Liquid Crystals

Effect of salt on the phase diagrams of two binary lyotropic liquid crystalline solutions

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Published online: 24 Sep 2006.

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Effect of salt on the phase diagrams of two binary lyotropic liquid crystalline solutions

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The effect of adding salts NH_4OH and $CsOH$ to aqueous solutions of NH_4PFO and $CsPFO$, respectively, was studied for concentrations in the range 0 to 2 wt %. In both systems, the isotropic to nematic and nematic to lamellar phase transition temperatures were elevated. There was an insignificant effect on the width of the nematic range in the NH_4PFO system, while the nematic phase was widened by as much as $\sim 3°C$ in the case of $CsPFO$. High-resolution X-ray scattering measurements were performed to determine the micellar size and its dependence on temperature for 52 wt % NH_4PFO solution in water.

1. Introduction

Binary solutions of ammonium perfluoro-octanoate (NH_4PFO)/water and caesium perfluoro-octanoate ($CsPFO$)/water have been the subject of several exhaustive studies because of the simplicity of their phase diagrams and their similarity to thermotropic liquid crystal systems. Much work has been done on the phase diagram and pretransitional effects at the weakly first-order isotropic (I) to nematic (N) and N to lamellar (L_α) phase transitions in these systems using microcalorimetry [1], nuclear magnetic resonance [2], light scattering [3], rotational viscosity [4], X-ray scattering [3, 5, 6], neutron scattering [7], and magnetic birefringence [8] techniques. Unfortunately, because of the high-Z of the element Cs, the absorption length for CuK_α radiation in CsPFO mixtures is very small. Consequently, X-ray studies require more intense and penetrating (short wavelength) radiation, often to the detriment of instrumental resolution and ease of experimentation. For this reason, NH_4PFO is more suitable for X-ray measurements. Previous work [6, 9] on NH_4PFO solutions probed the miscellar dimensions with low-resolution X-ray scattering. The micelles were found to have a disc-like shape and positive diamagnetic anisotropy. The phase diagram determined using NMR [6] was completely isomorphous to the CsPFO system, with the I, N, and L_α phases present.

A simple and well-characterized lyotropic system with a wide N range and an N–L_α phase transition is highly desirable for high-precision phase transition studies.
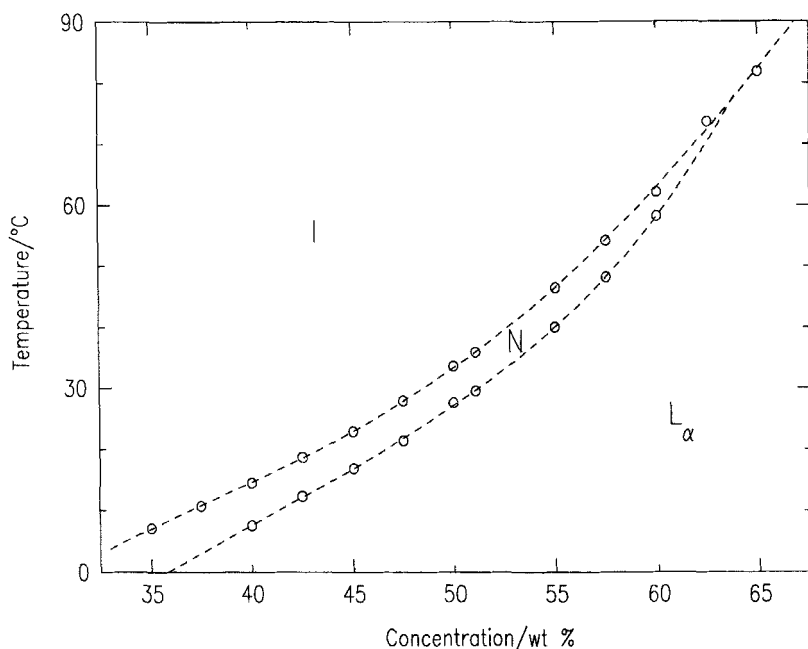
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Figure 1.   Phase diagram of NH$_4$PFO/water determined with polarizing microscopy. This system exhibits I, N, and L$_\alpha$ phases and an I/N/L$_\alpha$ triple point at 64 wt %.

The addition of small amounts of salt is known to have a profound effect [10] on the phase diagram of lyotropic systems, normally altering the transition temperatures and thereby changing the temperature ranges of various phases. In particular, magnetic susceptibility measurements performed on CsPFO/CsCl/water show stabilization of the lamellar phase and effective increase in T_{N-I} [11]. In some cases, new phases are made possible by the addition of a compatible salt. With the expectation of a wide N phase, we have studied the effect of suitable salts (CsOH and NH$_4$OH) on these two (CsPFO and NH$_4$PFO, respectively) lyotropic systems. The N–I and N–L$_\alpha$ transition temperatures, in both cases, were found to increase. The range of the N phase remained unaffected in the NH$_4$PFO system while it was broadened by 2 to 3°C for CsPFO/water solutions. Finally, we have examined a 52 wt % mixture of NH$_4$PFO/water using X-ray scattering to determine the temperature dependence of layer spacing and effective micelle diameter.

2.   Experimental

Starting materials were purchased from Aldrich, and the synthesis was performed at Kent State University. The compounds were purified by recrystallization from acetonitrile. The solutions were prepared by mixing the surfactant in distilled–deionized water and continuously stirring it with a magnetic stirrer for 24 h. Errors in concentration for CsPFO and NH$_4$PFO were ± 0.02 per cent, and for salts were ± 1.0 per cent of their respective concentrations. Samples were filled in 0.3×3 mm glass capillaries (Vitrodynamics) which were then fused to eliminate water evaporation during the measurements. The phases were identified and transition temperatures determined by observing the changes in the characteristic microscopic texture of the various phases with a Leitz polarizing microscope and a Mettler hot stage. The phase diagram for the

NH_4PFO and water system is given in figure 1. Transition temperatures were determined on both heating and cooling and differences between them were found to be within the limits of experimental temperature accuracy. Increasing NH_4PFO concentration resulted in narrowing of the nematic range until an $I/N/L_\alpha$ triple point was reached at approximately 64 wt %, a result similar to that obtained for the mixture CsPFO/water [12].

For X-ray measurements, the samples were placed in a $1 \cdot 5$ mm $\times$ 4 mm $\times$ 12 mm beryllium cell which was plugged with rubber stoppers at both ends and sealed with epoxy. It was placed in a home-made oven with temperature stability better than $\pm$ 10 mK. The sample was aligned by cooling from the I phase in a 6–7 kG magnetic field produced by a pair of permanent rare-earth magnets. Due to positive diamagnetic anisotropy, the nematic director aligned parallel to the field. X-ray measurements were performed using copper radiation from a rotating anode source and a Huber two-circle goniometer. A pair of Ge(111) single crystals were utilized as monochromator and analyser to achieve experimental resolution of $|\Delta q| = 4 \times 10^{-4}$ Å^{-1}. The experiments were conducted with two different director orientations. The lamellar spacing was
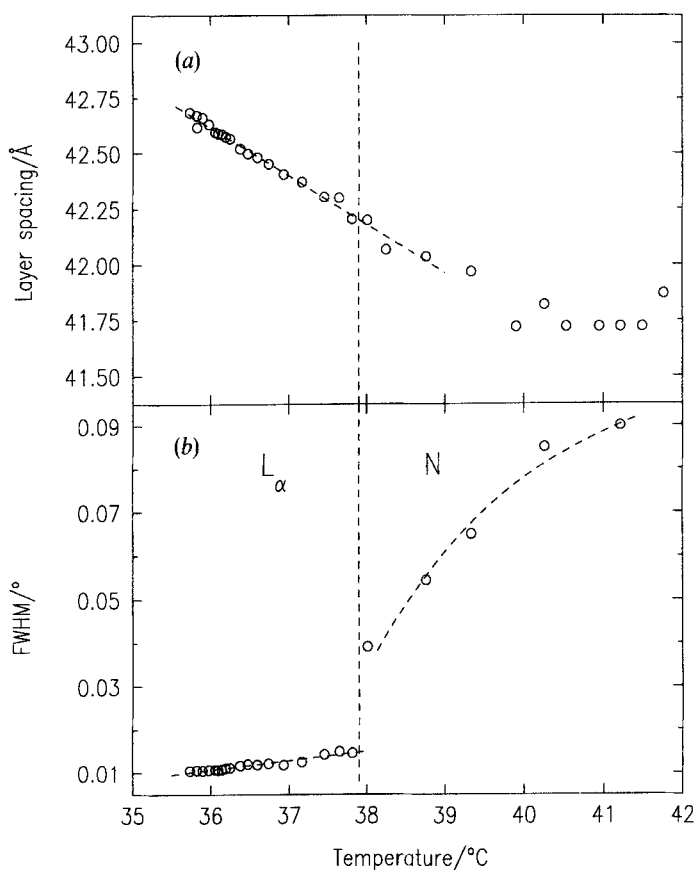
Figure 2.　(*a*) Temperature dependence of lamellar layer spacing for the 52 wt % NH_4PFO/water system measured by high-resolution X-ray diffraction. (*b*) The full-width half maximum (FWHM) of peak in the longitudinal scan also becomes narrow as the N–L_α transition is approached and eventually is resolution limited. Dashed lines are drawn as a guide to the eye. -

B. Cull *et al.*

Figure 3. Three-dimensional plots of the phase boundaries of the NH$_4$PFO/CsOH/water system.

Figure 4. Three-dimensional plot of the phase boundaries of the CsPFO/CsOH/water system.

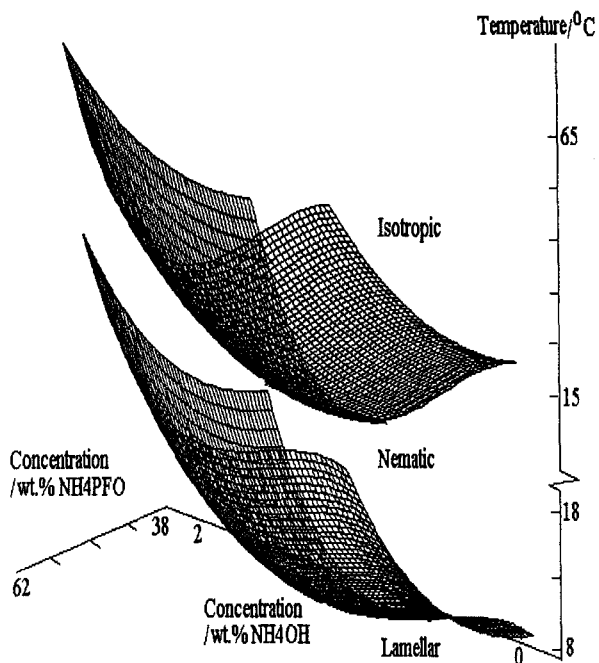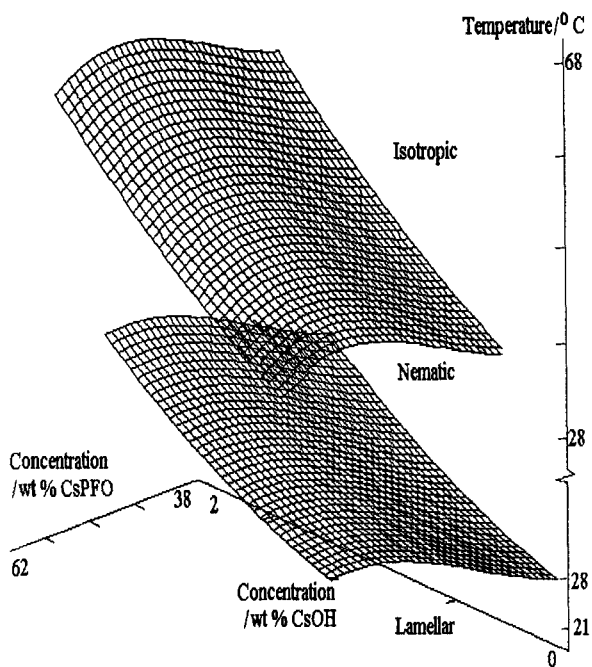determined by aligning the director so as to lie in the scattering plane. To determine the intermicellar distance perpendicular to their symmetry axis, the magnetic field was applied normal to the scattering plane.

3. Results

X-ray diffraction measurements were performed on a 52 wt % NH_4PFO/water mixture. The sample temperature was changed in 0·25°C steps and the position and width of the Bragg peak were monitored. Figure 2 (*a*) shows the measured layer spacing over a temperature range of 35 to 42°C. The peak grew sharp and its intensity increased continuously in the N phase as the L_α phase was approached. The peak width (FWHM) decreased by a factor of ten from 0·090° to 0·009° (see figure 2 (*b*)) within three degrees of the N–L_α transition at 37·8°C. The sample and the magnetic field were then

Table 1. The isotropic to nematic and nematic to lamellar phase transition temperatures (in °C) for the NH_4PFO, water, and NH_4OH system.

Amount of NH_4PFO wt %	Transition	Amount of NH_4OH/wt %				
		0·0	0·5	1·0	1·5	2·0
40·0	I–N	14·6	19·9	17·8	18·5	—
	N–L_α	7·8	13·2	11·1	11·7	—
45·0	I–N	24·5	27·0	20·7	25·1	25·3
	N–L_α	17·5	20·1	14·1	18·3	18·6
50·0	I–N	34·4	38·6	36·5	38·5	37·4
	N–L_α	27·7	31·5	29·5	31·4	30·5
55·0	I–N	50·7	47·4	48·4	45·9	52·9
	N–L_α	44·3	40·8	41·9	39·5	47·0
60·0	I–N	53·4	65·7	63·7	63·9	65·3
	N–L_α	48·6	61·8	58·3	56·9	58·2

Table 2. The isotropic to nematic and nematic to lamellar phase transition temperatures (in °C) for the CsPFO, water, and CsOH system.

Amount of CsPFO wt %	Transition	Amount of CsOH/wt %				
		0·0	0·5	1·0	1·5	2·0
40·0	I–N	27·3	31·3	33·6	34·2	36·9
	N–L_α	21·5	24·1	25·7	26·0	28·9
45·0	I–N	34·2	34·4	36·7	40·1	41·4
	N–L_α	27·9	27·4	29·2	31·9	33·1
50·0	I–N	42·7	45·4	45·9	47·4	51·2
	N–L_α	36·9	38·7	38·6	39·7	42·8
55·0	I–N	48·6	49·9	54·8	55·9	—
	N–L_α	42·9	43·5	47·7	48·8	—
60·0	I–N	62·5	64·0	66·8	63·0	68·7
	N–L_α	58·3	59·2	61·2	55·8	61·7

simultaneously rotated by 90° about the beam direction to probe the micelle diameter, which was found to remain essentially unchanged with temperature at an average value of $61 \cdot 2$ Å $\pm 0 \cdot 9$ Å. The ratio of the intermicellar distances in the two directions remained fairly constant at $1 : 1 \cdot 5$ for the temperature range explored, which differs from the previously obtained ratio of $1 : 1 \cdot 3$ for the CsPFO/water system at comparable concentrations and $1 : 1 \cdot 25$ for NH_4PFO/D_2O at $45 \cdot 2$ wt % [6].

We obtained partial phase diagrams of ternary systems of NH_4PFO/NH_4OH/water and CsPFO/CsOH/water to determine the effects of additive salts on transition temperatures and the stability of the N and L_α phases. Figures 3 and 4 show three-dimensional plots of temperature versus surfactant and salt concentrations. Concentrations are given in weight per cent of the surfactant in the solutions, and weight per cent of salt. Note that there are breaks in the vertical axes. These data are also given in tables 1 and 2. The two transition temperatures of the NH_4PFO and water system were equally affected by NH_4OH. It raised both transition temperatures equally by $1-3°C$, leaving the nematic range unaffected. For the CsPFO and water system, however, I–N temperatures increased by $6-10°C$ while N–L_α temperatures rose only by $3 \cdot 5-7°C$, thus resulting in a wider N phase, for the highest salt concentration, by $\sim 3°C$. This effective broadening of the N range by approximately 60 per cent may be very helpful in the study of pretransitional effects at the N–L_α phase transition.

4. Summary

To summarize, we have obtained partial phase diagrams of NH_4PFO/NH_4OH/water and CsPFO/CsOH/water by optical microscopy. For the NH_4PFO/water system, both transition temperatures rose by the same amount. The nematic range of CsPFO/water was significantly widened by the addition of CsOH.

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