Water Diffusion and Headgroup Mobility in Polymer-like Reverse Micelles: Evidence of a Sphere-to-Rod-to-Sphere Transition

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A pulsed gradient spin-echo FT ^{1}H NMR study on the system soybean lecithin/water/perdeuterated cyclohexane is presented. The self-diffusion coefficient of water, D_w, was measured as a function of the water content (W_0) and was found to show a bell-shaped trend. The composition at which the maximum in D_w occurs is the same at which the viscosity is the highest. We rationalize the rising part of the plot in terms of a water diffusion inside wormlike reverse micelles which increase their length upon increasing W_0. On the contrary, the descending part indicates a rod-to-sphere evolution of the aggregate's shape. This interpretation is supported by measurement on the headgroup rotation by dielectric spectroscopy. The composition at which a structural transition occurs and the location of the phase boundary can be predicted by a geometrical model in which the effective packing parameter is equal to 1.58. This value is in agreement with small-angle neutron scattering data in the literature.

I. Introduction

Reverse micelles at moderately high values of surfactant concentration and low values of the mole ratio of water to surfactant (W_0) are generally believed to have a droplet-like structure.[1] A remarkable exception can be found in some systems lecithin/organic solvents/water, where the formation of gel-like viscoelastic solutions can be observed.[2] In these systems it has been firmly established that the polymer-like properties are due to a water-induced one-dimensional growth of the micellar aggregates into very long and flexible cylindrical reverse micelles.[3] The resulting supramolecular aggregates should be formed of cylindrical lecithin (PC) film filled with water molecules and surrounded by the organic solvent. Above a crossover concentration c^* (or volume fraction ϕ^*) of the dispersed phase (surfactant *plus* water), a network of breaking and recombining cylindrical micelles ("living polymer") starts to build up. Like in polymer solutions the crossover concentration, c^*, above which the chains start to overlap, can be estimated as[4]

$$c^* \approx \frac{3M}{4\pi N_A R_g{}^3}$$

where N_A is the Avogadro's number and M and R_g are the aggregate's molecular weight and radius of gyration, respectively. For wormlike micelles, however, this crossover concentration is not so well defined due to the huge polydispersity. Extensive scattering studies, mainly using light scattering (LS) and small-angle neutron scattering (SANS) techniques, performed on these systems at $c < c^*$ (where the experiments probe individual aggregates properties) strongly suggest the presence of a water-induced sphere-to-rod transition at low W_0.[3,5] Moreover, there is the experimental evidence of a c^* decrease when W_0 is increased. As a consequence, at experimentally useful concentrations and for $W_0 > 14$, the system is always in the regime $c > c^*$. Under this condition LS is not sensitive anymore to the individual micellar properties but probes collective features of the network that are independent of the micellar size distribution. Dynamical properties such as the zero shear viscosity, on the other hand, show a peculiar behavior when measured as a function of W_0. Although at low W_0 the zero shear viscosity increases enormously in conformity with the water-induced micellar growth, observed by other techniques,[3,5] above a W_0 of 10 the viscosity falls dramatically again, and the whole W_0 dependence can be described as bell-shaped.[5] Similar effects in aqueous solutions of wormlike micelles have been attributed to branching of the micelles.[6] It has been argued that this would reduce the viscosity since branch points unlike chemical connections can slide along the branches.[7] Although theory predicts that this is an effect of only moderate importance,

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it has been suggested, in analogy with the bicontinuous L3 phase, that this could lead to very low viscosity.[8] An alternative explanation, however, is the transition to another structure of the aggregates like, for instance, large spherical droplets. In this paper we will show that, in the case of the lecithin/water/cyclohexane system, this latter possibility is consistent with both the self-diffusion data obtained by pulsed gradient spin-echo (PGSE) NMR measurements and the information on the mobility of the surfactant headgroups coming from dielectric spectroscopy.

II. Experimental Section

II.1. Materials. Soybean lecithin (Epikuron 200) was a generous gift of Lucas Meyer GmbH (Hamburg, Germany) and was used without further purification. Fully deuterated cyclohexane was purchased from Aldrich (>99.8% isotopic purity). Double distilled water in an all-quartz apparatus was employed. Samples were prepared as previously described.[9]

II.2. Measurements of Self-Diffusion Coefficients. Water self-diffusion coefficients measurements were carried out by the pulsed gradient spin-echo (PGSE) FT(^{1}H)NMR method[10] using the experimental setup described elsewhere.[11] The pulse sequence employed the Stejskal−Tanner sequence,[12] $90°−\tau−180°−\tau−$echo with two rectangular field gradient pulses of about 0.04 T m^{-1}, separated by a constant interval Δ. The echo amplitude recorded at 2τ is given by

$$A_{(2\tau)} = A_0 e^{-[\gamma^2 G^2 D \delta^2 (\Delta - \delta/3)]}$$

were γ is the gyromagnetic ratio of the observed nucleus (^{1}H), D is the self-diffusion coefficient of the species responsible of the spin-echo decay, and δ ranged from 2 to 40 ms depending on samples. The applied field gradient strength (G) was determined before each experiment by a separate calibration. For some samples, the self-diffusion coefficient of lecithin, D_{LEC}, was also measured by following the ^{1}H NMR signal of the $-N^+-(CH_3)_3$ group. For samples with W_0 in the range 6−18 D_{LEC} could not be measured because of the rapid transverse relaxation. For measurements at $\Delta < 100$ ms, gradient calibration was carried out before each experiment with aqueous $ZnCl_2$ solutions. The water self-diffusion coefficients values of these solutions were from the literature.[13] Using the right $ZnCl_2$ concentrations, it is possible to prepare solutions characterized by D_w values close to the water self-diffusion coefficients in the organogels. By means of this procedure, it is possible to obtain a strong reduction of the spurious, whose effects tend to alter the reliability of the diffusion coefficients measured by means of the PGSE-NMR technique.

II.3. Dielectric Spectroscopy. Dielectric spectra were recorded with an impedance analyzer, HP419A (Hewlett-Packard, San Diego, CA), in the high-frequency range (100 Hz to 100 MHz), and with a lock-in amplifier, SR510 (Stanford Research Systems, Sunnyvale, CA), in combination with an external signal generator HM3180 (Hameg GmbH, Frankfurt at Main, Germany), in the low-frequency range (from 1 Hz to 10 kHz). The analyzer was connected to cylindrical cells with various electrode spacings. The electrode spacing was chosen in such a way that the electrode polarization due to the accumulation of charges near the electrodes could be easily separated from other processes.[14] The measured impedance was interpreted in terms of parallel circuit of a capacitor and a conductance, yielding both the dielectric permittivity and conductivity versus frequency. The dielectric permittivity

spectra were fitted to the real part of the Cole−Cole function:

$$\epsilon = \epsilon_\infty \frac{\epsilon_s - \epsilon_\infty}{1 + (i\omega\tau)^\beta}$$

with ω being the circular frequency of the applied field, τ the characteristic relaxation time, and ϵ_s and ϵ_∞ the permittivity at $\omega\tau \ll 1$ and $\omega\tau \gg 1$, respectively. This function can be used to obtain a symmetrical distribution of relaxation times in which the broadness is described by the β parameter. The higher β, the narrower the distribution gets. For $\beta = 1$ the Cole−Cole function goes over in the Debye function, describing a dielectric relaxation process characterized by one single relaxation time.

III. Theoretical Background

In lecithin/water/cyclohexane solutions above c^* (semidilute regime) a characteristic static property is the correlation length,[4] ξ, which has been experimentally found[15] to be independent of W_0, decreasing with increasing lecithin concentration according to the power law $\xi \propto \phi^{-\gamma}$, with $\gamma = 0.70$. The contour length, L, of these wormlike micelles could be extremely large (more than 1 μm depending on W_0 and lecithin concentration[15]).

On the basis of the multiple chemical equilibrium models or scaling arguments, the averaged molecular weight, M, of the micellar aggregates is supposed to increase with the surfactant concentration through the end-cap energy, i.e., the free energy fee to be paid to build an end cap. In general, this increase can be written in the form of a power law as $M \propto c^\alpha$.[16] As stated by the mean field models, α ranges between $\alpha = 0.5$, based either on law of mass-action or Flory−Huggins lattice model calculations, and $\alpha \approx 0.6$, when a scaling theory approach for semidilute solutions is applied.[16] Scattering experiments on the lecithin/water/cyclohexane system demonstrate that the averaged molecular mass of the micelles depends not only on the surfactant concentration but also on the water-to-surfactant ratio W_0.[17] This can be rationalized by a negative affinity of the water to the end caps, which results in an increase of the end-cap energy with W_0. Theoretically this can be accounted for by a modified version of the Gibbs adsorption equation.[18] A simple depletion model based on this concept would include the assumption of ideal mixing of water in the micellar core and a linear dependence of the water depletion on W_0. This model predicts that the end-cap energy depends linearly on W_0, with, as a proportionality factor, the relative deficiency of water molecules in the end caps as compared to the cylindrical parts, ζ.[18] Since the average molecular weight depends exponentially on the end-cap energy, the dependence of the average molecular mass on W_0 becomes $M \propto \exp(\zeta W_0) + $ constant. The constant is related to the finite size effect due to the sphere-to-rod transition.

An empirical approach, based on the renormalization group theory, splits the water and lecithin contribution to the micellar growth giving $M = B_1(W_0)c^\alpha$.[17] In this expression c is the dispersed phase (water *plus* lecithin) concentration (in g/L) and $B_1(W_0)$ is a parameter which is function of W_0 and independent of the lecithin concentration, thus reflecting only the water-induced micellar growth.[17] The exponent $\alpha = 1.2 \pm 0.3$ and the values of $B_1(W_0)$ for $4 \leq W_0 \leq 14$ were calculated from LS data.[17] Furthermore, the values of the mass per unit length, $M_L(W_0)$, for the lecithin/cyclohexane reverse micelles as a function of W_0 have been calculated from SANS data.[15] Accordingly, the weight-average contour length, L, can be calculated: $L = G(W_0)c^\alpha$ with $G(W_0) = B_1(W_0)/M_L(W_0)$ a function only of the mole ratio water/lecithin that has been found
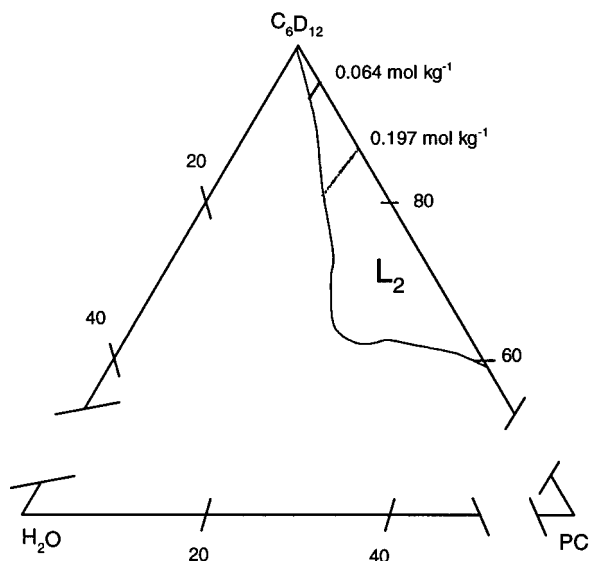
Figure 1. Phase diagram (wt %) of the system water/lecithin/C_6D_{12} (only the extension of the L_2 phase is shown). The sample's composition investigated by PGSE-NMR and by dielectric spectroscopy is shown by the dots (water dilution of PC/C_6D_{12} solutions 0.197 and 0.064 mol kg^{-1}, respectively). The phase diagram was redrawn from ref 47 after the correction for the difference in molecular weight between C_6H_{12} and C_6D_{12}.

to increase with W_0, ranging from 69 Å (g/L)$^{-\alpha}$ at $W_0 = 4$ to 9091 Å (g/L)$^{-\alpha}$ at $W_0 = 14$.

IV. Results

The NMR self-diffusion data presented here were collected along the water dilution line of a lecithin/perdeuterated cyclohexane 0.197 mol kg^{-1} solution (Figure 1). In Figure 2 the self-diffusion coefficients of water and lecithin vs the water content (W_0) are shown. The water self-diffusion coefficients, D_w, have been corrected for the contribution of the water molecules dispersed as monomers in the organic solvent, "free water", assuming a fast exchange between two sites according to[19]

$$D_{obs} = P_{free}D_{free} + (1 - P_{free})D_w \qquad (1)$$

where P_{free} is the mole fraction of the water dispersed in the continuous organic bulk, D_{obs} is the water self-diffusion coefficients experimentally observed, and D_{free} is the water self-diffusion in cyclohexane. P_{free} has been evaluated assuming a constant water concentration in cyclohexane equal to its solubility in the neat solvent (1 mM[20]) and a value of D_{free} of 2.3×10^{-9} m^2 s^{-1} (since at 25 °C both water and perdeuterated cyclohexane share the same viscosity). It should be noticed that, due to the high water content of samples with $W_0 > 5$, the correction can be neglected above this W_0 value. The D_w values show a bell-shaped trend when plotted against W_0 as found for similar water dilution lines of PC/perdeuterated cyclohexane solutions with lecithin concentration greater than 0.075 mol kg^{-1}.[21] At low W_0 (≤ 5) it is possible to perform PGSE ^{1}H NMR runs with $\Delta = 100$ ms, although increasing the W_0 the ^{1}H NMR signal of the trimethylammonium group of the lecithin was no more detectable (for $\Delta > 30$ ms) up to $W_0 \approx 18$ (see Figure 3). For higher W_0 values, the lecithin diffusion can be easily measured until phase separation occurs. It should be remarked that such a behavior is strongly related to the macroscopic viscosity of the solution (as judged by visual inspection), which increases with W_0 up to a maximum around
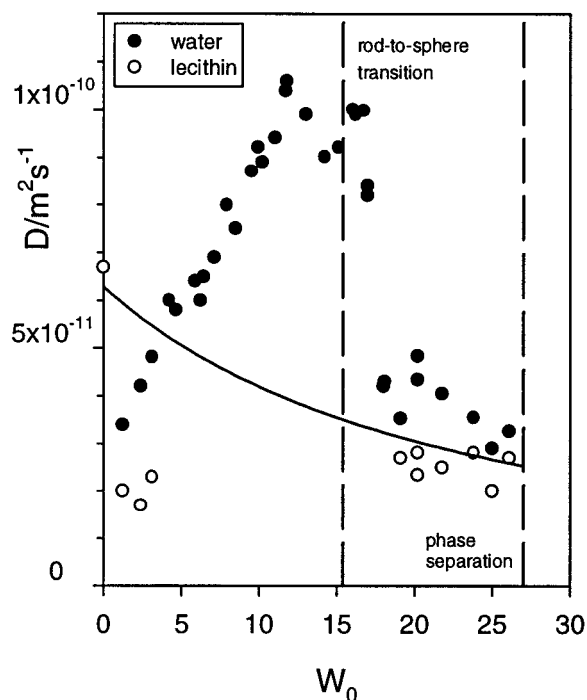
Figure 2. Water and lecithin self-diffusion coefficients of organogels as function of W_0 (water dilution of a PC/C_6D_{12} 0.197 mol kg^{-1} solution). The water diffusion was corrected taking into account the water solubility in cyclohexane (eq 1). The self-diffusion coefficient values expected for spherical reverse micelles at the same composition (according to eqs 2−4) are shown as continuous line. Also shown (as a broken line) are the position of the rod-to-sphere transition and the phase separation inferred from the geometrical model (see text for details). The experimental phase boundary corresponds to the point at the highest W_0 ($W_0 = 26$).

$W_0 = 10$ (where the sample is gel-like) and drops for $W_0 > 15$ to give a liquidlike solutions near the phase separation.

Figure 4C shows a typical dielectric spectrum of lecithin organogel. Two dispersions are clearly visible as reported for the isooctane-based system.[22] The characteristic relaxation time and the dielectric increment for both the high- and low-frequency dispersions (τ_1, $\Delta\epsilon_1$ and τ_2, $\Delta\epsilon_2$, respectively) can be easily extracted from the spectra. The low-frequency dispersion is related to the rotational diffusion of the micelles as a whole.[22] The characteristic relaxation time, τ_1, for this dispersion depends on W_0 with a bell-shaped trend (see Figure 4A) in analogy with other dynamical parameters. The increment of this dispersion ($\Delta\epsilon_1$) also exhibits a maximum in its dependence on W_0 at $W_0 = 10$ (Figure 4B). The distribution of relaxation times is rather broad ($\beta \approx 0.5$), which is a reflection of the high micellar polydispersity. The high-frequency dispersion was attributed to the lecithin headgroup rotation[22,23] in analogy with the conclusion from a systematic study of its dependence on the headgroup size in aqueous solutions of synthetic lecithin.[24] Until $W_0 = 15$ the characteristic relaxation time, τ_2, depends exponentially on W_0 (Figure 5A). For larger W_0 values this relaxation time jumps to a higher value. The increment related to this dispersion ($\Delta\epsilon_2$) increases with W_0 (Figure 5B), in contrast with the isooctane-based system where it is constant.[22] At $W_0 = 0$ the $\Delta\epsilon_2$ increment is almost zero and increases with W_0 up to $W_0 = 16$. For further water addition, a sharp decrease is observed. The distribution of relaxation times is always rather narrow, $\beta \approx 0.8-0.9$, except for the W_0 range from 10 to 16, where it is about 0.5. It is remarkable that the distribution is very sharp at high water content ($W_0 = 20$) where it cannot be distinguished from one single relaxation time ($\beta \approx 1$). Since
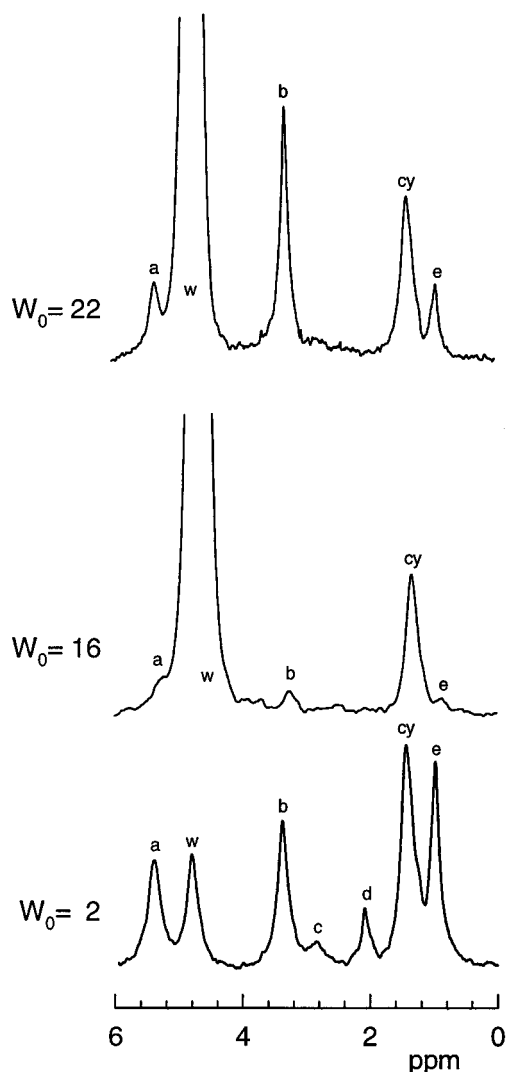
Figure 3. Organogel ^{1}H NMR pulsed gradient spin-echo spectra at three different W_0 (lecithin concentration = 0.197 mol kg^{-1}). Conditions: Δ = 100 ms, δ = 2 ms, G = 0.04 T m^{-1}. Lecithin peaks assignments: a, $-CH=CH-$; b, $-N^+(CH_3)_3$; c, $-CH=CH-CH_2-CH=CH-$; d, $-CH_2CO-$; e, $-CH_3$. Other peaks: w, water; cy, cyclohexane.

samples at low PC concentration are more easily handled, a complete investigation on the dependence of the dielectric properties on W_0 was performed on gels at PC concentration of 0.064 mol kg^{-1}. However, experiments performed at W_0 = 4, 14, and 20 below and above the concentration used in the NMR experiments reveal the same features of system with [PC] = 0.064 mol kg^{-1}. In particular, the τ_2 values are concentration-independent, and τ_1 decreases with the PC amount, but always conserving the maximum on its W_0 dependence.[25]

V. Discussion

It is interesting to compare the water self-diffusion coefficient to the diffusion expected, at the same composition, in the case of a translational displacement of spherical reverse micelles. If both the water and the lecithin are moving with the aggregate, and the predominant diffusion process is the Brownian motion of the aggregate itself, their self-diffusion coefficient will be the same, coinciding with the reverse micelles diffusion. For an ensemble of particles of spherical shape at infinite dilution, the self-diffusion coefficient ($D°$) is related to the particle
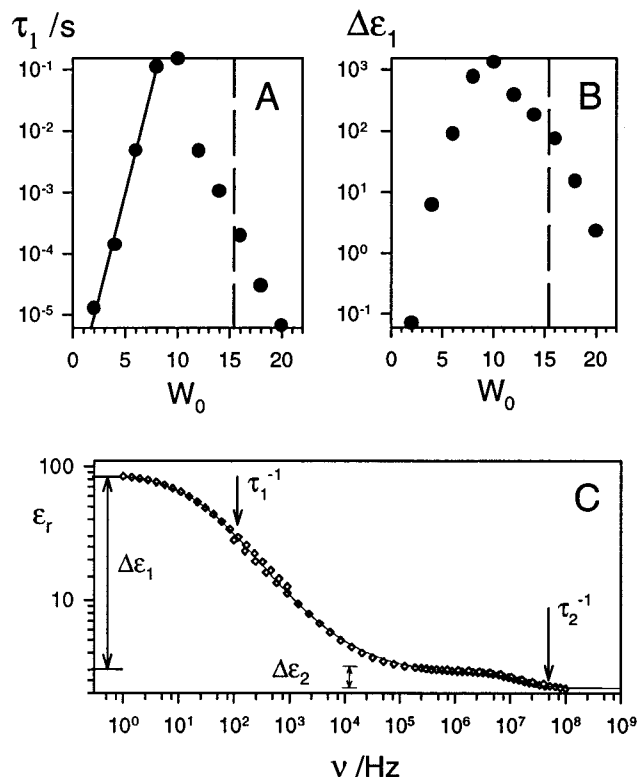
Figure 4. Dielectric spectroscopy for water dilution of a PC/C$_6$H$_{12}$ 0.064 mol kg^{-1} solution. The position of the rod-to-sphere transition inferred from the geometrical model is shown as a broken line (see text for details). Low-frequency dispersion: (A) The characteristic relaxation time, τ_1, as a function of W_0; the line shown is an exponential fit in the W_0 range from 4 to 9. (B) The dielectric increment, $\Delta\epsilon_1$, as a function of W_0. (C) Typical dielectric spectrum of organogel (lecithin concentration of 0.064 mol/kg, W_0 = 6). The line denotes a Cole/Cole fit to the data with two groups of relaxation times.
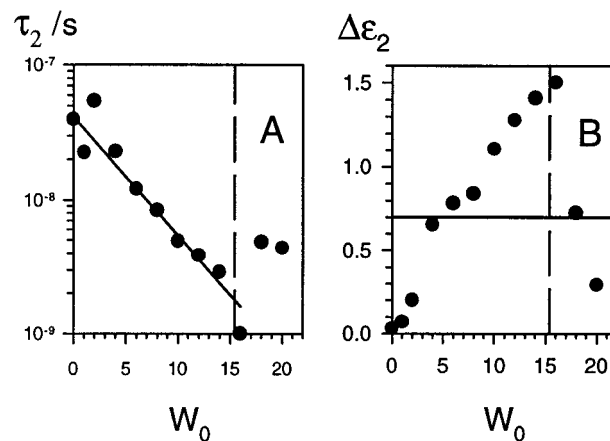
Figure 5. High-frequency dispersion in dielectric spectroscopy for water dilution of a PC/C$_6$H$_{12}$ 0.064 mol kg^{-1} solution. The position of the rod-to-sphere transition inferred from the geometrical model is shown as a broken line (see text for details). (A) The characteristic relaxation time, τ_2, as a function of W_0; the solid line is a guide to the eye. (B) The dielectric increment, $\Delta\epsilon_2$, as a function of W_0. The solid line shown is the average value of the increment found for the system PC/water/isooctane at the same lecithin concentration.[22]

hydrodynamic radius (r) via the Stokes−Einstein relation:

$$D° = KT/6\pi\eta r \qquad (2)$$

where K is the Boltzmann constant and η is the viscosity of the medium. If a monodisperse size distribution of the micellar aggregates formed by lecithin and water is assumed, it is simple

to demonstrate that their radius is related to the W_0 by the following relation:

$$r = l_c + (3/a_s)(v_w W_0 + v_h) \qquad (3)$$

where v_w is the water molecular volume (30 Å^3), v_h is the lecithin headgroup volume (204 Å^3, for the phosphorylcholine[26]), l_c is the PC hydrophobic tail length (22 Å, from SANS measurements[27]), and a_s is the PC polar head area (70 Å^2, a value found in lamellar phases at high water content[26] and consistent with SANS data in organogel at $W_0 = 14$[27]). Thus, using eqs 2 and 3, it is possible to calculate the self-diffusion coefficient at infinite dilution. Actually, the D_w at low and high W_0 are close to those predicted for spherical reverse micelles at infinite dilution. A more appropriate comparison requires a correction for the noninfinite dilution of the droplet's ensemble. Such a correction can be done using the first term in the virial expansion:[28]

$$D = D°(1 - k\phi) \qquad (4)$$

where ϕ is the droplet volume fraction (in the present case is the sum of water and lecithin volume fractions) and k is a constant that depends on the interaction among the particles. Assuming hard-sphere interaction ($k = 2$),[29] the D_w was calculated as function of W_0 (solid line in Figure 2). For the sake of clarity in the following discussion the W_0 range has been roughly divided into three region: low ($0 \leq W_0 \leq 4$), intermediate ($5 \leq W_0 \leq 15$), and high water content (from $W_0 = 16$ to the phase boundary).

V.1. Low Water Content. The good agreement existing between the prediction of eq 4 and the experimental value of the lecithin self-diffusion coefficient at $W_0 = 0$ (Figure 2) suggests that almost all the PC molecules reside on the aggregates and that the values of l_c, v_h, and a_s together with the choice of the hard-spheres interactions are satisfactory. The very low value of the high-frequency dielectric increment $\Delta\epsilon_2$ in the absence of added water (Figure 5B) is a further indication of the presence of particles of spherical shape. In water-in-oil droplets[30] the interface is curved toward the water so that the lecithin headgroup rotation gets severely restricted. This could be the reason in toluene, where the system is composed of discrete reverse micelles,[31] this dispersion cannot be detected.[22]

Despite the agreement found for $W_0 = 0$, for low and intermediate water content the calculated diffusion of the aggregates is incompatible with the measured D_w (see Figure 2). Although the calculations were carried out for a spherical geometry only, this conclusion is valid also for giant wormlike aggregates,[32] as well as for other shapes. In fact, the expression for a spherical particle represents an overestimation of the true diffusion of an asymmetrical particle since the interactions between nonspherical aggregates should increase the excluded-volume effect when compared to spheres already at low concentration. Accordingly, the D_w and D_{LEC} values (both lower than the prediction) measured at low water content are consistent with the presence of relatively small prolate (cylindrical) reverse micelles. The increment related to the high-frequency dispersion ($\Delta\epsilon_2$, Figure 5B) shows a very different behavior upon the addition of water as compared to the isooctane system, where no W_0 dependence has been observed.[22] This latter is a situation that would be expected if the number of surfactant headgroups contributing to the dispersion were W_0-independent. The observation that this seems not to be true in cyclohexane could be explained by a coexistence of cylindrical and spherical aggregates, the latter, as discussed before, not contributing to

the dispersion. In this case the increase in the $\Delta\epsilon_2$ increment is due to a decrease in the relative abundance of the spherical micelles, with the evolution from spherical to wormlike aggregates upon increasing the W_0 from 0 to 16. From this point of view the steep increase below $W_0 = 4$ could be a reflection of a relatively sharp water-induced sphere-to-rod transition as suggested by LS data.[3,5]

V.2. Intermediate Water Content. This has been the region most investigated by means of scattering techniques. In the present study both the D_w and the parameters (τ_1, $\Delta\epsilon_1$) related to the low-frequency dielectric dispersion reveal an increase of their values with the water content up to a maximum. On the contrary, both τ_2 and $\Delta\epsilon_2$ show a monotonic trend when plotted against W_0.

Below $W_0 = 10$ the low-frequency dispersion exhibits an increase of both the τ_1 (Figure 4A) and the corresponding increment ($\Delta\epsilon_1$, Figure 4B) with the water content, which seems to be a reflection of the water-induced micellar growth. Such an increase in the τ_1 values appears to be exponential (Figure 4A, solid line), which could be taken as an indication of the aggregate size exponential growth with W_0 discussed in the theoretical section.[18] According to this exponential dependence and the power law relation between the dielectric rotational correlation time and the mole mass for polymers,[33] $\tau \propto M^{9/5}$, the relative decrease of the end-cap water/PC mole ratio, ζ (see section III), can be calculated as 1.1 water molecules *per* PC molecule. Above $W_0 = 10$ both the τ_1 and the increment $\Delta\epsilon_1$ start to decrease (Figure 4). This seems to be related to the decrease in both D_w (Figure 2) and viscosity.[5] In this region the high-frequency dielectric relaxation time (Figure 5A) decreases exponentially with W_0 as found in the low water content region. In the isooctane-based system, the decrease of τ_2 was attributed to different mechanisms for the release of headgroups, namely, the swelling of the cylindrical part of the micelles (at low W_0) and the increase in the number of branch points[22] (predominant at higher W_0). For the cyclohexane system this would mean that only one of these mechanism is prevalent for the low and intermediate water content. The observation that in cyclohexane the relaxation times are shorter in comparison to the isooctane-based system relaxation times ($10^{-6}-10^{-8}$ s) seems to suggest that the mechanism for the release of the headgroups in cyclohexane is the increase in the number of branch points.

Extensive scattering studies (LS, SANS, mainly performed at lower concentrations) indicate that in this W_0 region the system is composed of flexible giant cylindrical reverse micelles, whose weight averaged contour length, L, increases with the water content.[3,15] The water inside such cylindrical reverse aggregates is characterized by a large local mobility[34] and consequently should be free-flowing inside the rodlike reverse micelles. The relatively high values of D_w found at the maximum of the bell-shaped curves suggest the presence of an extended path for the water molecules displacement. These features strongly suggest that the observed water diffusion is mainly due to the motion of water inside the aggregates. More accurate and repeated measurements (unlike the preliminary ones[9]) performed at different Δ's have not evidenced any time scale dependence of D_w. This point allows us to rule out any diffusional processes due to the motion along aggregate of infinite lifetime for which D_w should scale as Δ^{-1} or $\Delta^{-1/2}$ for restricted and unrestricted diffusion, respectively.[9] A direct proportionality between D_w and the expected (weight) averaged contour length, L, in the W_0 range 4−12 has been previously found by our group.[9] This behavior, as well as the time scale

independence of D_w, can be accounted for by different structural models of the network. The first one foretells a branched network in which the density of cross-linking point is proportional to L, while a second views an entangled network of disconnected tubular micelles[35] that undergo reaction of end interchange.[36] A third explanation invokes the exchange of water molecules between different polymer-like micelles (most likely in the correspondence of entanglement points). It was proved that in concentrated w/o emulsions this latter mechanism gives raise to a Gaussian diffusion[37] (which remains time independent as long as the water lifetime inside the aggregate is shorter than Δ).[38] It should be noticed that, at low PC concentrations (water dilution of a 0.064 mol kg^{-1} lecithin solution), the water diffusion behavior is fully consistent with the presence of branches and/or with intermicellar water exchange.[39] The low value of the characteristic relaxation time for the high-frequency dispersion in dielectric spectroscopy is an indication for branching in this system. It has been postulated that τ_2 reflects the mobility of the surfactant headgroups.[22] Therefore, the presence of branch points, in which the interface is curved toward the water, should shift the relaxation times to lower values. The values obtained in this work are even lower than those obtained in the regime in which the isooctane system reveals the presence of branch points (Figure 5B). The infuence of the lecithin concentration on the water diffusion is the subject of a forthcoming paper,[21] while the present one is focused on the drop in water diffusion, viscosity, and the lecithin polar head mobility for $W_0 > 15$ and at high PC concentration. Thus, for the purposes of the present discussion, it is sufficient to say that the increase in the D_w values with W_0 in the intermediate water content is related to the presence of an extended network of wormlike micelles (it does not matter if branched or not).

V.3. High Water Content. In the investigated composition range, the aggregates are extremely long. It is therefore possible, at least in a first approximation, to neglect any contribution of the end caps to both the total interfacial surface and to the total (water *plus* headgroup) internal volume. The volume-to-surface ratio for the (infinite) cylinder is $r_c/2 = (W_0 v_w + v_h)/a_s$. In this way it is easy to evaluate the maximum water uptake compatible with a cylindrical geometry, $W_0(cyl)$, by the following relation:

$$W_0(cyl) = \left(\frac{a_s r_c}{2} - v_h\right)\frac{1}{v_w} \tag{5}$$

being the cross-sectional radius of the aqueous core, r_c, known from scattering measurements ($r_c \approx 19$ Å[27]). Therefore, it has been possible to calculate the maximum water uptake compatible with a cylindrical geometry, namely $W_0(cyl) = 15.4$. For water content greater than 15.4 water molecules *per* PC polar head, cylindrical reverse micelles cannot accommodate all the water molecules (as long as there is not any variation in the effective packing parameter of the lecithin), and a transition toward a shape with a greater volume/surface ratio is expected.

The water diffusion and the viscosity actually drop for $W_0 > 16$, the former assuming values expected for *quasi*-spherical aggregates (see Figure 2). Furthermore, for $W_0 > 17$ the D_w and D_{LEC} values become very close to each other, and above this threshold the ^{1}H NMR line width of the trimethylammonium moiety of the lecithin decreases significantly (see echo-NMR spectra of Figure 3). Since the line width is the most immediate criterion for molecular mobility, this latter evidence represents a hint of the decrease in the ^{1}H NMR T_2 of the lecithin polar head. This phenomenological interpretation is further supported

by the similar trend observed for the ^{31}P NMR signal of the phosphorylcholine group in cyclohexane organogels.[34] The results from dielectric spectroscopy too seem to confirm the ideas based on the NMR data. In the high water content region, the high-frequency dispersion clearly shows a peculiar behavior. The τ_2 jumps to a value higher than in the intermediate region, and the increment $\Delta\epsilon_2$ decreases sharply. This could be very well explained by the rod-to-sphere transition suggested by the diffusion data. The increase in the τ_2 could be due to a decrease in the number of branch points (or deswelling of cylindrical parts) in the coexisting network due to the adsorption of water in the relatively large droplets. Also, the LS data suggest that, despite the rod-to-sphere transition, the spherical reverse micelles must coexist with a network at $W_0 = 20$.[40] In fact, at a lower lecithin concentration, the LS results show an almost constant correlation length in this W_0 range.[5] A further indication of the coexistence of aggregates with different geometries and tumbling times can be inferred observing that at $W_0 = 16$ the ^{1}H NMR water signal is split[34] and that also the ^{31}P NMR lecithin spectrum presents a sharp resonance on the top of a broad one.[34]

The above-discussed data are indicative of a transition in the shape and size of the aggregates. The reverse micelles experience a water-induced monodimensional growth when the W_0 increases from 0 to 14, while they evolve from cylinders (rods) to spheres for $W_0 > 15-16$, the lecithin effective packing parameter, $(v/a_s l_c)_{eff}$, being unchanged. Consequently, it is possible to predict the maximum water uptake of the system (i.e., the phase boundary). The spherical geometry allows a higher volume/surface ratio, and for a spherical inverted system the maximum droplet radius permitted is fixed by the packing parameter.[41] It can be shown that this parameter is related to the mean and Gaussian curvature of the interface.[42] In the case of spherical and cylindrical geometries the following equalities were demonstrated[42] to hold: $(v/a_s l_c)_{eff} = 1 + l_c/r_s + (l_c/r_s)^2/3 = 1 + l_c/2r_c$, where r_s and r_c are the radius of the aqueous core referred to a sphere and to a cylinder, respectively. Accordingly, it is possible to write[42,43]

$$\frac{r_c}{r_s} = \frac{3r_s}{2(3r_s + l_c)} \tag{6}$$

Since both r_c and l_c are known from scattering experiments, it is possible to evaluate the effective packing parameter, $(v/a_s l_c)_{eff} = 1.58$, and the radius of the aqueous core of a spherical aggregate, $r_s = 44$ Å. Moreover, from the latter value it is possible to obtain an estimation of the maximum W_0 compatible with a spherical geometry before phase separation, by means of eq 3 and of the relation $r_s = r - l_c$, so obtaining $W_{0,max} \approx 27$, in fairly good agreement with the phase boundary experimentally found ($W_0 = 26$).

VI. Conclusion

The self-diffusion coefficients of both the water and the lecithin along a water dilution line of a lecithin/perdeuterated cyclohexane 0.197 mol kg^{-1} solution can be rationalized in terms of wormlike reverse micelles which increase their contour length upon increasing the W_0, up to $W_0 = 15-16$. For further water addition, the cylindrical micelles start to evolve toward spherical aggregates, and the dominating diffusion process becomes the aggregate motion. A drop in the D_w is indeed found, and the diffusion coefficients of both the water and the PC become very close, as shown in Figure 2. For $W_0 > 20$, the water and PC diffusion behavior is in agreement with the

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prediction for spherical monodispersed reverse micelles (taking into account the obstruction factor). The viscosity of the sample also drops together with the line width of both the $-N^+(CH_3)_3$ ^{1}H NMR (Figure 3) and of the phosphorylcholine ^{31}P NMR signals of the lecithin.[34] Thus, it may be suggested the presence of a rod-to-sphere transition. The dielectric data support this conclusion and suggest the presence at low W_0 (≈ 4) of another transition in the shape and dimension of the micelles. Thus, the overall effect of the addition of water to the system can be depicted as a sphere-to-rod transition at $W_0 \approx 4$ and a rod-to-sphere transition at $W_0 \approx 16$. It is interesting to outline that an analogous behavior was found in the case of the Co(AOT)$_2$/water/cyclohexane system.[44] The composition at which the rod-to-sphere transition occurs and the location of the phase boundary can be predicted by a geometrical model in which the effective packing parameter is equal to 1.58. The same packing parameter can be evaluated from SANS data at $W_0 = 14$ (in the presence of cylindrical geometry[27]) and in correspondence of the phase boundary (where spherical droplets are present[45]), thus confirming the validity of the proposed model. This evidence can be useful in order to reconcile scattering experiments performed at low (LS,[3,15] SANS[27] which are fully consistent with a wormlike model) and at high (SANS,[46] where the presence of spherical droplets is suggested) PC concentration.

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