

## Deuterium NMR Study of Slow Relaxation Dynamics in a Polymer-like Micelles System after Flow-Induced Orientation

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We present a first time-resolved deuterium NMR study on wormlike micelles under shear. For the investigation, a micellar system made of soybean phosphatidylcholine (lecithin), D<sub>2</sub>O, and cyclohexane was studied in the concentrated regime, in the vicinity of the isotropic/nematic transition but positioned in the equilibrium isotropic phase. The D<sub>2</sub>O dispersed in the micellar core was used as a probe to study the relaxation of a shearing-induced nematic phase back to the isotropic liquid state, after cessation of shear. The whole process was followed through time-resolved deuterium spectra and was characterized by a continuous decrease of the measured quadrupolar splitting, proportional to the nematic order parameter.

### Introduction

Of the many different forms of surfactant aggregates, wormlike micellar solutions have stimulated considerable theoretical and experimental interests during the last years because of their unique and fascinating rheology.<sup>1,2</sup> Wormlike micelles—whose main features can be described by the theoretical model developed by Cates and coworkers<sup>1</sup>—bear a structural similarity to polymers and are therefore often called “living” or “equilibrium” polymers to emphasize the fact that the aggregates are dynamic objects which can break and recombine. Moreover, they provide valuable systems to test different models of flow-induced liquid crystal ordering. While most investigations on wormlike micelles to date have been performed on direct aggregates we, here, consider *reverse* micellar (water-in-oil) systems. Reverse threadlike micelles form, e.g., when a small amount of water is added to organic solutions of the biological lipid phosphatidylcholine (soybean lecithin)<sup>3</sup> giving rise to highly viscoelastic liquids. The structure and dynamics of these *organogels* show substantial differences, depending on the chemical structure of the oil component producing, e.g., large and entangled micelles in cyclohexane,<sup>4</sup> or branched and connected in isooctane.<sup>5</sup> Furthermore, the differences in the rheology observed for lecithin organogels with cyclohexane and isooctane can be attributed to the different structure of the micellar network, as has been ascertained by NMR self-diffusion<sup>4,5</sup> and phase equilibria investigations.<sup>6,7</sup> In cyclohexane, the persistence length is roughly 700 nm, whereas the overall contour length is not precisely known, because of a broad length distribution, but is probably much longer than 2  $\mu\text{m}$ , with a cross-sectional radius of about 30 Å.<sup>8</sup> Another critical parameter

for the lecithin-based micellar solutions is the amount of water, quantified by the mole ratio of water and lecithin,  $W_0$ . By tuning of this parameter, it is possible to vary dynamical properties, such as viscosity<sup>3</sup> and self-diffusion coefficients,<sup>9</sup> markedly, indicating the strong variation of the microstructure of the micellar system. The special interest in this system is due to the great resemblance to polymer solutions, to the specific viscoelastic properties and their particular flow behavior. Indeed, viscoelastic, isotropic micellar solutions of the system lecithin/cyclohexane/water, like other systems of wormlike micelles, show a shear-induced transition to a state of nematic order, evident from small-angle neutron scattering (SANS) experiments.<sup>10</sup> It has been already shown in direct systems that the shearing of an isotropic (I) solution of wormlike micelles can induce a first-order phase transition toward a nematic (N) phase.<sup>11</sup> Under the influence of a mechanical flow, the micellar entanglements are subject to disruption and the chains align in the direction of flow, giving rise to the shear thinning effect observed also in our system. Early experimental evidence of the shear-induced I–N transition was due to SANS under shear for solutions of CPClO<sub>3</sub>–NaClO<sub>3</sub>,<sup>12</sup> CPCl–hexanol–brine,<sup>11</sup> and very recently for lecithin–water–cyclohexane as well,<sup>10</sup> but no studies have been reported on NMR investigations of a shear-induced phase transition, to our best knowledge. In a recent paper,<sup>10</sup> we demonstrated that the unusually slow relaxation of shear-aligned wormlike micelles back to the isotropic phase state could be followed using time-resolved SANS measurements. It was found also that the relaxation is characterized by a gradual decay of the orientational order, quantified in terms of the second rank order parameter  $P_2 = \langle 3 \cos^2 \theta - 1 \rangle / 2$ . Here,  $\theta$  is the local angle between the tangent of the micellar contour and the director of the phase. The slow time scale of the structural relaxation, of the order of tenths of minutes, is consistent with the view that micellar breaking and/or formation of branch points connecting two or more aggregates, are unusually rare events in this lecithin system.

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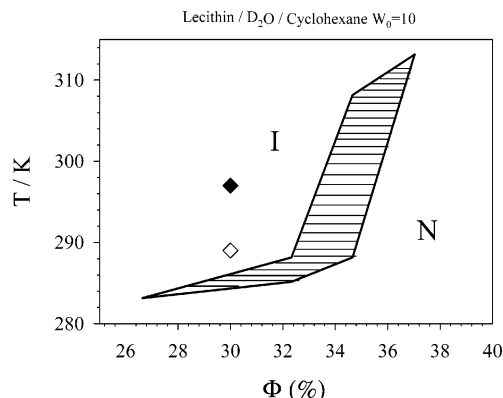
Although the relaxation may be expected to involve a stretched-to-coil transition of the micelles, with additional influence of micellar reptation, it is not clear by which mechanism the overall process occurs from the ordered state back to the equilibrium isotropic system. In our previous SANS study,<sup>10</sup> we concluded that the relaxation of the shear-induced nematic structure, after cessation of shear, was characterized by a continuous monotonic decay of  $P_2$ , in contrast to a nucleation and growth process. In the present Letter, we demonstrate that the shear alignment of wormlike micelles also can be investigated using  $^2\text{H}$  NMR spectroscopy in combination with a miniature shear cell. We revisit the problem of the shear-induced structure and its relaxation, where  $^2\text{H}$  NMR actually has the advantage, compared to, e.g., small angle scattering, in that it is more sensitive in detecting coexisting phases, in particular the coexistence of isotropic and anisotropic domains. In this way, the NMR experiment is more suitable to distinguish between a continuous relaxation and a process involving nucleation and growth.

This Letter is structured as follows: First, we describe features of the equilibrium phase diagram near the isotropic/nematic transition, and the experimental conditions. Then we present steady state NMR data at two different shear rates demonstrating that a sufficiently high shear rate has to be reached in order to obtain a homogeneously aligned sample. Finally, we investigate the relaxation of the sample after cessation of shear and draw conclusions regarding the relaxation mechanism.

### Sample and Experimental Section

The material was a concentrated organic solution of the biological amphiphile phosphatidylcholine (soybean lecithin Epikuron 200), which was a generous gift from Degussa Bioactives A.G., with a purity of 95% and average molecular weight of 772 Da. To convert the sample compositions in volume fraction units, the value of 1.0198 kg/L has been used for lecithin density.<sup>13</sup> The organic solvent cyclohexane, of purity >99%, was obtained from Fluka and deuterated water (99.9%  $^2\text{H}$ ) from Cambridge Isotope Laboratories Inc. Here, we have used the same composition investigated in our previous SANS study,<sup>10</sup> i.e., a water-to-lecithin molar ratio  $W_0 = 10$  and the volume fraction,  $\Phi$ , of micelles (sum of water and lecithin) is 30%. For  $W_0 = 10$ , the system forms at 298 K an isotropic phase (I), where the micelles are highly entangled in a transient network, up to approximately  $\Phi = 33\%$ , followed by a nematic phase (N) stable up to  $\Phi = 45\%$ .<sup>6</sup> The temperature dependence of the I/N phase boundary has been checked by varying  $\Phi$  at fixed  $W_0 = 10$  (Figure 1).

$^2\text{H}$  NMR measurements were performed on a Bruker MSL 300 spectrometer operating at a deuterium resonance frequency of 46.073 MHz. Recently, NMR spectroscopy coupled with shearing devices has merged as a potential tool to study the microscopic behavior of complex fluids subjected to shear.<sup>14</sup> For the present study, a special home-built NMR probe head with an integrated miniature shear-rate controlled Couette cell (concentric cylinders) was employed. The outer and inner diameters of the shear tool are 15 and 14 mm, respectively, and the amount of sample used for each experiment was about 0.4 mL. Shear has been applied by driving the outer cylinder with an external rotor located below the superconducting magnet. The vorticity direction was parallel to the external magnetic field. An O-ring placed in the uppermost part of the gap prevented solvent evaporation and experiments could be run for days without detectable loss of  $\text{D}_2\text{O}$  from the shear cell. All data were obtained applying a  $90_x - \tau - 90_y$  pulse sequence; typically, 16 transients were averaged before Fourier transfor-



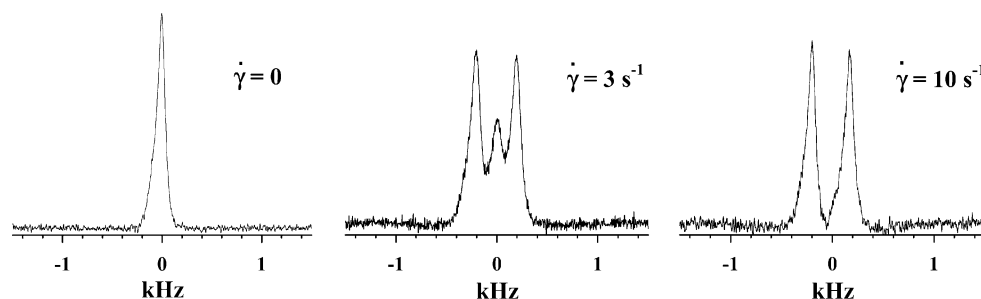
**Figure 1.** Region of the lecithin/ $\text{D}_2\text{O}$ /cyclohexane phase diagram, temperature  $T$  vs composition  $\Phi$ , with fixed water/lecithin molar ratio  $W_0 = 10$ , showing the structural sequence, reverse liquid-isotropic (I)/biphasic region (hatched area)/reverse nematic (N), related to the orientational micellar arrangement. Volume fractions  $\Phi$  (lecithin plus water) are given in percent. At the composition  $\Phi = 30\%$ , which refers to the present investigation, the system belongs to the isotropic phase (*at rest*) for both the reference temperatures, 297 (◆) and 289 K (◇), respectively.

mation. The  $90^\circ$  pulse length was  $15 \mu\text{s}$  and the pulse separation  $\tau$  was  $70 \mu\text{s}$ . The sample temperature was controlled by a Eurotherm temperature unit. For the basic concepts of  $^2\text{H}$  NMR in anisotropic fluids see, e.g., ref 15. The dominant interaction for a deuterium nucleus is the electric quadrupolar interaction, which splits the resonance line into a doublet. Also, the macroscopic ordering of a system may in principle be inferred from the distribution of splittings observed in the spectrum. The maximum component of electric field gradient is approximately along the O—D chemical bonds, with an interaction constant  $\nu_Q$  of the order of 250 kHz. The measured splitting is given by an expression of the form:  $\Delta\nu \propto \nu_Q P_2$ , where  $P_2$  is the nematic order parameter. The present NMR study was performed at 297 K, while the previous SANS study was performed at 289 K. For some reason, we were unable to obtain a stable flow of the sample in the NMR shear cell below 293 K. This may be a consequence of different shear histories in the two experiments, but the issue remains to be investigated in more detail.

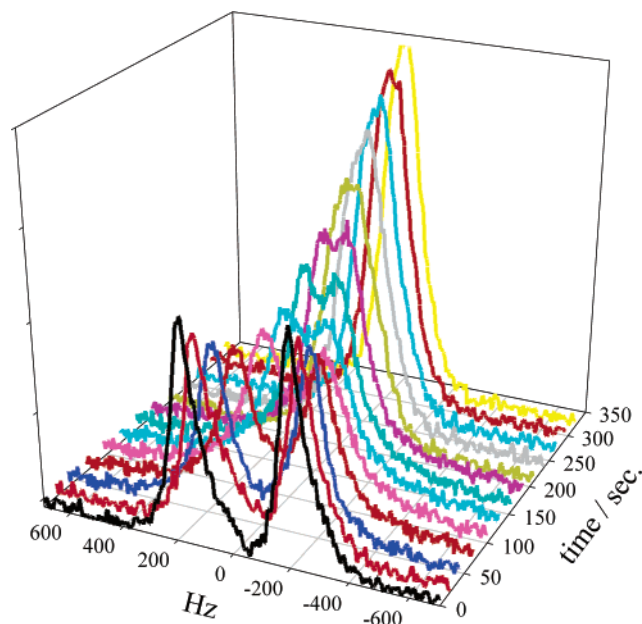
### Data Analysis and Discussion

To be able to measure the relaxation process of a shear-induced nematic sample back to isotropic state, the observation of a well-resolved doublet of deuterated water must be reached first. A large number of NMR experiments have been performed to assess the best operational conditions and reproducibility. The composition of the sample was fixed at  $\Phi = 30\%$ , belonging to the isotropic micellar phase in correspondence of the two reference temperatures, 289 and 297 K, respectively (see the phase diagram in Figure 1). A well resolved doublet was found stable and reproducible only in a narrow range of temperature, 296–298 K, characterized by a constant splitting of  $400 \pm 10$  Hz obtained for  $\dot{\gamma} = 10 \text{ s}^{-1}$ , whereas at intermediate  $\dot{\gamma}$  a coexistence I + N was observed (Figure 2).

After the optimum experimental conditions, i.e., flow and temperature, were fixed under which a homogeneous flow of shear-induced nematic sample is obtained in the form of well resolved and reproducible NMR doublet, a time-resolved experiment has been performed to measure the relaxation back to equilibrium (isotropic) state. In detail, we presheared the sample at steady shear rate  $\dot{\gamma} = 10 \text{ s}^{-1}$  and constant temperature of 297 K to orient the wormlike micelles in the direction of the flow; this was done by directly controlling the line shape of

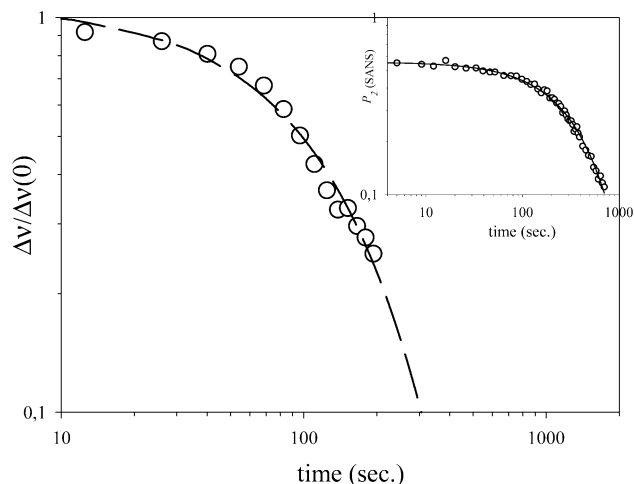


**Figure 2.** Left: typical isotropic NMR spectrum of deuterated water dispersed in the lecithin/D<sub>2</sub>O/cyclohexane sample at equilibrium ( $T = 297$  K). The micellar volume fraction (lecithin *plus* water) is  $\Phi = 30\%$  and  $W_0 = 10$ . The signal width at half-height is about 50 Hz. Middle: partially shear-induced nematic state obtained with applied shear rate in the Couette cell of  $\dot{\gamma} = 3 \text{ s}^{-1}$ . Right: fully aligned sample for  $\dot{\gamma} = 10 \text{ s}^{-1}$ , after the isotropic sample has been presheared at 297 K for about  $\gamma = 1 \times 10^4$  strain units in both the experiments, respectively. The observed deuterium splitting is independent of  $\dot{\gamma}$ , being  $\Delta\nu = 400 \pm 10$  Hz. The spectra have been averaged over 16 scans.



**Figure 3.** Time-resolved deuterium NMR spectra of water for the sample lecithin/D<sub>2</sub>O/cyclohexane with  $\Phi = 30\%$  and  $W_0 = 10$ , measured at 297 K after cessation of steady shear with  $\dot{\gamma} = 10 \text{ s}^{-1}$ . A continuous coalescence of the shear-induced doublet (first spectrum at  $t = 0$ ) is completed over almost 5 min.

deuterium signal of water in our sample until a stable and resolved doublet was reached. Then, the rotor was stopped after the solution had been sheared for more than  $1 \times 10^4$  strain units, and the subsequent relaxation was followed by saving several spectra developing after the cessation of the flow. Each spectrum was averaged over 16 scans and the time-window fixed at 14 s. The complete relaxation took almost 300 s, during which a continuous coalescence of the initial splitting ( $400 \pm 10$  Hz), obtained under flow, was recorded up to the final period of relaxation where the splitting narrowed toward the instrumental resolution (50 Hz). In Figure 3, the whole set of time-resolved spectra, taken after cessation of steady shear, is shown in a stacked plot. The whole experiment was repeated and the results were found to be reproducible. The continuous decrease of  $\Delta\nu$  vs  $t$  and the lack of any single peak coming out in the center of the doublet corroborate the fact that the nematic phase, induced by shear flow, “remelts” to the isotropic phase over time following shear cessation, thus confirming the absence of two-phase regime isotropic/nematic during the relaxation process. Furthermore, the time evolution of deuterium line shapes qualitatively supports the features observed in the analogous rheo-SANS investigation,<sup>10</sup> where a continuous increase of the angular width in the two-dimensional scattering pattern was



**Figure 4.** Log–log plot of the time dependence of measured  $\Delta\nu$  (open circles) after cessation of shear, normalized with  $\Delta\nu(0) = 400$  Hz related to the sample under flow. The dashed line is a nonlinear best fit to the single-exponential decay with  $\Delta\nu/\Delta\nu(0) = 1.06 \pm 0.05$  for the extrapolated value at  $t = 0$  and  $\tau_{\text{NMR}} = 130 \pm 10$  s for the time constant ( $r = 0.99$ ). In the inset we show, for comparison, the data reported in ref 10, regarding the decay of the order parameter  $P_2$  in the range 0.6–0.1, obtained from SANS measurements at 289 K on the same system. Here, a single-exponential fit (solid line) gives  $P_2(0) = 0.57 \pm 0.01$  and  $\tau_{\text{SANS}} = 415 \pm 5$  s ( $r = 0.99$ ).

observed. Finally, the decay of the ratio  $\Delta\nu/\Delta\nu(0)$  during the relaxation process is reported in Figure 4 as a function of time, where  $\Delta\nu(0)$  is the measured splitting for the sample under shear (400 Hz). In the inset, the exponential decay of  $P_2$  in the range 0.6–0.1 from the SANS study<sup>10</sup> has been shown as well. The comparison between the time constants,  $\tau_{\text{NMR}} = 130 \pm 10$  s and  $\tau_{\text{SANS}} = 415 \pm 5$  s, obtained from nonlinear exponential fits to the data <sup>2</sup>H NMR at 297 K and SANS at 289 K, respectively, would suggest an activated mechanism for this relaxation process, which may be driven by a diffusive and/or micellar breaking mechanisms. However, both diffusion (through reptation) and micellar scission, are affected by the average micellar length  $\bar{L}$ , which is function of temperature<sup>1</sup> through  $\bar{L} \propto \exp(E/k_B T)$ , where  $E$  is the scission energy of the chain and  $k_B$  the Boltzmann constant. Due to the different molecular weight distributions of the polymer-like micelles at 289 and 297 K, it is not trivial to draw a suitable temperature dependence of the kinetic of micellar reentanglement upon cessation of steady shear flow, and a more detailed study is needed. Accordingly, further investigations are required to settle NMR experiments in order to obtain stable flow at lower temperatures than 297 K, which in turn would allow us to better match the structural dynamic information coming from SANS and <sup>2</sup>H NMR techniques.

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