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Confinement Effects Induced by a Solubilized Polymer on the Micellar Nematic-Lamellar Transition

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We studied the effect of polyethylene-oxide (PEO, molecular weight from 10^5 to 4×10^6) dissolved in the micellar nematic (N) and lamellar (L) phases of the surfactant system cesium perfluoro-octanoate (CsPFO)/water by microscopy and calorimetry. Replacement of water by PEO suppresses the lamellar phase above a critical concentration (w_c) which depends on the molecular weight of the polymer by a power law. In a limited range below w_c a reentrant nematic is observed. The N-L transitions become less sharp with increasing concentration. The observed effects are due to the disruption of the lamellar order by the polymer.

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Polyethylene-oxide (PEO) is a water soluble polymer that has been extensively studied in surfactant solutions (for a review see Nagarajan [1] and references given there). Neutron scattering experiments in dilute sodium dodecylsulfate (SDS)/water solutions by Cabane and Duplessix [2] established that the polymer clings to the micelles forming necklacelike strings of micelles. The binding energy of PEO to the micelles in dilute solutions is approximately $0.3kT$ per surfactant molecule. The attraction is due to electrostatic forces. In water the polymer acquires a positive charge due to the addition of protons while the micellar aggregates carry a negative charge. Experiments on the lamellar phase for concentrated SDS solution [3] (75 wt.% SDS) show that the dissolved polymer penetrates the layers and forms coils with a layered distribution of the segments. The mixtures remain homogeneous until about 5% of the water is replaced by PEO; at higher concentrations of PEO a separation into lamellar, isotropic, and other uncharacterized phases occurs. The cesium perfluoro-octanoate/water system has a relatively simple phase diagram [4]. Over a wide concentration range (32–62 wt.% CsPFO) it has a lamellar phase (L) separated from the isotropic (I) micellar solution by a 6–8°C wide nematic range (N_L). The lamellar phase is stable at lower temperatures and extends down to the Krafft boundary.

The effects of polymers when surfactant concentrations are near the phase boundaries, where micellar nematic and lamellar smectic phases are formed, has not been studied previously, experimentally or theoretically. In this concentration range micellar structures in general depend strongly on additives and it is reasonable to expect that the addition of polymers would significantly affect the liquid-crystalline properties. The nematic phase of the CsPFO solutions is formed from more or less disklike surfactant aggregates. We assume that the dissolved PEO also clings to the micelles in these solutions but, as we shall see, the insensitivity of the N_L -I transition to added polymer shows the orientational order is indifferent to the decoration of the micelles with the polymer.

Electric conductivity measurements [4,5] and transmission electron micrographs [6] show that the bilayers of a

lamellar phase near the N_L -L transition have many defects, or possibly consist of layers or separate disks. In any case the lamellae can easily be penetrated by the polymer but a random coil configuration will interfere with the layered structure of the solvent and disrupt it. This should lead to a separation into nematic and smectic fractions unless there is a repulsive (electrostatic) interaction that prevents aggregation.

In the following, we describe the effect of PEO on the stability of the nematic and lamellar phases of CsPFO/water using optical microscopy to classify the phases and scanning microcalorimetry to explore changes in transition properties. CsPFO was obtained by neutralizing perfluoro-octanoic acid with CsOH and purified by recrystallization from ethanol. PEO was obtained from Aldrich with molecular weights of 10^5 , 2×10^5 , 3×10^5 , 6×10^5 , 9×10^5 , and 4×10^6 , as determined by viscometric methods. It was used without further purification. No data are available on the molecular weight (MW) distribution. Since PEO degrades in time [7], we used only samples that were less than 10 days old and stored in the dark at room temperature. Degradation effects were observed by us only for very large molecular weights with samples that were kept for more than a month. A 4×10^6 MW sample displayed after 2 months a significant reduction in viscosity.

We compare, in the following, compositions of constant surfactant concentrations in which the weight percentage of water replaced by PEO varies. The compositions are accordingly characterized by the weight percentage of the surfactant in the sample and the weight percentage of water replaced by PEO. We first prepared stock solutions of the polymer in distilled water with PEO concentrations in the range of 0 to 1.5 wt.%. The final samples were then prepared by mixing the surfactant and the stock solutions at room temperature using a magnetic stirrer. The total preparation time was typically 3 days.

For microscopy the solutions were filled into flat capillaries (Microslides, Vitrodynamics, NJ) of a width of 4 mm and a thickness of 0.2 mm which were sealed with a torch. The microscopic observations were made with a Leitz polarizing microscope equipped with a Mettler

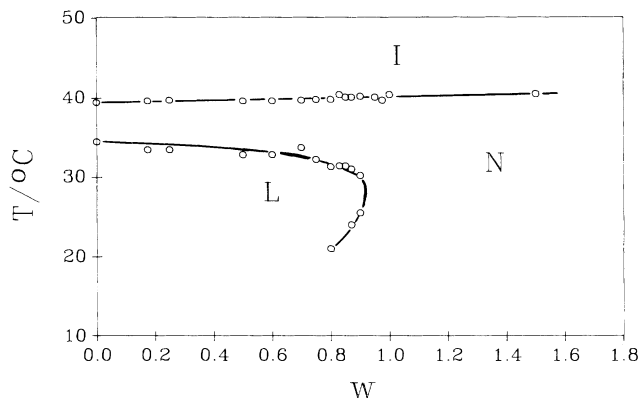


FIG. 1. Transition temperatures vs the weight percentage of water replaced by PEO; MW 10^5 , CsPFO concentration 49 wt.% (I, isotropic micellar solution; N, nematic solution; L, lamellar phase).

heating stage. The temperature was changed typically at a rate of 0.2°C per minute for the determination of the transition temperatures. At the nematic-lamellar smectic transitions, the formation of smectic textures in samples containing PEO could take hours. In these ranges the temperature was changed stepwise, typically by 1°C , in intervals of $\frac{1}{2}$ to 2 h.

Heat capacities were measured with a MC-2 calorimeter (Microcal Incorporated) equipped with a large capacity (1.2 ml), airtight cell. The results are independent of the scan rates at rates slower than 80 mK/min. The scans reported here were taken at rates between 33 and 34 mK/min. The heating and cooling scans gave similar results.

Figure 1 shows the phase diagrams determined by microscopy for PEO of a molecular weight of 10^5 in a 49 wt.% surfactant solution. The salient features are that a lamellar smectic phase is stable only below a critical PEO concentration w_c , that there is a concentration range near w_c with a reentrant nematic phase, and that the isotropic-nematic transition temperature is not affected by the polymer, except for a slight increase. Figure 2 summarizes results for the critical concentrations obtained at 25°C for a sequence of molecular weights with a 49 wt.% CsPFO sample. The polymer affects not only the stability of the lamellar phase but it also changes the properties of the N_L -L transition. The I- N_L transition is clearly recognizable under the polarizing microscope at all PEO concentrations. On cooling from the isotropic phase a schlieren texture forms that changes at elevated temperatures to a pseudo-isotropic texture within 1 to 2 days.

The N_L -L transition is indicated by the appearance of focal conic domains. The transition is sharp and well defined at low PEO concentrations but with PEO concentrations near w_c this transition is gradual, like a glass transition. The experimentally determined transition temperatures therefore have a large error (2-3 $^\circ\text{C}$). (The temperature of reentrance is particularly difficult to

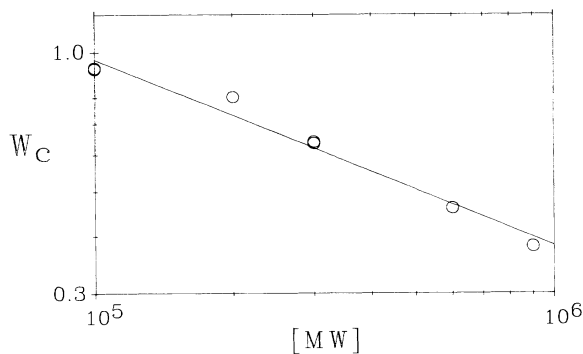


FIG. 2. Critical concentration vs molecular weight of PEO.

determine since the relaxation of the textures is slow. For that reason we could not establish reentrance much below 20°C .) Figure 3(a) shows the texture of the lamellar phase with typical focal conic defects of a sample containing 0.83 wt.% of 10^5 MW PEO. The micrograph of Fig. 3(b) is taken with a sample that has a slightly higher PEO concentration, 0.87 wt.%, at the same temperature. This sample is in the nematic phase close to the lamellar

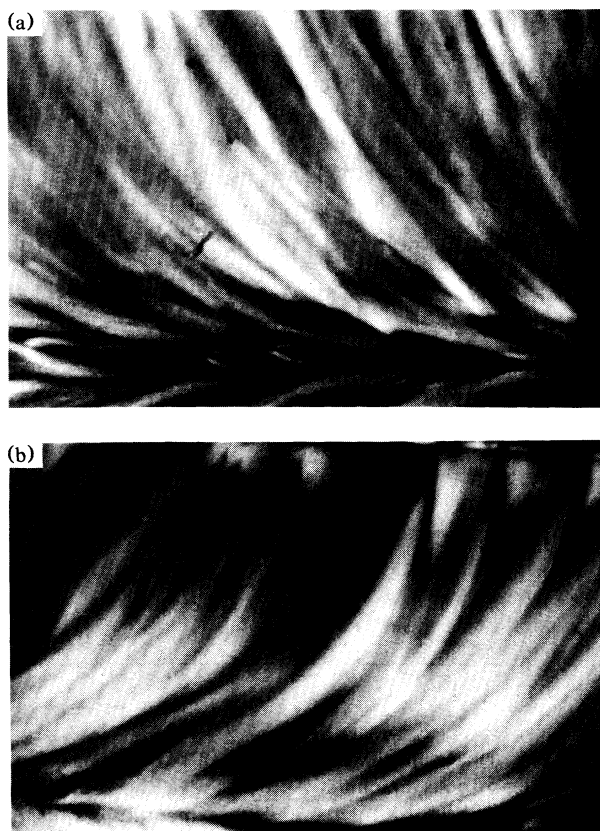


FIG. 3. Micrographs of PEO 10^5 MW solutions at 25.4°C , 49 wt.% CsPFO; crossed polarizers, magnification $325\times$. (a) 0.83 wt.% PEO; (b) 0.87 wt.% PEO.

transition. It has also a texture with stripe patterns but focal conics do not form.

The change of the sharpness of the L - N_L transition is also clearly documented by calorimetric measurements made on a sequence of 49 wt.% CsPFO samples with 10^5 MW PEO. The critical concentration for this mixture is $w_c = 0.91$ wt.%. The changes in heat capacities, at six different PEO concentrations, are shown in Fig. 4 as a function of temperature. Estimated linear backgrounds have been subtracted from the data. The curves have been shifted vertically to facilitate comparison with each other.

The difference in the effects of PEO on the two phase transitions is striking. The N_L -I transition temperature and the sharpness of the heat-capacity peak remain essentially unchanged, although the N_L -I peak height shows a decrease with increasing PEO concentration. On the other hand, the N_L -L peak shape and height and the transition temperature are strongly affected. The peak flattens out and shifts to lower temperature with increasing PEO concentration. The peak broadening is significant even at concentrations well below w_c , where microscopy still clearly indicates a well-developed lamellar phase. It is also remarkable that there is a broad hump in heat capacity even at concentrations higher than the

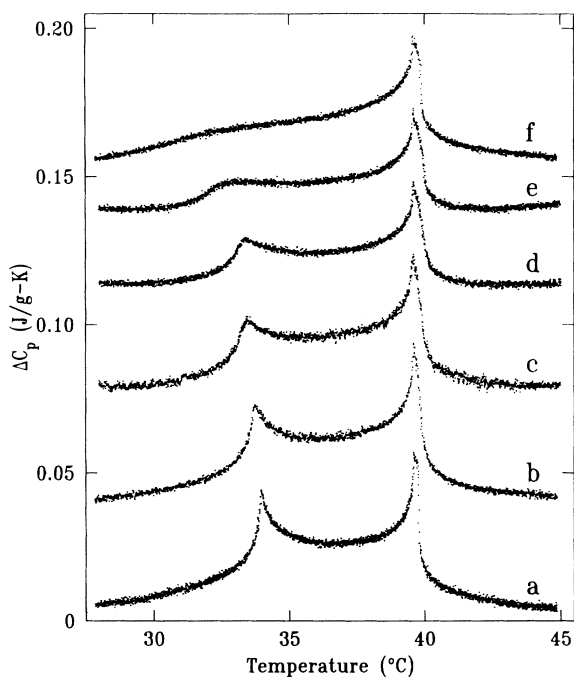


FIG. 4. Heat capacity of 49 wt.% CsPFO solutions in water containing various amounts of 10^5 MW PEO. Linear backgrounds have been subtracted and the temperature scales have been adjusted slightly (by less than $\pm 0.5^\circ\text{C}$) so that the N -I transitions are at the same temperature. Weight percentage of water replaced by PEO: (a) 0.0 wt.%, (b) 0.1 wt.%, (c) 0.175 wt.%, (d) 0.25 wt.%, (e) 0.5 wt.%, (f) 1.0 wt.%.

critical concentration. It indicates a temperature range over which a short-range smectic order develops in a fraction of the sample.

The coils formed by PEO in the micellar solutions are much larger than the dimension of a micelle or the layer distance in the lamellar phase. The radius of a random PEO coil in water is estimated to be of the order of 200 Å for a MW of 10^5 and may be as large as 1300 Å for a MW of 4×10^6 . In micellar solutions the interaction with the micelles will affect the local coil structure but the radius should have a similar magnitude. A polymer coil is relatively large compared to typical intermicellar distances or to the layer distance of 50 Å [4]. Within the coil the structure of the surfactant aggregates and their order will be more or less modified. In dilute polymer solutions the effect of the coils on the lamellar phase formation may be similar to an impurity confined to small droplets that are randomly distributed. In semidilute solutions the coils overlap and act like an impurity that is spread homogeneously over the volume.

The experimental results show that PEO has little effect on the stability of the nematic phase but it reduces the stability of the lamellar phase and suppresses it completely above a critical PEO concentration. These observations indicate that the nematic order develops unhindered in the PEO coils while the smectic order cannot develop. We have, accordingly, the following conditions for the formation of the lamellar phase.

In dilute PEO solutions the lamellar phase develops nearly unhindered. It is interrupted only by a number of nematic droplets confined to the polymer coils. Therefore, a fraction of the sample, equal to the total volume of the polymer coils, does not take part in the N_L -L transition and the transition enthalpy will be reduced in proportion to the polymer concentration. The transition will also change its critical properties, especially when the critical PEO concentration is approached. Near the transition, when the smectic coherence length becomes comparable to or larger than the minimum distance between the coils, confinement effects become important and change the sharpness of the transition [8]. The spaces between the coils are quite irregular which further reduces the sharpness. With increasing polymer concentration the connections between the lamellar domains become weaker until at sufficiently high PEO concentration the smectic domains are disconnected and no macroscopic smectic order can develop.

In Fig. 5 the data of Fig. 1 are combined with the data for 3×10^5 MW PEO solutions and plotted versus the reduced polymer concentration w/w_c . It shows that the nematic lamellar transition lines have similar features for the two PEO weights but there is no universal curve. For the higher molecular weight the cutoff is sharper than for the lower molecular weight. This is to be expected because the dimensions of the interstitial smectic domains are larger for higher polymer weights at the same reduced concentration.

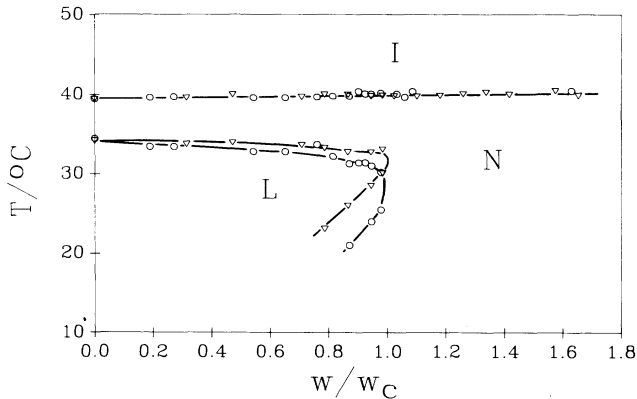


FIG. 5. Transition temperatures vs reduced PEO concentration; \circ , 10^5 MW; ∇ , 3×10^5 MW.

The specific-heat measurements are also in good agreement with the confinement model. The transition enthalpy decreases with increasing polymer concentration and the transition peak broadens with a small downshift in temperature. There is no sudden change in the thermal properties when the critical concentration is reached. A very broad and weak peak exists even above the critical concentration, showing that locally a lamellar structure is still formed.

The critical concentration should follow the same power law in the molecular weight dependence as the overlap concentration. The exponent should accordingly be between 0.5 and 0.8. The value that we obtained for the exponent 0.43 ± 0.07 is somewhat smaller. In part, the deviation may be due to errors in the molecular weight of PEO samples and due to the unspecified width of the weight distribution. Another problem is that the smectic order may penetrate into the coils to an extent that depends on the molecular weight. The penetration

may be deeper for larger molecules which would explain why the critical concentration is not as strongly dependent on the molecular weight as expected. The observation of a reentrant nematic phase indicates that the persistence length and the size of the polymer coil increases with decreasing temperature.

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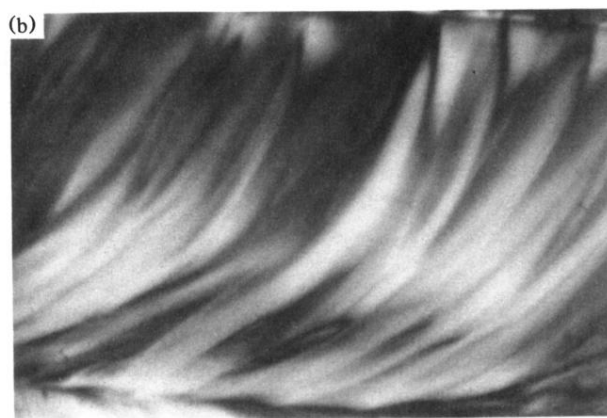
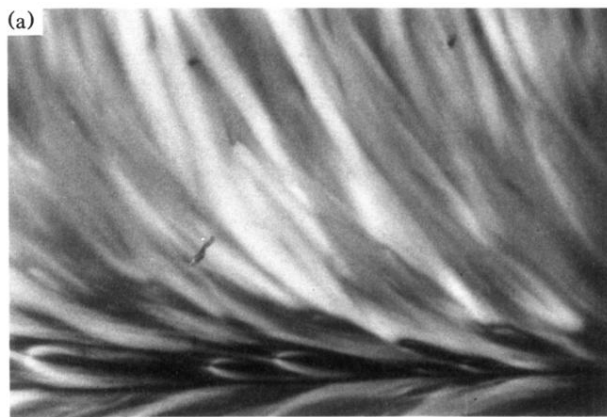


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