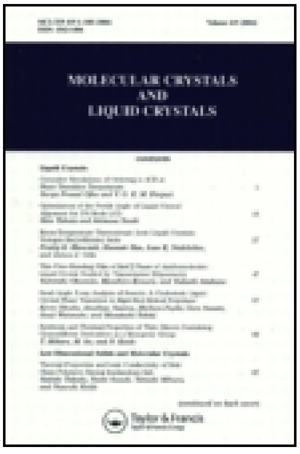

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A Smectic-A Type Lamellar Amphiphilic Lyotropic Liquid Crystal Phase

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A SMECTIC-A TYPE LAMELLAR AMPHIPHILIC LYOTROPIC LIQUID CRYSTAL PHASE

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ABSTRACT
Preliminary polar micrographic studies suggest in the binary cesium perfluoro-octanoate/heavy water system more than one smectic type phase exists in the lamellar region. The lamellar phase on the low water side of the nematic was examined and from the micrographic textures it is suggested the structure of the phase is related to the classical thermotropic smectic-A S_A mesophase.

Recently evidence has been put forward which suggests that when there is a transition in a amphiphilic lyotropic liquid crystal system from a hexagonal phase to a nematic phase, there is an intermediate phase, which has a smectic-A type structure corresponding to layers of orientational ordered cylindrical micelles[1]. It would seem possible the same situation might arise with a lamellar phase. A good model system is available for investigation, i.e., the binary cesium perfluoro-octanoate CsPFO/ D_2O system. A reliable phase diagram has been published[2]. In this system the lamellar phase region is large and undergoes two types of transitions to the isotropic micelle phase. The first type is a first order transition indirectly via a nematic phase or directly to the isotropic phase, while the second type is a second order transition via the nematic phase to the isotropic micelle solution. The two types of transitions are separated by a tricritical point which has been theoretically predicted[3,4].

CsPFO was prepared by dissolving perfluoro-octanoic acid (PFO) in methanol and adding a slight excess of Cs_2CO_3. The solution was filtered and evaporated to dryness. The crude detergent was then recrystallized from a ethanol/n-butanol mixture four times and dried under vacuum. Samples were prepared by weighing out CsPFO and D_2O into a test tube with a constriction in the middle. The test tube was then heat sealed. The mixture was homogeneously mixed by repeated heating and centrifuging.

Polar micrographic studies were made using a polarizing microscope set up with a heating stage and an electromagnet in a way similar to previously described[5]. Retardation studies were not possible with lamellar phases because these phases have a tendency to align perpendicular to the surface of the glass slide. This sort of study requires planar aligned samples as would be obtained from middle soaps[1].

X-ray studies[6], nmr studies and electrical conductivity[7] made on the 45% CsPFO sample do not give a clear indication of a smectic-smectic phase transition in the large lamellar region of the phase diagram. The results do confirm the nature of the nematic-lamellar transition which has characteristics of nematic-smectic-A transition[4]. When the samples of the CsPFO/D_2O mixtures were examined after mixing, it was observed the viscosity of the mixtures increased with decreasing temperature and water content which is indicative of a corresponding increase in order.

Figure I and II are polar micrographs of concentration gradients set up between CsPFO and D_2O. Figure I, where the concentration gradient has been set up by evaporating D_2O from a 80% CsPFO isotropic solution held between a microscope slide and a cover slip, shows four main areas. The black area is presumably an isotropic micelle solution. The area furthest away from the black area has an oily-streak texture which is a classical lamellar texture[8]. Next to the dark area is a texture typical of a nematic phase which shows a response to a magnetic field (positive diamagnetic nematic). Between the oily streaks and the nematic region is a region with some nematic characteristics but the phase shows a lack of response to a magnetic field. This is consistent with a dimensionally ordered smectic-A type liquid crystal. Figure II shows a polar micrograph where the concentration gradient was set up by running D_2O against a 30% CsPFO lamellar sample held between a microscope slide and a coverslip. There is clearly two distinct oily streak regions where the oily streaks have different dimensions derived from two different smectic phases. The water-rich phase which, on close inspection, is seen to be next to a nematic phase could be a smectic-A type. The two smectic phases and nematic phase in the above micrographs eventually give rise to pseudo-isotropic textures. When these pseudo-isotropic textures were observed under the polarizing microscope through a Bertram lense and a full wave plate, all three phases gave rise to interference figures which indicated positive birefringent mesophases. This is consistent with a nematic phase which has a structure of disk-shaped micelles and a lamellar phase with a bilayer structure.

Preliminary polar micrographic evidence shows that in the large lamellar region of the binary CsPFO/D_2O phase diagram there are at least two smectic type phases. One of these undergoes a second order transition to a nematic phase. This phase, it is suggested, has a structure corresponding to layers of orientational ordered disk-shaped micelles similar to the thermotropic classical smectic-A S_A mesophase. There are probably many other types of smectic phases in this binary detergent system including the tilted S_c phase.

In amphiphilic lyotropic liquid crystal systems there seems to be good evidence to suggest that the lamellar phase as well as the hexagonal phase are dimensionally ordered arrays of micelles. When there is a transition to a nematic phase it would seem it takes place via a less ordered phase. It seems reasonable to suggest that these less ordered phases have structures which are layers of orientation ordered micelles similar to the thermotropic classical smectic-A S_A mesophase.

LAMELLAR bilayers	→	Fluid Lamellar	↘	Disks
				NEMATIC
HEXAGONAL Arrays of infinitely long cylinders	→	Fluid Middle Soap S_A	↗	Clylinder
Symmetry Ordered Layers		Orientational Ordered Layers		Orientational order only.

If a smectic-A type phase can be found in the lamellar and middle soap regions of amphiphilic/D_2O phase diagrams, it would seem reasonable that similar ordered phases should be found in the cubic and reverse liquid crystal regions. The latter seems especially attractive in view of the recent discovery of a reverse micelle nematic fluid in an oil continuous system[9]. This is an area of the amphiphilic lyotropic liquid crystal research field which certainly warrants a more intensive investigation.

Figure 1. Photomicrograph of a concentration gradient has been set up by evaporating D_2O from a 80% CsPFO isotropic solution. Temperature 20°C. The dark area on the right has the highest D_2O concentration.

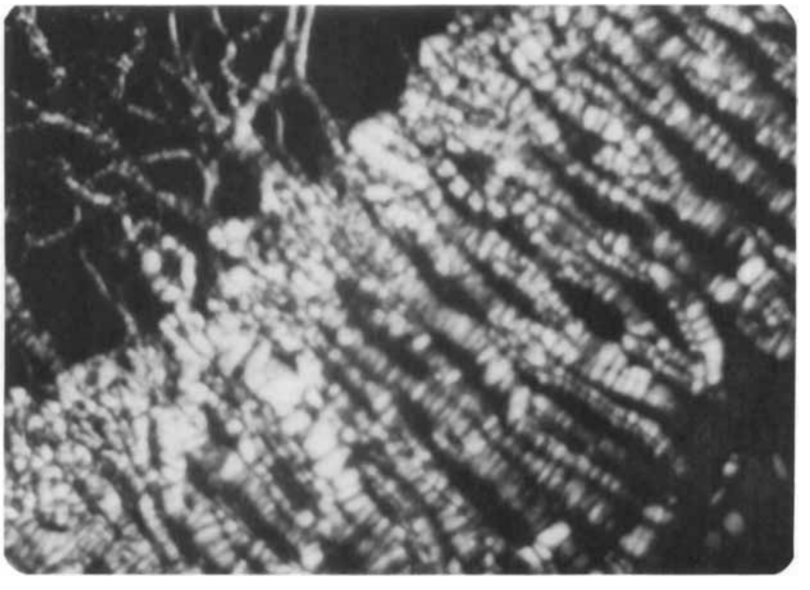

Figure II. A photomicrograph of a concentration gradient set up by running D_2O against a 30% CsPFO lamellar sample. Temperature 20°C. The right lower corner has the highest D_2O concentration.

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