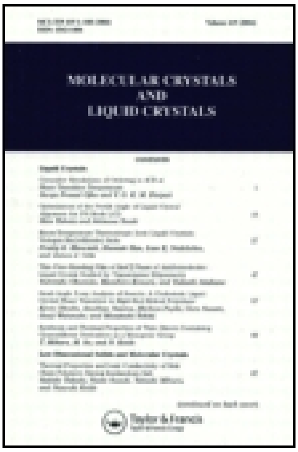

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

A Study of the Lyotropic Liquid Crystal Phases of Caesium Pentadecafluorooctanoate(CsPFO)/Poly (Ethylene Oxide) (PEO)/Water System

Andrew M. Smith [a] & Michael C. Holmes [a]

[a] Department of Physics & Astronomy, University of Central Lancashire, Preston, Lancashire, UK, PR1 2HE

Version of record first published: 23 Sep 2006.

To cite this article: Andrew M. Smith & Michael C. Holmes (1995): A Study of the Lyotropic Liquid Crystal Phases of Caesium Pentadecafluorooctanoate(CsPFO)/Poly (Ethylene Oxide) (PEO)/Water System, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 260:1, 605-609

To link to this article: http://dx.doi.org/10.1080/10587259508038733

Mol. Cryst. Liq. Cryst. 1995, Vol. 260, pp. 605–609
Reprints available directly from the publisher
Photocopying permitted by license only

A STUDY OF THE LYOTROPIC LIQUID CRYSTAL PHASES OF CAESIUM PENTADECAFLUOROOCTANOATE (CsPFO) / POLY (ETHYLENE OXIDE) (PEO) / WATER SYSTEM.

ANDREW M. SMITH & MICHAEL C. HOLMES
Department of Physics & Astronomy, University of Central Lancashire, Preston, Lancashire, UK PR1 2HE

Abstract The binary lyotropic liquid crystal system CsPFO / water is one which has been extensively studied in recent years [1] since the system contains a nematic phase, (N_D), over an unprecedented range of temperature and concentration of exceptional stability. This phase is bordered at higher temperatures by an isotropic micellar phase, (L_1), and at lower temperatures by a defected lamellar phase (L_α^H).

A non-ionic hydrophilic polymer, poly(ethylene oxide) (PEO), has been added to the system replacing some water molecules. Optical microscopy agrees with previously reported results [2] showing that at 0.9% PEO the lamellar phase is replaced by a phase with a nematic-type texture, (N*). This system is unusual in polymer-surfactant systems in that the polymer addition causes a phase change from a lamellar phase to a magnetically orientatable phase. We have used small angle neutron scattering (SANS), optical microscopy and ^2H NMR to investigate both the L_α^H and N* phases in order to understand the structural changes that are taking place.

INTRODUCTION

The addition of polymer to surfactant/water systems has received considerable attention for two important reasons. Firstly these systems are explored with the aim of producing artificial particles of comparable complexity to those found in biological systems [3]. Secondly, the solubilization power as well as the viscosity of an aqueous solution of polymer bound micelles is higher than those of the separate polymer and surfactant solutions [4] and has potential industrial applications. In this paper we present some initial measurements on the addition of a non-ionic hydrophilic polymer PEO to the caesium perfluorooctanoate (CsPFO) / ^2H_2O system. It exhibits a nematic phase bordered to higher temperature by an isotropic micellar phase and to lower temperature by a defected lamellar phase. In a recent study, Kuzma et al. [2] presented optical microscopy and DSC evidence showing that when 0.9% by weight of water is replaced by PEO the lamellar phase is replaced by a nematic phase, N* which is also reentrant at lower temperatures. This effect was explained by a model, suggested by Nagarajan [5], in which the polymer disrupts the lamellar order. However, the results also indicated a substantial degree of positional order might be still present in the nematic phase. The aim of this work is to delineate the structure of this nematic phase.

RESULTS

Optical microscopy, small angle scattering and deuterium NMR results are presented for the CsPFO/PEO/^2H_2O system in which the water is progressively replaced by PEO with a molecular weight of 3 x 10^5. The weight ratio of surfactant to (^2H_2O + PEO) was held constant at 1:1.

The phase diagram, determined by optical microscopy, for the ternary system is shown in figure 1 and is in qualitative agreement with that presented by Kuzma et al. The nematic phase, N* is identified optically as a *softening* of the lamellar texture. The isotropic-nematic transition temperature is almost independent of polymer concentration and molecular weight.

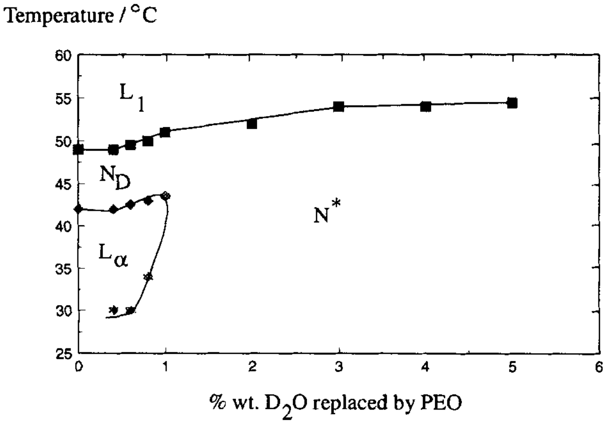

FIGURE 1 Phase diagram of the CsPFO/PEO/^2H_2O system. L_1, isotropic micellar; L_α, lamellar; N_D, nematic of disk micelles and N^*, polymer induced nematic.

The ^2H NMR splitting of solvent ^2H_2O in the nematic phase of a disordered 0.8% PEO sample showed alignment by a magnetic field within 8 minutes in a magnetic field of 5.3T, even in the reentrant part of the phase diagram. This behaviour is characteristic of that associated with a lyotropic nematic phase and contrasts to that in the lamellar phase where the sample remained unaligned by the field after several hours. The ^2H NMR splitting measured as a function of temperature through nematic, lamellar and reentrant nematic regions shows very little change in the behaviour of the splitting with temperature at the latter phase boundary, implying that there is little change in local order.

A typical series of SANS spectra, at a fixed temperature of 35°C and varying PEO content, are shown in figure 2. They are characterised by two scattering peaks; a sharp peak at larger Q corresponding to the bilayer spacing, $d_{\|}$ parallel to the lamella normal and a broader reflection at smaller Q corresponding to the distance, $d_{\perp}$ between defects within the lamella plane. Each experimental scattering curve has been fitted by two gaussian line shape functions. The position of $Q_{\|}$ is independent of polymer concentration whilst $Q_{\perp}$ increases with PEO so that the two scattering peaks move together. The areas from under the two line shape functions are independent of PEO concentration indicating that the number of scattering centres contributing to each remains constant.

As a function of temperature, there is a rapid decrease in the line width of $Q_{\|}$ as the upper nematic phase is crossed with decreasing temperature. This marks a rapid increase in positional order which is complete by the time the lamellar phase is entered [6]. Both lamellar and N* phases show sharp Bragg reflections characteristic of a high degree of positional order. The transition from lamellar to re-entrant nematic, seen by decreasing the temperature, is only marked by a short interval of 2^oC over which $d_{\|}$ remains constant before resuming its steady increase with decreasing temperature seen in the binary system. Both $Q_{\|}$ and $Q_{\perp}$ remain present to low temperature whether in the lamellar phase of the binary system or in the N* phase of the ternary system. Qualitatively the scattering curves are similar for both phases.

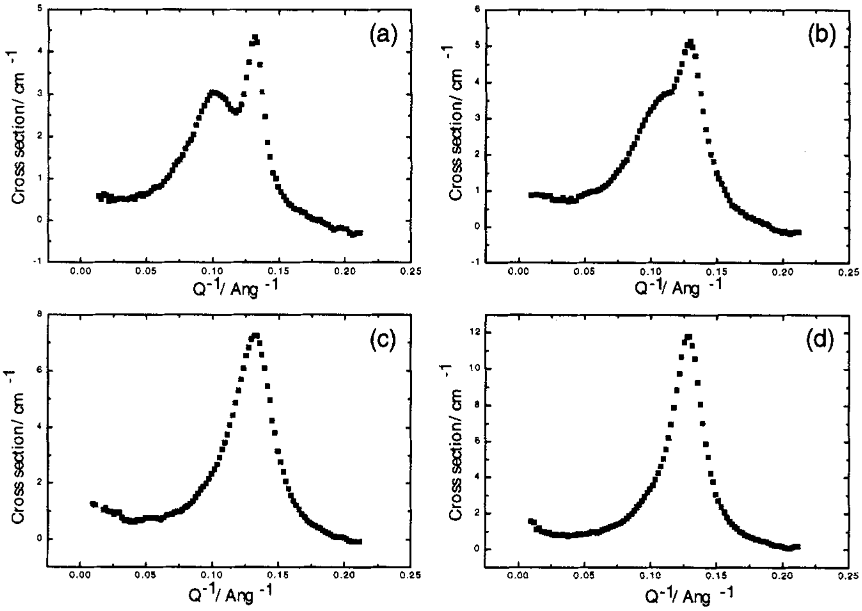

FIGURE 2 SANS scattering patterns recorded as a function of PEO concentration at a fixed temperature of 35°C ; (a) 0% PEO, (b) 0.9% PEO, (c) 2.0% PEO and (d) 5.0% PEO.

CONCLUSION

These results provide conflicting evidence for the structure of the nematic phase, N*. Polarising optical microscope textures and the response of the phase to a magnetic field suggest that it is a lyotropic nematic phase and might suggest that the polymer is causing the lamellar bilayers to break up into the disk shaped micelles which have been associated with this type of phase. However, small angle scattering and ^2H NMR show that locally both phases have rather similar structures and that both possess a high degree of positional order. The N* phase, although macroscopically similar to the N_D phase is microscopically different. It should be remembered that the lamellar phase in this system is not a classical lamellar phase but one in which the lamellae are broken by elongated water filled defects. We have already shown that adding electrolyte, cosurfactant and changing surfactant concentration has the effect of changing the size and density of defects [7,8]. It may be that the added polymer increases the density of defects in the lamellar structure to the extent that a transition is induced to nematic in the way described theoretically by Toner & Nelson [9] and Helfrich [10]. We are continuing to characterise the structure of these phases by contrast variation SANS experiments, TEM and water self diffusion measurements.

REFERENCES

[1] M. C. Holmes & N. Boden, Mol. Cryst. Liq. Cryst., 124, 131, (1985).
[2] M. R. Kuzma, W. Welder, A. Saupe, S. Shin & Satyendra Kumar, Phys. Rev. Letts., 68, 3436, (1992).
[3] E. D. Goddard, Colloids Surf., 19, 255, (1986).
[4] M. M. Breuer & I. D. Robb, Chem. Ind. (London), 13, 530, (1972).
[5] R. Nagarajan, J. Chem. Phys., 90 (3), 1980, (1990).
[6] A. Guinier, X-ray Diffraction in Crystals, Imperfect Crystals & Amorphous Bodies, W. H. Freeman & Co., London, (1963).
[7] M. S. Leaver & M. C. Holmes, J. Phys. II France, 3, 105, (1993).
[8] M. C. Holmes, A. M. Smith & M. S. Leaver, J. Phys. II France, 3, 1357, (1993).
[9] J. Toner & D. R. Nelson, Phys. Rev. B, 23 (1), 316, (1981).
[10] W. Helfrich, J. de Physique, 39, 1199, (1978).