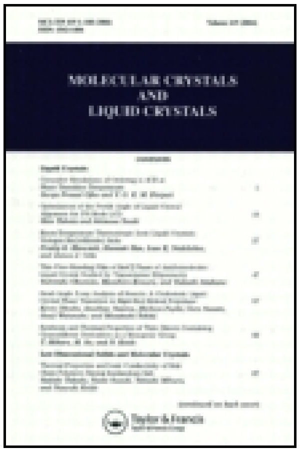

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THE LIQUID CRYSTALLINE PHASE BEHAVIOUR OF PERFLUOROCARBON SURFACTANTS IN ORGANIC SOLVENTS

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Abstract The behaviour of ammonium perfluorooctanoate (APFO) and caesium perfluorooctanoate (CsPFO) in polar, organic solvents has been investigated. Only the APFO/ ethylene glycol system exhibits any mesophases (a lamellar phase). This phase occurs at high concentrations (mass fraction w >0.65) and at temperatures below 250 K, which are accessible only by supercooling below the solubility curve. The phase behaviour of APFO in mixtures of ethylene glycol and water has also been established. The nematic-to-isotropic transition in the APFO/ water system is found to be displaced to lower temperatures on incrementally replacing water with ethylene glycol. This is shown to arise from a contraction in the size of the disk-like micelles brought about by a lowering of the interfacial energy, an effect countered by lowering the temperature. Generally, the temperatures required fall well below the solubility curves preventing access to mesophases in perfluorocarbon surfactant/organic solvent systems.

INTRODUCTION

Salts of short chain perfluorocarboxylic acids form aqueous solutions of disk-like micelles which are stable over wide concentration and temperature intervals[1-8]. With increasing concentration the disk-like micelles undergo ordering transitions to form, first, a nematic N_D phase and, subsequently, a smectic lamellar L phase[2,5,8]. The N_D phase is characterised by long-range correlations in the orientation of the symmetry axes of the micelles. At low concentrations, where the N_D-to-L transition is apparently second order, the first-formed lamellar phase is a smectic-A-like state comprised of micelles arranged on equidistant planes[1,9] . This phase behaviour has been explained in terms of phase transitions which are predominantly driven by hard particle interactions between disk-like micelles, i.e. the isotropic-to-nematic transition occurs when the surfactant volume fraction ϕ reaches a critical value of the axial ratio a/b of the micelle, where a is the height of the disc and b its diameter[7,10] Changes in the phase behaviour may, therefore, be brought about by perturbing the self-assembly of the micelles. For example, we have previously shown that at a given temperature an increase in the length of the fluorocarbon chain leads to a displacement of the isotropic to nematic phase transitions to lower ϕ as a consequence of a concomitant decrease in a/b, whilst at any given ϕ the transition is shifted to higher temperatures since the micelles become smaller as the temperature is increased[10]. Changes in the counter-ion also affect the self-assembly to a significant degree with consequent large changes in the phase transition temperatures[7]. Thus, the electrostatic repulsion between charged head groups, the curvature dependence of the fluorocarbon chain packing and the interfacial energy of the micelle all influence the size and shape of the micelles[7,10,11]

In this paper we investigate the importance of the solvent in determining micellar self-assembly by observing the effects on the phase behaviour of substituting water by non-aqueous solvents. We would expect such a solvent exchange to affect the interfacial free energy and the electrostatic repulsion between head groups. A decrease in the interfacial tension will favour smaller micelles[11] as will a decrease in the relative permittivity of the solvent due to reduced screening of the coulombic forces between neighbouring carboxylate groups. Thus, generally, in non-aqueous solvents a/b is expected to be significantly larger than in water with a concomitant shift of the phase transitions to higher concentrations/lower temperatures. It will be shown that for perfluorocarbon surfactants in a wide range of polar organic solvents mesophases are not accesible at temperatures above the solubility curve. Only in the case of the APFO/ ethylene glycol system where supercooling below the solubility curve is practicable can liquid crystals be observed.

EXPERIMENTAL

The perfluorocarboxylate salts were prepared as previously described[2,3] and had a purity of at least 99.7 % by microanalysis. Samples were prepared using either triply distilled water or distilled ethylene glycol held over 4 Å molecular sieves. All other solvents were of analytical grade.

The presence of mesophases was investigated using an Olympus BH2 polarising microscope fitted with a Linkam THM600 hot/cold stage. The coolant used for all experiments was liquid nitrogen. The samples were contained in 0.2 mm microslides (Camlab, England).

X-ray scattering experiments were conducted with a simple pinhole camera, nickel-filtered Cu K_a radiation of wavelength $\lambda=0.154$ nm, Lindemann sample tube (0.5 mm i.d.)-to-plate distance of 113.5 mm, and with a magnetic field of 0.4 T applied parallel to the z-axis (equator) and perpendicular to the x-axis (meridian) which is the direction of the long axis of the Lindemann tube.

RESULTS AND DISCUSSION

The behaviour of APFO and CsPFO were investigated in a variety of polar organic solvents (ethylene glycol, formamide, glycerol, methanol and dimethylacetamide), but a mesophase was only seen for APFO in ethylene glycol (EG). A lamellar phase (Figure 1) is observed, but only at high surfactant concentrations and by supercooling well below the solubility curve. This is possible for the APFO/ethylene glycol system because of strong hydrogen bonding between the ammonium ion and the solvent.

The phase transition temperatures T_{IL} and T_{LI} for samples with $w>0.65$ ($\phi>0.49$) are compared with those for the APFO/H_2O system ($w\leq0.65$, $\phi<0.50$) in Figure 2. The nematic phase in the APFO/H_2O system finishes at $\phi=0.45$ and thereafter only a lamellar phase is present. In the case of the APFO/ethylene glycol system only a lamellar phase region is accessible. Interestingly a singular point is seen at ϕ=0.56. Such a point could exist for the APFO/H_2O system but at higher concentrations than those accessible.

Figure 1. Optical micrograph showing the characteristic batonnette texture of a lamellar phase for the APFO/EG system (w=0.65) at 213 K (magnification 200x).

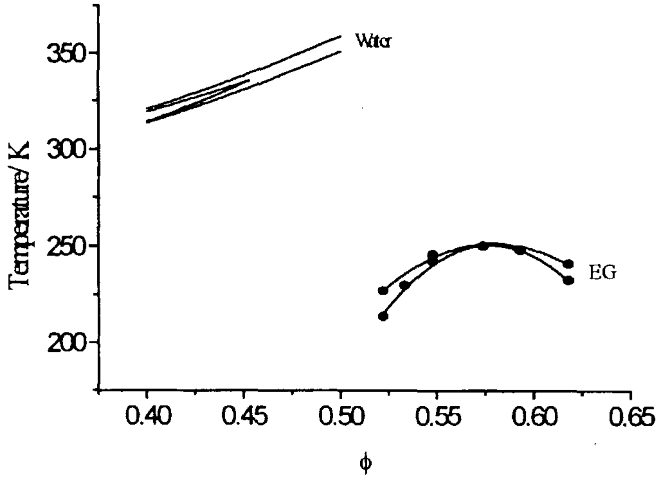

Figure 2. Comparison of the phase behaviour in the APFO/EG and APFO/H_2O systems.

However, the most significant difference between the two systems is a lowering of the T_{IL} and T_{LI} phase transition temperatures in the ethylene glycol system by approximately 140 K. Samples with w<0.65 could not be supercooled below the solubility curve and so it was not possible to establish whether a nematic phase exists at lower concentrations. The *depression* of the phase transition temperatures will be a consequence of the effect temperature has on one or more contributions to the micellar energy: namely, the micelle/solution interfacial energy, counter-ion binding energy and entropy of mixing, all of which will cause the micelle to grow as the temperature is lowered. On substituting ethylene glycol for water a decrease in the micelle size is expected either as a consequence of a reduction in the micelle/solvent interfacial tension $\gamma_{fc/s}$ or a reduction in the relative permittivity ε of the solvent [8,11]. We have shown for perfluorinated surfactants that changes in ε do not have a significant effect on the self-assembly of the disk-like aggregates, whilst changes in $\gamma_{fc/s}$ can have a profound effect (to be published). A reduction in $\gamma_{fc/s}$ will give rise to a larger average area a_o occuppied by a surfactant molecule at the micelle/solution interface: that is, to a smaller micelle.

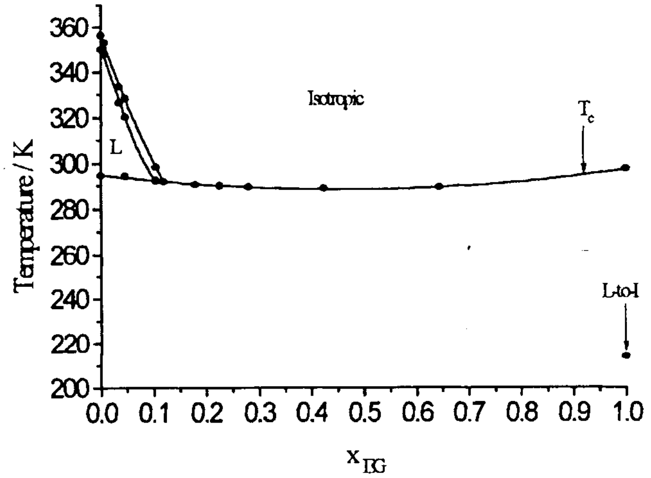

Figure 3. Phase diagram of the APFO/ H_2O/ EG (w=0.65) system showing the effect of increasing the solvent mole fraction x of ethylene glycol on the T_{LI} and T_{IL} phase transition lines. Tc is the solubility curve.

Thus, to obtain the critical axial ratio characteristic of the isotropic-to-mesophase transition it becomes necessary to increase the interfacial energy by lowering the temperature. As there are no surface tension data available for ethylene glycol at 250 K, we have tested this hypothesis by observing the effect of adding small amounts of ethylene glycol to the APFO/H_2O system. Figure 3 shows how these additions have a spectacular effect on the phase transition temperatures. At solvent mole fractions of ethylene glycol inexcess of 0.12 the *L*-to-*I* transitions occur below the solubility curve Tc and are inaccessible.

Confirmation that the micelles do, in fact, decrease in size with increasing concentration of ethylene glycol is obtained from small angle x-ray scattering measurements performed on an APFO/H_2O/EG (w=0.5) sample in the isotropic phase at 311 K. This APFO concentration was chosen for ease of sample preparation and an easily accessible isotropic phase. For APFO/H_2O w=0.65 the transition temperature to the isotropic phase is 360 K, which would have necessitated working at quite a high temperature.

The scattering pattern for a sample in the isotropic phase is a single diffuse ring[1,3]. Assuming the x-rays are scattered from the (111) planes of a fcc lattice with plane separation d_o, we obtain the micelle volume $V_m = \frac{3}{4}\sqrt{3}\,\phi d_o^3$, from which an estimate of the axial ratio a/b can be calculated, assuming the micelle is an oblate ellipsoid with half-thickness (a/2)=13.2 Å corresponding to the length of the PFO^- ion. The a/b values increase (Figure 4) with increasing ethylene glycol concentration, i.e. the micelles decrease in size as the ethylene glycol concentration increases. Interestingly, in pure ethylene glycol the a/b ratio is close to unity implying the micelle is almost spherical. To recover the critical size necessary for the phase transition to occur requires going to lower temperatures as is shown in Figure 5.

The significance of the role of interfacial tension is illustrated in Figure 6. It shows that the *I*-to-*L* transitions lie along a line of equi-interfacial tension $\gamma_{fc/s}$. The values for $\gamma_{fc/s}$ have been calculated using the Zisman-Good equation (Appendix A). This behaviour supports the idea that the decrease in the micelle size on addition of ethylene glycol is due to the concomitant decrease in the surface energy of the micelle.

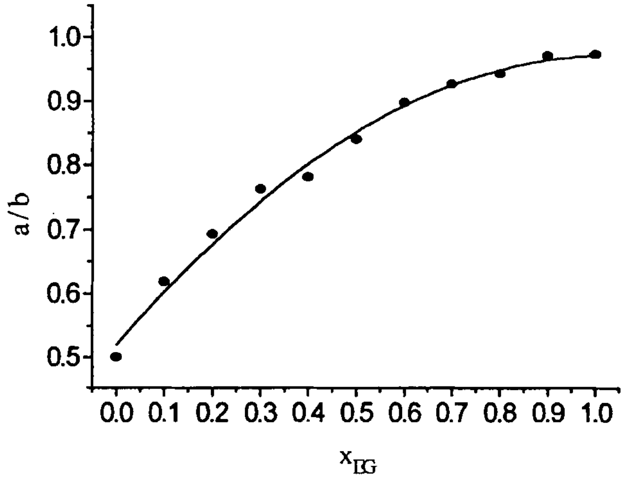

Figure 4. The axial ratio a/b of the micelles, in the isotropic phase, at 311 K, of APFO/H_2O/EG (w=0.5) as a function of the solvent mole fraction of ethylene glycol x_{EG}.

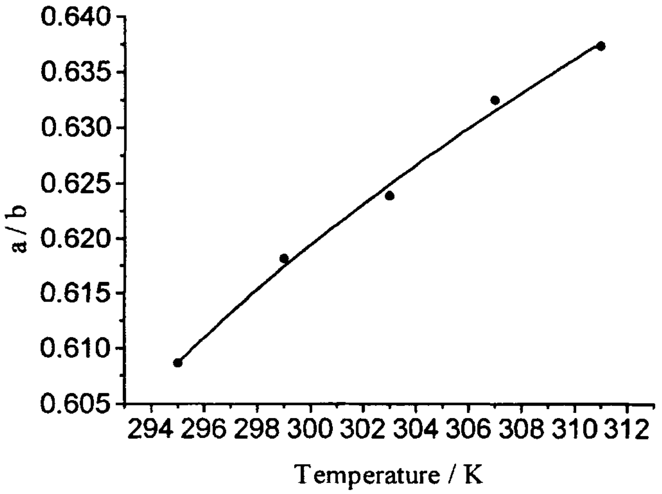

Figure 5. The axial ratio of the micelles in the isotropic phase of APFO/H_2O/EG (w=0.5; x_{EG}=0.1) as a function of temperature.

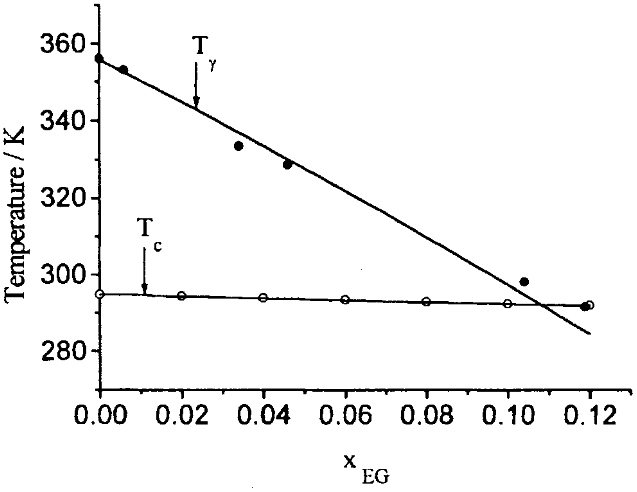

Figure 6. Experimentally measured *I*-to-*L* phase transition temperatures (closed circles) and the line of temperatures T_γ at which the fluorocarbon/ solvent interfacial tensions are constant ($\gamma_{fc/s}$=44mN m^{-1}). Experimental points on the solubility curve Tc are marked using open circles.

CONCLUSION

The inaccessibility of mesophases for perfluorocarbon surfactants in non-aqueous solvents stems from the reduction in the size of disk-like micelles due to the lowering of the fluorocarbon/ solvent interfacial energy. Whilst this effect can be reversed by lowering the temperature, the temperatures required fall well below the solubility curves.

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APPENDIX

The fluorocarbon/solvent interfacial tension $\gamma_{fc/s}$ is calculated using the Zisman-Good equation[13], $\gamma_{fc/s} = \gamma_{s/a} + \gamma_{fc/a} - 2\sqrt{\gamma^{d}_{fc/a}\gamma^{d}_{s/a}}$, where γ^{d} represents the dispersive contributions to the surface tensions. Values for both the pure and mixed solvent/air interfacial tensions $\gamma_{s/a}$ were taken from published data[12]. The fluorocarbon/air interfacial tension is assumed to be completely dispersive, i.e. $\gamma^{d}_{fc/a} = \gamma_{fc/a} = 10$ mN m^{-1} (using the critical interfacial tension, obtained from a Zisman plot, determined from contact angles between a self-assembled perfluorocarbon monolayer and a range of polar solvents, including ethylene glycol). The dispersive contribution to the surface tension of ethylene glycol is taken to be the same as the interfacial tension between ethylene glycol and tetradecane[13] and the previously published value[14] for the dispersive contribution to the water/air interfacial tension is used. In both cases the value is 20mN m^{-1} and this value is also taken for the dispersive contributions in the solvent mixtures. In this calculation the dispersive contributions were taken to be independent of temperature.