Magnetically Doped Hexagonal Lyotropic Phases

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Received: November 30, 1993; In Final Form: February 17, 1994 , 1994•

We describe in this paper the formation, structure, and magnetic properties of a new system which consists of a lyotropic hexagonal phase doped with colloidal magnetic particles. The initial nondoped lyotropic system is cyclohexane/SDS/water/pentanol, in which we replace the cyclohexane by a ferrofluid. The lattice parameter of these new phases is determined by small-angle X-ray scattering to be about 27 nm and thus significantly larger than that in the hexagonal phases of the nondoped system. The first magnetic experiments performed on the doped phase put into evidence an orientation effect of the whole structure and thus indicate a strong magnetic anisotropy, suggestive of intimate incorporation of the magnetic particles into the hexagonal lyotropic structure.

The first realizations of lyotropic phases doped with solid particles, or *amphicolloids*, have been recently reported.[1,2] In these systems, which are obtained from a lamellar phase and a colloidal suspension, the particles are confined in a bidimensional way between lyotropic membranes. When the colloidal suspension is a *ferrofluid*,[3,4] which contains magnetic particles, the doped lamellar phase, called the *ferrosmectic phase*, presents interesting properties due to its magnetic anisotropy.[5] We report here the first proofs of the existence of a doped lyotropic phase presenting a different structure: a hexagonal phase, where the particles are expected to be confined in a unidimensional way.

The nondoped phases are obtained with the quaternary system cyclohexane/sodium dodecyl sulfate (SDS)/water/pentanol described in refs 1 and 2. We dope the system by replacing the cyclohexane with a ferrofluid; this suspension in cyclohexane of magnetic particles,[4] whose typical diameter is 7 nm, is the nonpolar medium of the phases. We will first describe the hexagonal phase of the nondoped system, and then we will expose the elements of knowledge we have on its magnetically doped colleague. Finally, we will present the first magnetic experiments performed on this new magnetic fluid phase.

The Nondoped System

The phase diagram of the SDS/pentanol/water ternary system presents a hexagonal phase[6] in which the surfactant molecules form cylinders organized on a hexagonal lattice. We added cyclohexane (which we call *oil*) to the hexagonal phase obtained with a weight ratio of water to SDS equal to 2.5, thus moving the system towards the oil-rich region of the phase diagram water + SDS/pentanol/oil, and stayed in the same hexagonal phase region up to a volume fraction of oil equal to $\Phi_{cyclohexane} = 0.35$ (with $\Phi_{pentanol} = 9\%$), as displayed in Figure 1. We call this operation *swelling* the phase.

The hexagonal structure of the phase was first recognized by optical microscopy, in the same way as is explained later on, and confirmed by small-angle X-ray scattering[7] (Figure 2): three Bragg peaks, whose positions are in the ratio $1:\sqrt{3}:2$, indicate a hexagonal structure. The position q_0 of the first peak is related to the distance between the centers of adjacent tubes by $d_c = 2/\sqrt{3}2\pi/q_0$.[8] For the most swollen phase, we find $d_c = 14.8$ nm.

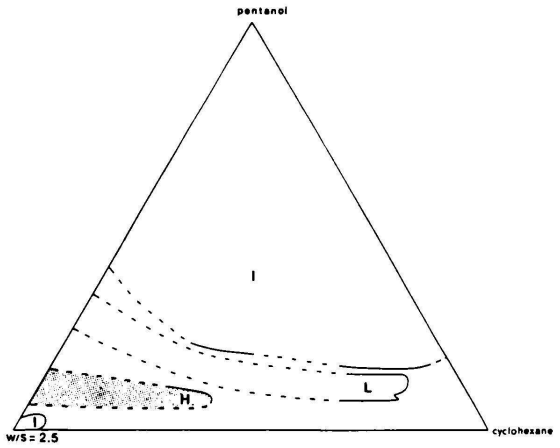

Figure 1. Phase diagram (volume percent) of the pseudoternary system SDS + water/pentanol/cyclohexane for a weight ratio water/SDS = 2.5. L = lamellar phase; I = isotropic (micellar or microemulsion); grey zone = hexagonal nondoped phase.

Let us recall that, in a general way, three geometries can be envisioned for the lyotropic hexagonal phases: direct (nonpolar tubes in a polar medium), inverse (the opposite disposition), and complex (a surfactant bilayer curves in pipes that separate an *inside* and an *outside*, either both polar or both nonpolar).[8] A detailed analysis of the X-ray spectrum of our phase, using a modeling of the form factor,[9] shows that it has a *direct* structure: the phase is composed of nonpolar tubes (oil and surfactants tails) in a polar medium (water and heads). By adding cyclohexane to the ternary direct hexagonal phase, we thus inflate the nonpolar tubes and increase the periodicity. The size of the tubes is deduced from the phase composition; for the previous phase, the external diameter is 12.1 nm, which corresponds to an internal diameter of about 9 nm, with a mean surfactant length of 1.5 nm.

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• Abstract published in *Advance ACS Abstracts*, April 1, 1994.

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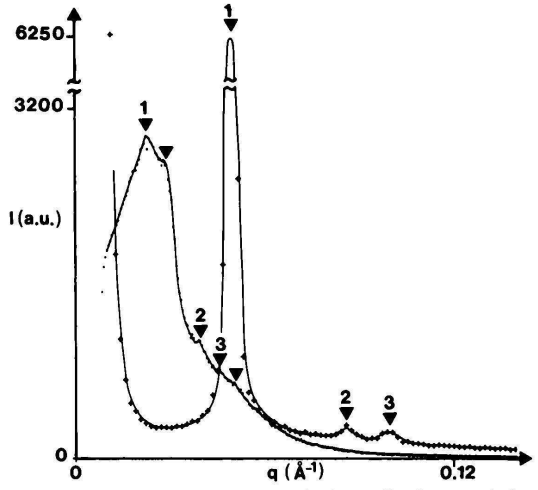

Figure 2. X-ray scattering spectrum (+) of a swollen hexagonal phase of the nondoped system (weight ratio water/SDS = 2.5, $\Phi_{cyclohexane}/\Phi_{water}$ = 0.85, $\Phi_{pentanol}$ = 9%). Positions of the peaks: q_0 = 0.49 nm^{-1}; q_1/q_0 = 1.76; q_2/q_0 = 2.04. Spectrum (●) of a hexagonal-isotropic biphase of global composition water/SDS = 2.5, $\Phi_{ferrofluid}/\Phi_{water}$ = 1.8, $\Phi_{pentanol}$ = 7%, φ = 5%. Positions of the hexagonal peaks: q_0 = 0.24 nm^{-1}; q_1/q_0 = 1.74; q_2/q_0 = 1.98. Two additional peaks, probably due to the presence of the isotropic phase, could not be interpreted. The base line is not flat due to small-angle scattering by the particles.

The Ferrosystem

For the doped phase, swelling of the ternary hexagonal phase with the ferrofluid cannot be done continuously since a stable doped phase needs to have a nonpolar medium spacious enough for the particles. In particular, when trying to obtain with a ferrofluid the phase equivalent to the undoped one described above, we observe a separation between an undoped phase and aggregates of particles expelled from it, presumably because the 9-nm diameter of the cylinder is too small.

In the phase diagram of the system ferrofluid/SDS/water/pentanol, however, we have shown in multiphasic mixtures the existence of birefrigent phases whose texture is characteristic of hexagonal phases, as explained below. Since the ferrofluid has a deep red color (because the magnetic particles are iron oxyde), we can confirm that the particles are incorporated inside the lyotropic structure from the color of the obtained phase. In fact, the strong color of these hexagonal phases tells us that they reach a particle volume fraction φ larger than 3%. By gas chromatography analysis of these samples, we have determined the composition of a biphasic mixture, in which a hexagonal phase and an isotropic phase coexist, both very viscous and having the same concentration in particles and the same density. Because of these similarities, it has been impossible up to now to separate the two phases mixed in macroscopic samples (they are, however, separately observable in thin samples such as capillaries). The global composition of this system is water/SDS = 2.5 (weight ratio), $\Phi_{ferrofluid}/\Phi_{water}$ = 1.8, $\Phi_{pentanol}$ = 7%, swollen with a ferrofluid of volume fraction in particles φ = 5%.

Figure 3b displays a picture of the hexagonal part of the biphasic isotropic-hexagonal sample, held in a glass capillary of rectangular section 1 × 0.1 mm and observed between crossed polarizers. The observed texture forms spontaneously between the plane glass boundaries and is commonly referred to as *fan-shaped*.[10] It corresponds to an orientation of the tubes parallel to the limiting glass plates, which can be explained in terms of an anchoring energy.[11] The orientation of the tubes, which locally defines the optical axis, is however two-fold degenerate in the plane, which results in domains of different orientations observed in the fan-shaped texture. This texture, characteristic of a two-fold degeneracy, is comparable to the one observed with smectics in a planar orientation, and we will consequently designate the corresponding orientation of the hexagonal phase as *planar*. We can, however, identify the hexagonal texture without ambiguity, as it displays typical striations (Figure 3a); such defects are due to a slight cooperative undulation of the lyotropic tubes, their average orientation being perpendicular to the striations.[12,13]

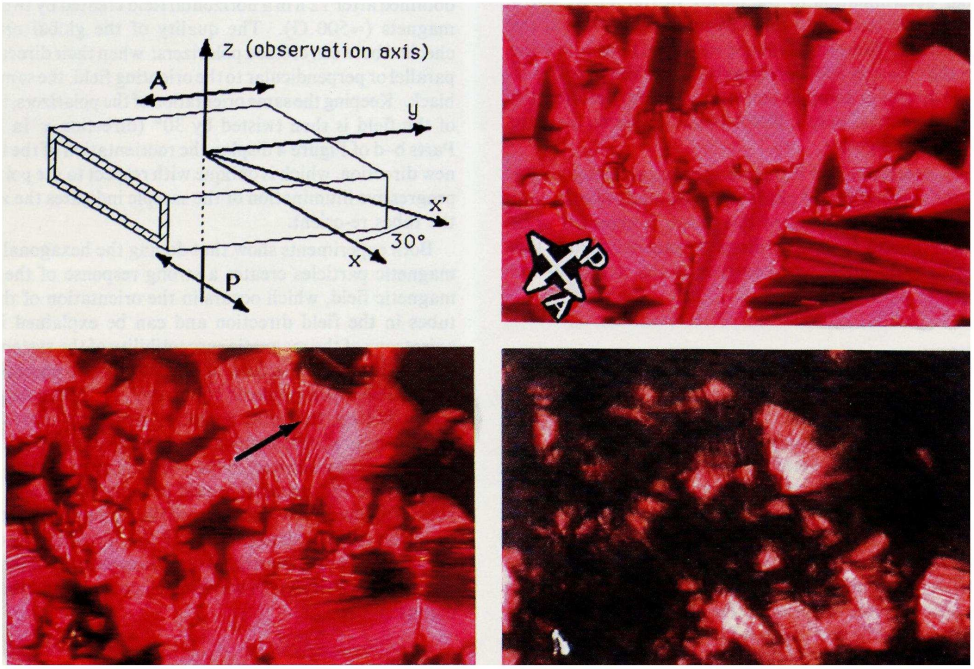

Figure 3. (a, upper left) Observation geometry: the magnetic field (~100 G) is applied at t = 0 in the z-direction, which is also the observation axis. (b, upper right) Optical microscopy picture of the hexagonal part of an isotropic-hexagonal biphasic sample without field. (c, bottom left) Same view as in part b, with the sample being subjected to the 100-G field along the z-direction for 40 s. (d, bottom right) Same view as in part c, t = 4 min.

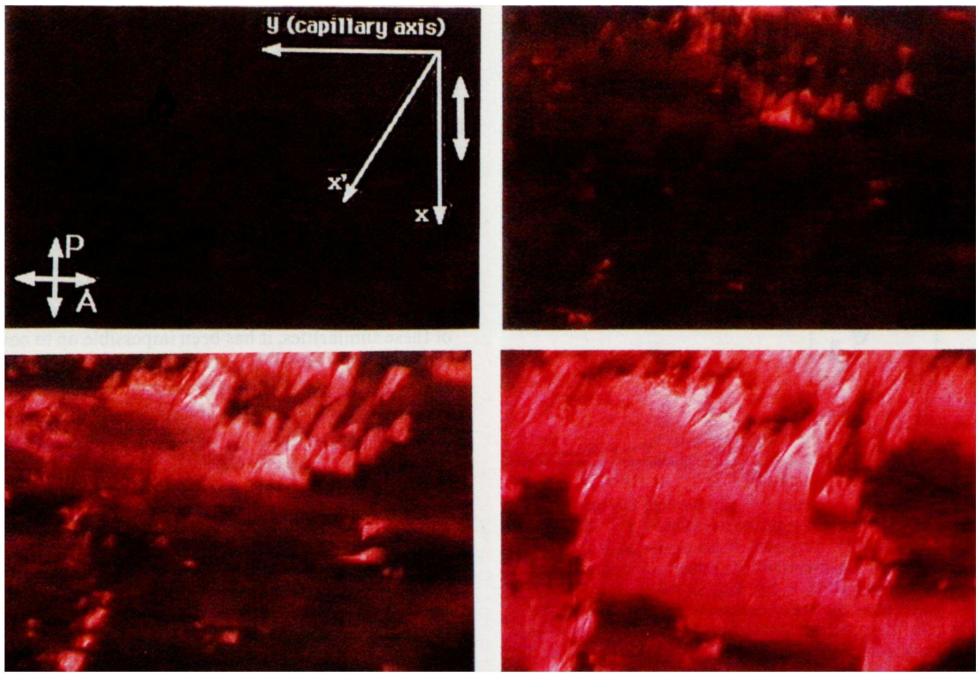

Figure 4. (a, upper left) Geometry described in Figure 3a. On this black picture obtained when the orientation is complete, we have represented the direction of the hexagonal tubes with a double arrow. The direction of the magnetic field is twisted at $t = 0$ from x to x'. (b, upper right) $t = 10$ s: the reorientation begins in the top part of the picture. (c, bottom left) $t = 4$ min. (d, bottom right) $t = 13$ min: reorientation is almost complete.

The X-ray scattering experiments (Figure 2) show that the tubes have their centers separated by $d_c = 30.2$ nm, which is larger than the distances observed in the nondoped phases. Detailed study of the shape factor of the X-ray scattering spectrum provides precious indications on the nature of the phase (direct, inverse, or complex). This method is not selective enough for an unambiguous determination of the nature of the phase, but it does indicate, in the case of all three hypotheses, the size of the lyotropic elements. Simple geometric considerations allow the observation that there is apparently no room for the particles to insert into the inverse or complex structures without deformation of the lyotropic matrix; only a direct structure seems likely to welcome 7-nm-sized guests.

We plan to determine the diffusion coefficient tensor of the particles in the isolated doped phase by using quasi-elastic light scattering.[14] As the anisotropy of this tensor is expected to be much stronger in the case of a direct hexagonal phase, this measurement should allow us to determine the nature of the hexagonal phase definitively.

Field Effects

We have observed the behavior of this new hexagonal phase in the presence of a magnetic field using polarized optical microscopy. Figure 3a displays the geometry of the first experiment: a magnetic field created by a wire bobbin (≈100 G) along the z-direction (see Figure 3) is applied on a planar sample in which the lyotropic tubes are oriented in the x–y plane. The texture of this initial state is presented in Figure 3b. When the field is applied, we observe that the illuminated zones between crossed polarizers become progressively darker (Figure 3c,d) and completely black after a few hours. This implies the obtention of a *homeotropic* orientation of the tubes, where the optical axis is perpendicular to the main glass walls; i.e., the tubes are parallel to the observation axis. As shown in Figure 3c, fine striations (arrow) appear when the field is applied and stress previously existing defects. This is likely to indicate the creation of disinclination walls[12,15] which allow a modification of the orientation of the tubes in order to align with the field direction.

Figure 4 presents another reorientation experiment, in a different geometry: the initial state is planar, as in the experiment of Figure 3, but the whole studied zone of the sample is a single-orientation domain (in the direction x shown in the Figure 3a), obtained after 12 h in a horizontal field created by two permanent magnets (≈500 G). The quality of the global orientation is checked between crossed polarizers: when their direction is either parallel or perpendicular to the orienting field, the sample appears black. Keeping the same orientation of the polarizers, the direction of the field is then twisted by 30° (direction x' in Figure 4a). Parts b–d of Figure 4 display the reorientation of the tubes in this new direction, which is oblique with respect to the polarizers: the progressive illumination of the sample indicates the zones where the tubes re-orient.

Both experiments show that doping the hexagonal phase with magnetic particles creates a strong response of the phase to a magnetic field, which occurs in the orientation of the lyotropic tubes in the field direction and can be explained in terms of anisotropy of the magnetic susceptibility of the system.[16] Notice that whatever the nature of the hexagonal phase, it must be compatible with a magnetic anisotropy. A direct hexagonal phase, which is here the most probable structure, corresponds to a unidimensional confinement of the magnetic particles inside the nonpolar tubes, whereas in the eventuality of inverse or complex geometries, the material would present anisotropic amagnetic holes (full- or hollow-tube shaped) in a magnetic matrix. In any case, the superparamagnetism of the ferrofluid has gained an anisotropic nature from the lyotropic structure, which shows that a strong solidarity exists between the particles and the surfactant matrix.

Conclusion

We have demonstrated the existence of a hexagonal lyotropic phase doped with solid particles, whose periodicity is much higher

than that of known undoped phases.[17] We have inferred that a direct structure is the most probable, which leads to a unidimensional confinement of the particles. The first experiments performed on biphasic mixtures containing this new phase show that magnetic particles confer to it anisotropic magnetic properties so that it completely aligns in a few hours when subjected to a weak magnetic field. These magnetic properties give, in particular, new opportunities to study the yet largely unknown elastic properties of lyotropic hexagonal phases.

Acknowledgment. We thank Madeleine Veyssié and Pascale Fabre for numerous discussions, Marie-Alice Guedeau-Boudeville and Célia Casagrande for their precious help in chromatographic analysis, and Raymond Ober for cooperation in the X-ray experiments.

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