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The Effects of Polyethylene Oxide on the Curvature Elasticity of Micellar Nematic Cesium Perfluorooctanoate Water Mixtures

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This study focuses on the effect of polyethylene oxide (PEO) on the elastic properties of the micellar nematic formed in cesium perfluorooctanoate (CsPFO) water mixtures. We used PEO with molecular weights of 100,000 and 300,000 and prepared samples with CsPFO concentrations of 49 wt% in water containing small amounts of PEO. The weight fractions of PEO in water were 0.0, 0.25, 0.60, and 1.0%. We determined the splay and bend elastic constants by analyzing the optical response of surface aligned films to magnetic fields. The splay constants, compared at corresponding temperatures, are nearly independent of the PEO concentration. The birefringence decreases slightly. The bend elasticity which depends on the smectic coherence length shows the strongest effects.

Keywords: Curvature elasticity; micellar nematic; cesium perfluorooctanoate water mixtures

INTRODUCTION

The binary system cesium perfluorooctanoate (CsPFO) and water has a relatively simple phase diagram. It forms a lamellar phase (L) and a micellar nematic (N) liquid crystal over a concentration range from 32 to 62 wt% CsPFO [1–4]. The L phase is separated from the isotropic micellar solution (I) by a 6–8°C wide nematic range. The addition of small amounts of

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polyethylene oxide (PEO) can suppress the formation of the lamellar phase but has little effect on the temperature stability of the micellar nematic.

Theoretical [5] and experimental [6–8] work on polymer solutions in micellar systems was reported earlier considering in particular the interactions between polymers and micelles and the effects on the micellar structures. The micellization of sodium dodecylsulfate (SDS) in aqueous solutions containing polyethylene oxide (PEO) was explored extensively using NMR, X-ray and neutron scattering experiments [6–9].

In the micellar solutions sections of PEO wrap around the SDS-micelles. A long polymer can attach to many aggregates and form a necklace-like string of micelles [9]. In the L phase the periodicity of the lamellar structure changes little upon addition of PEO. The polymer can penetrate the bilayers. The interaction of PEO with the micelles in the present system will be similar since CsPFO is an anionic surfactant like SDS.

In this work birefringence measurements on thin films of nematic mixtures of CsPFO are reported in dependence on temperature, magnetic field, and PEO concentration. The data are evaluated to determine the splay and bend elastic constants.

EXPERIMENTAL

The surfactant CsPFO ($C_7F_{15}COO^-Cs^+$) was synthesized by neutralizing perfluorooctanoic acid with CsOH and purified by recrystallization from ethanol. Two different molecular weight polyethylene oxide polymers (PEO, $(-CH_2-CH_2-O-)_n$) were purchased from Aldrich Chemical Co. The sample cell with a film thickness of 0.2 mm ± 2.5% was from Helma Cells Inc.

Binary solutions of CsPFO in water were prepared and ternary solutions for three PEO concentrations. The CsPFO concentration was in all samples kept at 49 wt%. The PEO concentrations were 0, 0.25, 0.6 and 1.0%. They are given in weight percent of PEO in water. Two different molecular weight PEO were studied, 1×10^5 and 3×10^5 MW PEO. In the following referred to as PEO100 and PEO300. Above a critical concentration the polymer suppresses the formation of a lamellar phase [10]. The critical concentration depends on the molecular weight. It is 0.91 wt% for PEO100 and 0.67 wt% for PEO300.

Curvature elastic properties were determined by birefringence measurements made on homeotropically aligned 0.2 mm thick films. The birefringence for vertical incidence was measured as a function of temperature and magnetic field. The field was applied under an angle of 80° to the normal of the film. The equipment allowed relatively fast high precision birefringence measurement. The temperature control was better than 1 mK.

The data were fitted with an iterative program that minimized the rms error for the phase shifts. The adjustable parameters were the birefringence of n_a, the critical field H_c, and the ratio of splay and bend elastic constants k_{11}/k_{33}. Strong anchoring of the homeotropic alignment was assumed. For more details on the data reduction see T. Haven [11] and E. Zhou [12]. The anisotropy of diamagnetic susceptibility χ_a measured for a PEO free mixture by Kim [13] was used to calculate values of the splay and the bend constants. We assumed for the evaluation that $\chi_a = 1.55 \times 10^{-6}\ n_a$, independent of the PEO concentration and temperature. Mainly because of the uncertainty in χ_a the uncertainty of k_{33} is estimated to be 6%. In k_{11} an additional error of up to 10% may occur.

RESULTS AND DISCUSSION

In Table I the compositions of the studied samples are listed together with the transition temperatures. The temperatures for the L-N transitions were determined by extrapolation in plots of $(1/H_C)^2$ versus temperature (see Fig. 4). As the table shows, there is a small increase of T_{NI} with increasing polymer concentration. The L-N transition is shifted little at PEO concentrations below the critical value where the formation of the lamellar phase is suppressed [10] rather abruptly. The 1.0 wt% solutions are above the critical concentrations and form no lamellar phase.

In Figures 1 and 2 some results of the birefringence measurements are compared at corresponding temperatures. (The temperature scales are shifted here in all following figure so that the N-I transition for all mixtures

TABLE I Phase transition for 49 wt% CsPFO solutions in H_2O containing various amount of 1×10^5 or 3×10^5 MW PEO. T_{NL} was determined by extrapolation in plots of $(1/H_C)^2$ versus T

PEO wt%	*PEO MW*	*T_{NI}(°C)* (*Transition range*)	*T_{NL}(°C)*
0	0	40.2 – 40.4	34.95
0.25	1×10^5	40.6 – 41.0	34.52
0.25	3×10^5	40.4 – 40.8	34.63
0.6	1×10^5	41.1 – 41.4	34.06
0.6	3×10^5	41.4 – 41.8	34.70
1.0	1×10^5	41.8 – 42.2	
1.0	3×10^5	42.4 – 42.8	

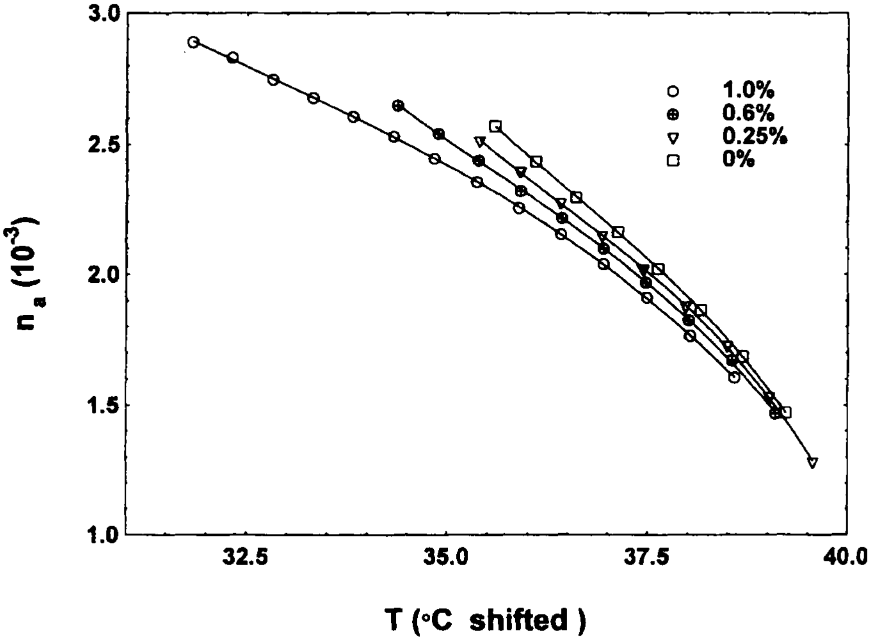

FIGURE 1 Birefringence of CsPFO (49 wt%) in water containing the indicated amounts of PEO (MW 3×10^5) The temperature scale is shifted so that the beginning of N-I transition is at 40°C for all mixtures.

starts on heating at 40°C). Figure 1 shows the birefringence for different PEO300 concentrations. The polymer reduces the birefringence slightly when compared at corresponding temperatures. The birefringence is determined by the order parameter of the surfactant molecules since the orientational order of water and presumably also the order of the polymer segments are small. Accordingly, the polymer reduces the order parameter of the surfactant. Probably this is connected with some reduction in the size of the micelles [5].

For the two lower PEO concentrations the birefringence is within error limits independent of the molecular weight, but for the 1.0 wt% solutions there is a significant difference in the lower temperature range. The higher molecular weight PEO is more effective in reducing the anisotropy. The stronger reduction is apparently correlated to the reduction of the smectic order.

Figure 3 summarizes the results for the critical field, $H_c = (\pi/d)(k_{33}/\chi_a)^{1/2}$. ($d$ denotes the film thickness and χ_a the diamagnetic susceptibility). The

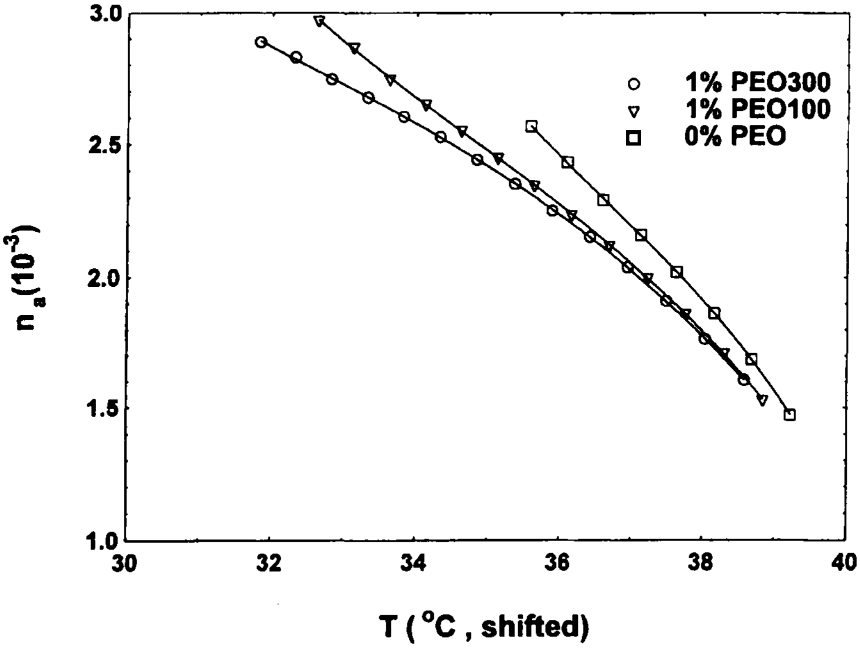

FIGURE 2 Birefringence of solutions containing 1.0% PEO of 1 and 3 × 10^3 MW. Temperature scale shifted as in Figure 1.

figure shows that at corresponding temperature the polymer lowers the critical field. The reduction is again independent of the molecular weight except, see Figure 3, at 1.0 wt%.

Figure 4 shows the temperature dependence of $(1/H_C)^2$ for the PEO100 mixtures. The dependence below 38°C is in good approximation linear indicating a critical exponent of -1 for the bend elasticity. However, there are insufficient data to make reliable statements on the critical properties of the transition. The linear relation seems to hold even for the 1.0% PEO100 concentration which is above the critical value of 0.91%. Only for the 1.0% mixture of PEO300 are the deviations from linearity apparent.

Results for the bend elasticity are summarized in Figure 5. The data for the 0.6% and 0.25% PEO300 mixtures are not shown. They coincide within error limits with the corresponding PEO100 data. PEO has little effect near T_{NI} but quite strong effects in the lower temperature range, as expected, because k_{33} depends on the smectic coherence length.

The splay elasticity shows no divergence at the L-N transition and no significant dependence on the PEO concentration. On a reduced temperature

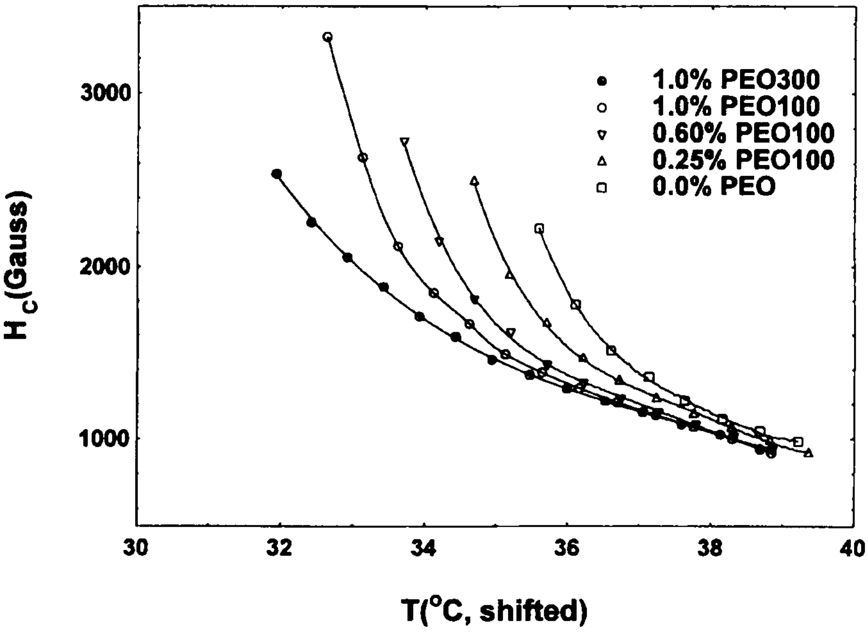

FIGURE 3 Critical fields for Frederiks transition.

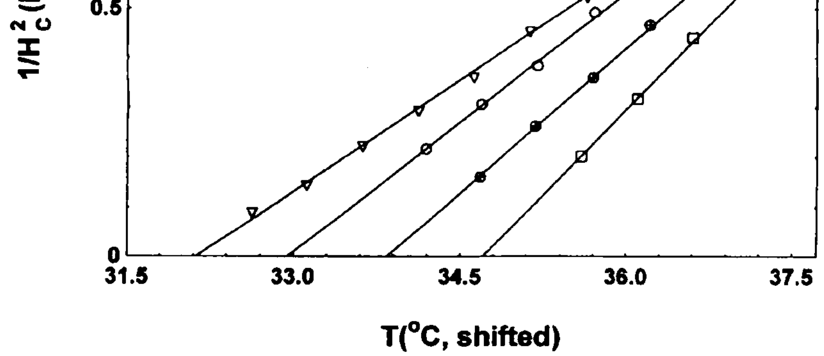

FIGURE 4 $(1/H_c)^2$ and linear fits for the PEO 100 solutions.

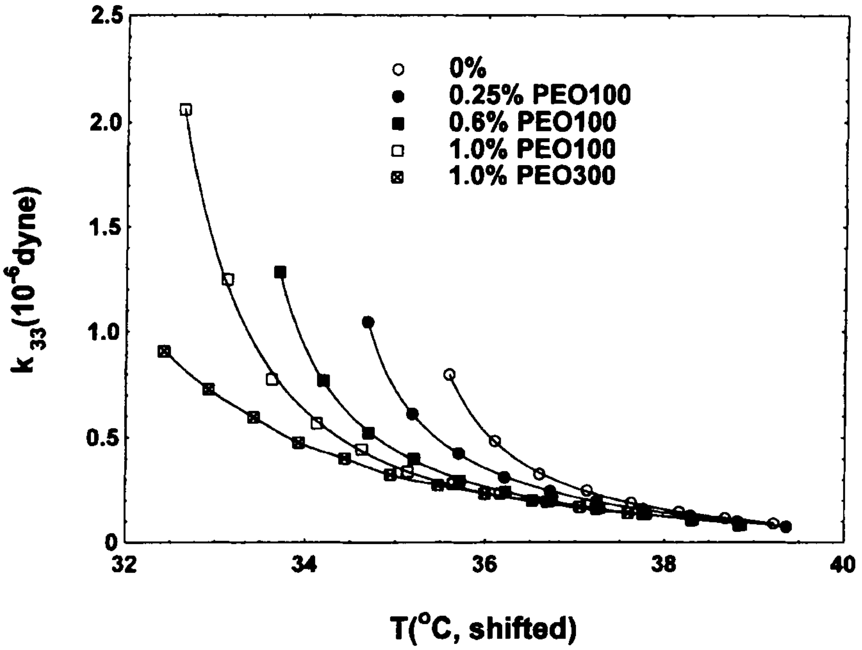

FIGURE 5 Bend elasticity.

scale all k_{11} values fall within error limits on the same curve (see Fig. 6). The error becomes however rather large in the lower temperature range.

SUMMARY AND CONCLUSIONS

As mentioned in the introduction PEO attaches to aggregates of cationic surfactants and it has a significant effect on the formation of liquid crystalline phases. With CsPFO as surfactant there is a rather strong effect on the formation of a lamellar phase but surprisingly little effect on the temperature stability of the nematic phase. Properties of the nematic phase as birefringence and bend elasticity depend on the polymer concentration but, in the lower concentration range ($w < w_C$), the induced changes do not depend on the molecular weight of the polymer. This independence indicates that the structure of the associated micelles is the same and that the fraction of polymer segments attached to the micelles is also the same. Both are probably also independent of the polymer concentration in this range

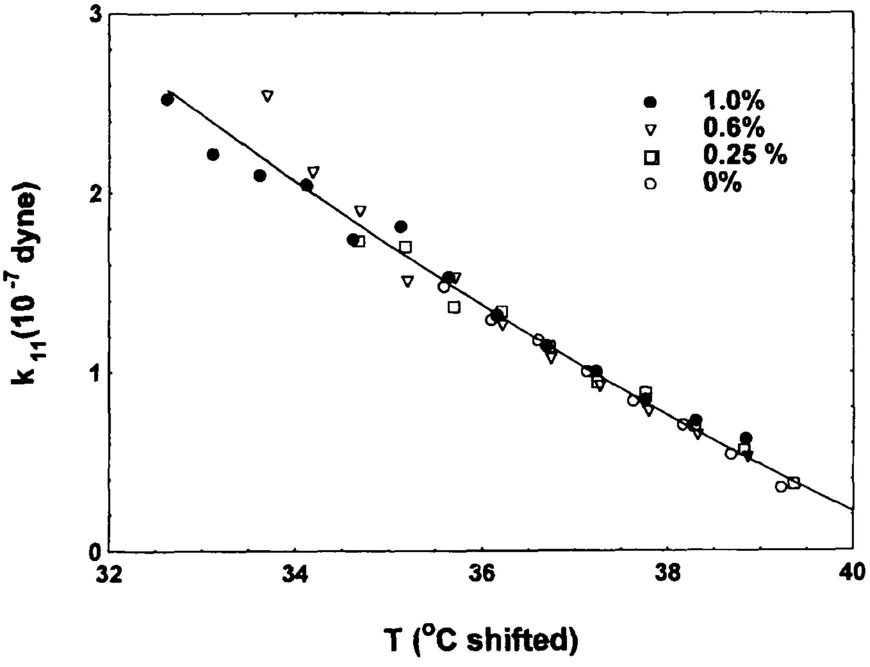

FIGURE 6 Splay elasticity for the PEO 100 solutions.

because the surfactant concentration is high so that the polymer is always saturated.

The bend elasticity k_{33} depends sensitively on the smectic short range order. But for the lower two concentrations the experiments show no dependence of k_{33} on the molecular weight even near the L-N transition because the transition temperatures for the two mixtures are the same.

The earlier proposed model [10] explains the molecular weight dependence of the critical concentration by the assumption that the lamellar structure is suppressed within the polymer coils. Accordingly a lamellar phase can only exist in dilute solutions where there is no overlap between the coils. The data obtained for k_{33} with the 1% solutions which are both above w_c show that there is still significant smectic short range order possible. They indicate that smectic short range order can exist within the coils.

For future research it will be interesting to study different surfactant concentrations in order to obtain further information on the polymer surfactant interactions.

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