalized and the intensity from d_{12}-cyclohexane was scaled for the solvent concentration in the gel phase. The nonadditivity of the solvent contribution is evident (see text).

V. THERMODYNAMICS OF THE AGGREGATION PROCESS

From the quasi-elastic scattering results, no evidence is found of bulk water, which means that almost all the water molecules participate to the building up of the correlated structure experimentally observed. At the same time, it appears evident that in the gel phase the high macroscopic viscosity observed is associated with a local arrangement, not too different from that observed in the sol phase ($R=0$), and with a large local mobility of the water molecule. A water mobility increasing with the water content could be rationalized in terms of a blowing up process of the micelles under the addition of water: in such an instance, when the R value increases, the volume of water that is seen as bulk liquid increases too. But such an idea is not consistent with a picture in which the micelles are thought of as long flexible cylinders whose lengths depend on the water content and on the concentration but whose cross-sectional radius is almost a constant. On this basis, it becomes clear that water is playing, in the aggregative phenomena taking place in the system, a more complex role than up to now understood. With the aim of gaining a deeper insight on the topic, we investigated the energetics of the intermicellar aggregation process by means of the calorimetric probe. We performed both measurements of heat of dilution, at different R values, and of enthalpy of solution of water, at fixed lecithin volume fraction. The two sets of data will be separately analyzed elsewhere.

A. Dilution enthalpies

For the measurements a fixed quantity of gel, at fixed volume fraction ϕ_i, was diluted in cyclohexane down to a final concentration ϕ_f. In the analysis of the experimental data it was assumed that (i) the main contribution to the measured enthalpy comes from the breaking process of the aggregates preexisting in the system; (ii) the aggregates are cylindrical or wormlike, in agreement with the current belief, and their size scales with concentration according to

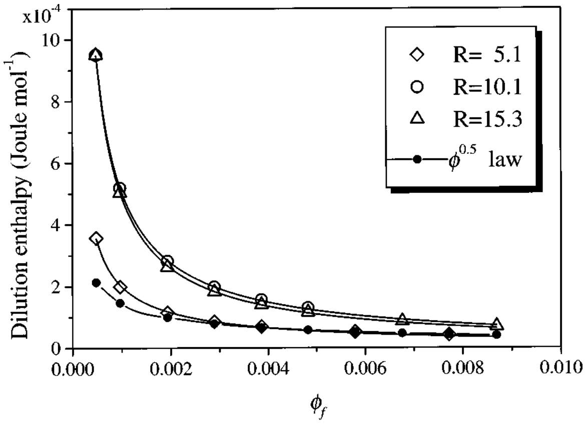

FIG. 9. Experimental dilution enthalpies as a function of the final concentration ϕ_f. Data are reported for samples at different water content. Continuous lines: fitting with Eq. (7). The behavior of Eq. (7) when the parameter α assumes the conventional value of 0.5 is also reported for a comparison.

$$L \propto \phi^{\alpha}. \tag{5}$$

When an aggregate of length L_i breaks in N_p points along the chain, it gives N_p+1 aggregates of mean length L_f, and thus

$$(N_p+1)L_f = L_i,$$

which can be rewritten as

$$N_p = L_i L_f^{-1} - 1 = \phi_i^{\alpha}\phi_f^{-\alpha} - 1. \tag{6}$$

If n_l indicates the number of lecithin moles in the solution, N_{agg} the aggregation number of the chain with length L_i, and E the thermal energy required to break one mole of chains of mean length L_i into two pieces, then one can write

$$\frac{Q_d}{n_i} = \frac{E}{K_R}(\phi_f^{-\alpha} - \phi_i^{\alpha}), \tag{7}$$

where K_R is a proportionality constant representing the aggregation number at unitarity lecithin concentration and is defined by $N_{\mathrm{agg}} = K_R \phi_i^{\alpha}$, and Q_d is the measured heat flux. In such a way it is implicitly assumed that the mean aggregation number depends on the water content through K_R. In Fig. 9, we report the experimental values of the dilution enthalpy as a function of ϕ_f, at different water contents. The data were fitted with Eq. (7), and the values of α and E/K_R were obtained (see Table I). It can be observed that (i) the α value is definitely higher than 0.5 [the behavior of Eq. (5) with $\alpha=0.5$ is reported in Fig. 9 for comparison]; (ii) the R dependence of the α values seems to suggest a more pronounced growth process at $R=15$ (or, at least, that at $R=15$ the growth process is not less pronounced than at $R=10$) while the shear viscosity exhibits the maximum value at $R \cong 10$. In addition, since the values of E/K_R are positive and due to the fact that the quantity K_R is positive by defi-

TABLE I. Values of the parameters in Eqs. (7) and (9), as obtained by the fitting with the experimental dilution enthalpies and enthalpies of solution.

R	α	E/K_R (kJ mol^{-1})	E/N_0 (kJ mol^{-1})	K_R/N_0
5.1	0.77	0.099	11.07	111.8
10.1	0.85	0.140	13.59	97.1
15.3	0.90	0.097	14.97	154.3

nition, also the scission energy E will be positive; i.e., the micellar aggregation is an exothermic process.

B. Water solution enthalpy

For the measurements, different amounts of water were dissolved in a fixed quantity of a solution of lecithin in cyclohexane at $\phi=0.135$. In the interpretation of the obtained data, it was assumed that the main contribution to the observed thermal effect comes from the micellar aggregation process induced by the water addition. In such a way, the effect arising from interactions between water and lecithin head groups is disregarded. However, it is to be stressed that the values of the solution enthalpy observed in analogous system, but in the absence of aggregation processes, are much smaller [19] and become even smaller as R increases. In addition it was assumed that (i) our system at $R=0$ consists of lecithin micelles, that are arranged in aggregates with a mean aggregation number N_0; (ii) the addition of water induces the aggregation of N moles of micelles with aggregation number N_0 to produce one mole of micelles with an average aggregation number $N_{\text{agg}}=NN_0$.

The thermal effect should be equal to $-(N-1)E$. The enthalpy changes for one lecithin mole is

$$\Delta H_L=-\frac{(N-1)E}{NN_0}=-\left(\frac{1}{N_0}-\frac{1}{N_{\text{agg}}}\right)E. \tag{8}$$

Taking into account that $\Delta H_L=\Delta H_W R$, we obtain

$$\Delta H_W=-\left(\frac{1}{N_0}-\frac{1}{K_R\phi^{\alpha}}\right)\frac{E}{R}. \tag{9}$$

In Fig. 10, the experimental values of the enthalpy of solution as a function of R are reported in a log-log plot. From the fitting procedure the values of the quantity E/N_0 are obtained (see Table I). Note that the data are well fitted by a straight line (also reported in the figure). The best fit slope of the latter is used to obtain the quantity E/N_0, by means of Eq. (9), when the previously determined values of E/K_R and α are used. From the values of E/N_0 and E/K_R we can obtain the quantity K_R/N_0, which, remembering the definition of K_R, is proportional to N_{agg}. From the data reported in Table I, it becomes clear that the micellar aggregation number is the lowest at $R=10.1$, where macroscopic viscosity assumes its maximum value and where, if the current models should be working, the micellar length should reach its maximum value.

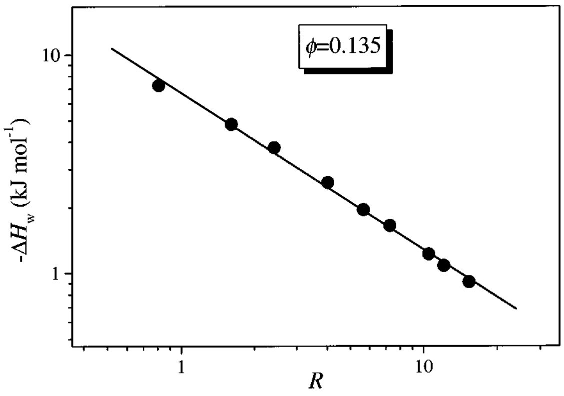

FIG. 10. Experimental values of the water solution enthalpy ΔH_W. The straight line represents the fitting with Eq. (9).

VI. CONCLUDING REMARKS

The current idea of a simple polymerlike picture for the gel structure is definitely confuted by the whole body of the presented experimental results. The most direct contradiction between the current model and the experiment lies in the occurrence that while the hypothesis of a random (neutral) network of polymerlike chains should be reflected in a Lorentzian structure factor [6,7], when the semidiluted region is investigated, the results from SANS [8,9,11] show the appearance of an intense interference maximum that is typical of any conventional micellar solution [20,21]. The static experiment reveals that the addition of water in a system at high volume fractions is not reflected in any significant structural change. The only effect one can observe is the progressive shift of the maximum position towards lower Q values: a result that is consistent with the usual blowing process of the reverse micelles after the addition of water, and that would suggest that the macroscopically observed sol-gel transition is not determined by the existence of wormlike micelles that are becoming long enough to entangle. The above considerations are in agreement with IR-spectroscopy results in which no changes in the C-H antisymmetric stretching of the methylene group of lecithin is observed [22]. This band, in fact, is particularly sensitive to the variation of the intermolecular chain-chain interactions [23] and hence of a variation of the packing order of the lecithin alkyl chains located in the micellar layer. Of course, an extensive entanglement of long cylindrical micelles should involve a change of the lateral packing order in the micellar interface and such a change should be easily detected in the IR spectra. A further argument against the hypothesized growth process is furnished by the calorimetric probe: if one assumes the current model as the basis for data analysis, i.e., if one assumes that the only intermicellar aggregation process that is taking place is the linear growth of polymerlike chains, then one reaches the contradictory result that the average micellar size is minimum where the macroscopic shear viscosity reaches its maximum value.

A similar result has been found by NMR experiments [13], in which the ^{13}C linewidth did not point out any alkyl chain entanglement. In contrast, NMR have shown that the increasing of the macroscopic viscosity is correlated with a strong stiffening of the phosphorus atom of lecithin and of the adjacent trigliceride moiety. This is a surprising result, because the phosphorus atom is far from any possible point of entanglement. A possible explanation of the above results was given by Shchipunov and Shumilina [24], who have shown that water molecules can interact simultaneously with phosphate groups of neighboring lipid molecules via hydrogen bonding, acting as a bridging between them: in such a way, water molecules and lecithin phosphate groups can self-arrange giving rise to a hydrogen bonding network. Such a structural hypothesis fit well with the experimental results that the water contribution to the QENS spectra of the jelly-like phase of our system is essentially coherent and follows the same Q dependence of the scattering from lecithin. The idea that almost all the water molecules are involved, together with the lecithin molecules, in the structure observed by SANS could agree with the structural hypothesis proposed in Ref. [24], but the observed increase of the water mobility with R seems to be interpretable with an increasing of the water molecules that are seen as bulk liquid and not as an increasing of the number of water molecules involved in the building up of the extended (interfacial) hydrogen bond network.

The presence of water not involved in the formation of the interfacial structure of the gel is also suggested by recent dielectric measurements performed by Cirkel and co-workers on isooctane/lecithin/water systems [25], where a percolation phenomenon has been indicated as possibly responsible of the observed dependence of the conductivity on the lecithin concentration at relatively high water contents. The proposed analogy of the system under study with conventional micellar solutions (for which the observed percolation at high enough volume fractions is usual) agrees well with the conclusions previously drawn from SANS [8–11]. Cirkel, van der Ploeg, and Koper also find some inconsistency in the assumption that the mean micellar length scales as ϕ^{α}; in particular they find $\alpha \approx 0$ at very low concentrations, in agreement with recent arguments [12] that point out inconsistencies in the assumption that $\alpha = 0.5$.

In summary, we can conclude that no correlation was detected between the observed sol-gel transition and the local structural arrangement of the gel. We have not been able to detect any structural transition associated with a growth process of the micelles, occurring in the crossover of the sol-gel boundary. On the contrary, all the experimental evidences seem to give support to the hypothesis that the rheological properties of the lecithin-based microemulsions could originate from some dynamical property of the micelles themselves on which water plays a preminent role. This is the main point suggested in this paper. On these bases, if a role is played by any shape whatsoever of micelles, our results show that it is not so crucial and directly responsible of the rheology of the system as thought before. A definite answer requires further theoretical and experimental examination.

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