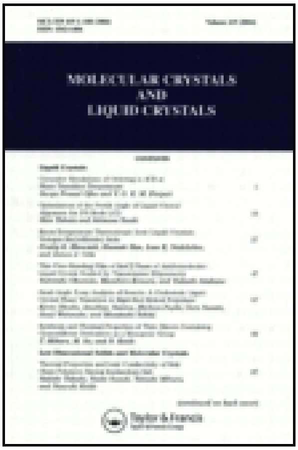

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Colloidal Dispersions in a Liquid Crystalline Medium

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COLLOIDAL DISPERSIONS IN A LIQUID CRYSTALLINE MEDIUM

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Abstract We have prepared stable colloidal suspensions in a lyotropic liquid crystal exhibiting an isotropic-nematic-lamellar phase sequence. Small angle neutron scattering (SANS) and dynamic light scattering (DLS) studies show the existence of attractive interparticle interactions in the nematic phase, which lead to a gas-liquid transition of the particles. The resulting liquid phase is weakly anisotropic. Further, the nematic-lamellar transition of the liquid crystal is found to be accompanied by a liquid-solid transition of the particles.

The structure of charged colloidal particles in an isotropic liquid is governed mainly by screened Coulomb interactions between them[1]. On the other hand, if a nematic liquid crystal (NLC) is used as the dispersing medium, at least three additional interparticle interactions can be expected to come into play. Each suspended particle disturbs the orientational ordering in the nematic phase, giving rise to disclinations in the director field. The interactions between the disclinations result in an effective interparticle interaction. Recent calculations show that this interaction is highly anisotropic, being attractive along certain directions with respect to the axis of symmetry. Further, it is found to be proportional to r^{-5}, r being the interparticle separation [2]. The particle surfaces can also induce a gradient in the magnitude of the nematic order parameter in their neighbourhood, leading to an attractive interparticle interaction [3]. Finally, there can also be interactions arising from the fluctuations in the director field, which are long-ranged compared to the van der Waals interaction[4].

In this paper we present studies on colloidal particles in a lyotropic system exhibiting an isotropic (I) - nematic (N) - lamellar (L_α) phase sequence on decreasing the temperature. In addition to direct microscopic observations on the suspensions, we have also probed them using small-angle neutron scattering (SANS) and dynamic light scattering (DLS) techniques.

The material used was a binary lyotropic system containing the surfactant CsPFO (Cesium pentadecafluorooctanoate) and water [5]. The micelles formed by the surfactant molecules have a discoid shape with the aspect ratio a/b in the range 0.2-0.55 depending on the temperature with a $\approx$ 22 Å. The colloidal particles used are polymeric latex particles of diameter 600 Å, with a surface charge density of about 260 μEq/g. The details of the phase diagram of the mixtures is published elsewhere [6]; here we shall briefly describe its main features. As the concentration of the particles in the mixture is increased, the I-N coexistence range increases, while the N-L transition temperature is not significantly affected. The highest particle concentration obtained was about 8% by weight. The most interesting feature of the phase diagram is the appearance, under a polarising microscope, of a frozen spinodal-decomposition-like texture at lower temperatures in the nematic phase. The onset of this texture is not very well defined and as the temperature is lowered in the nematic phase, it becomes gradually more conspicous at lower temperatures. This behaviour is found to be reversible on increasing the temperature.

Phase contrast microscopic observations indicate that the particles are well dispersed in the isotropic phase. On cooling the sample to the nematic phase, small clusters of particles appear, with liquid-like ordering within them. When the temperature is further lowered, these clusters grow incorporating more and more particles from the bulk. In the lamellar phase, the movement within the clusters is drastically reduced and all the suspended particles seem to be expelled into the clusters.

The SANS experiments were carried out on the neutron line PAXY at Laboratoire Léon-Brillouin, CEN-Saclay, France. The neutron wavelength was 8 Å with a sample to film distance of 6.78 m. A mixture with 1.5 wt.% polyballs was used in these studies. Contrast enhancement between the polyballs and the solvent was achieved by using D_2O instead of H_2O in the mixtures. Figure 1(a) shows the angle averaged scattered intensity profiles due to the latex particles obtained from unoriented samples at a few temperatures. The scattered intensity due to the micelles themselves falls outside the range of q shown. Even in the isotropic phase of the dispersing medium, there is a shoulder in the intensity profile at q $\approx 6\times 10^{-3}$ Å^{-1}, which corresponds approximately to the particle size, indicating the presence of short range order in the latex fluid. The shoulder becomes more pronounced and becomes a well-defined peak at lower temperatures in the nematic and lamellar phases.

The intensity profiles due to the colloidal particles obtained from oriented samples are shown in Fig.1(b). The sample was aligned with the nematic director normal to the incident beam. The figure shows two slices of the two dimensional profile in directions parallel and perpendicular to the director. In the isotropic phase, I(q) is isotropic and decays smoothly with q. In the nematic phase, on the other hand, it becomes anisotropic, with the anisotropy increasing with decreasing temperature. However, when the sample was aligned with the nematic director along the beam, the scattering was isotropic at all temperatures.

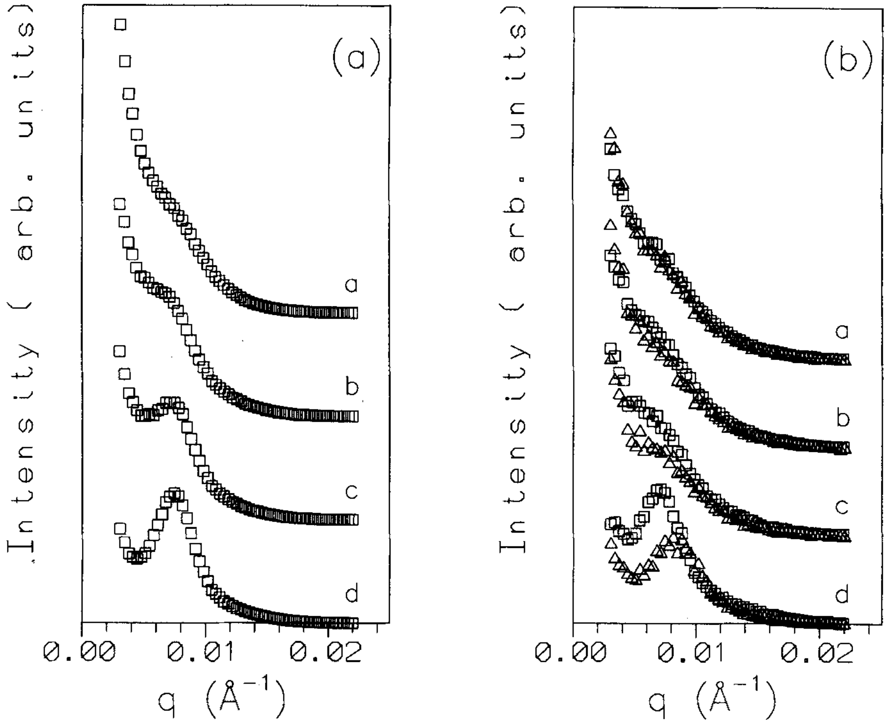

FIGURE 1 (a) Variation in the SANS intensity from the latex suspension in the CsPFO-water system with the wavevector q for a few temperatures corresponding to the isotropic (a), nematic (b), nematic with texture (c) and lamellar with texture (d) phases of the system. Particle concentration: 1.5 wt%. Surfactant concentration: 37 wt%. (b) The anisotropy in the scattered intensity from these four phases. The squares correspond to the direction normal to the nematic director and the triangles to that parallel to it.

The structure factor of the latex particles calculated from the SANS data are shown in Fig.2. It is clear from the figure that there is some structure in the particles even when the medium is in the isotropic phase. The peak in S(q) is not very pronounced ($S_{max} \approx 1.1$) and the phase can be identified as a gas. On lowering the temperature, the degree of order in the particles increases and the peak in S(q) grows, becoming very pronounced at the N-L_α transition of the solvent. We can thus conclude that the particles first undergo a gas-liquid transition in the nematic phase and then solidifies when the solvent goes into the lamellar phase, as indeed suggested by the phase contrast microscopic observations.

The single particle diffusion coefficient (D_o) of the polyballs in very dilute solutions was measured using DLS. In suspensions with larger particle concentrations, the interparticle interactions come into play and the intensity correlation function shows deviation from a single exponential decay. The short time decay in the correlation of the scattered light gives an effective diffusion coefficient D_{eff}, which is related to (D_o) by [7] $D_{eff} = \frac{D_o}{S(q)}$. The temperature dependence of D_o arises from that of the viscosity. Therefore, the additional temperature dependence of D_{eff} is due to that of S(q). We have measured the viscosity of the solvent using a plate-cone viscometer and D_o was calculated from the known values of the particle radius. The T-dependence of S(q) obtained this way from a mixture with 46 wt% surfactant concentration is shown in Fig.3 for two values of q.

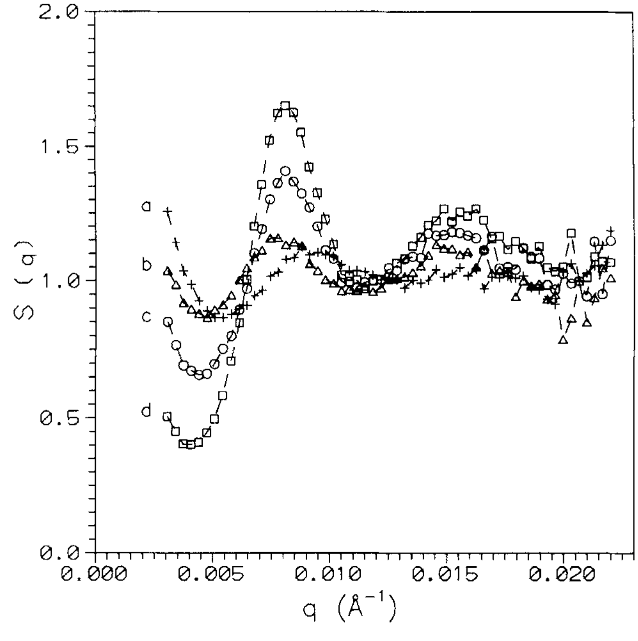

FIGURE 2 The structure factor of the latex particles at four different temperatures obtained from the SANS data. The labels have the same significance as in figure 1.

In the nematic phase at higher temperatures as well as in the isotropic phase, S(q) ≈ 1 and not sensitive to T. However, at lower temperatures in the nematic phase, it begins to decrease for $q_2 \approx 2.6\times 10^{-3}$ Å^{-1} and increase for $q_1 \approx 7.0\times 10^{-4}$ Å^{-1}.

This trend sets in near the temperature where the texture is seen under a microscope. The decrease in S(q) at q_2 continues with decreasing temperature and it reaches a plateau below the N-L_α transition, where the polyballs form a solid phase. We were unable to determine S(q) at q_1 in the lamellar phase, as the decay of the correlation function is very slow. It may be noted here that the temperature dependence of S(q) at q_2 is similar to that obtained from the SANS data for comparable values of q (Fig.2).

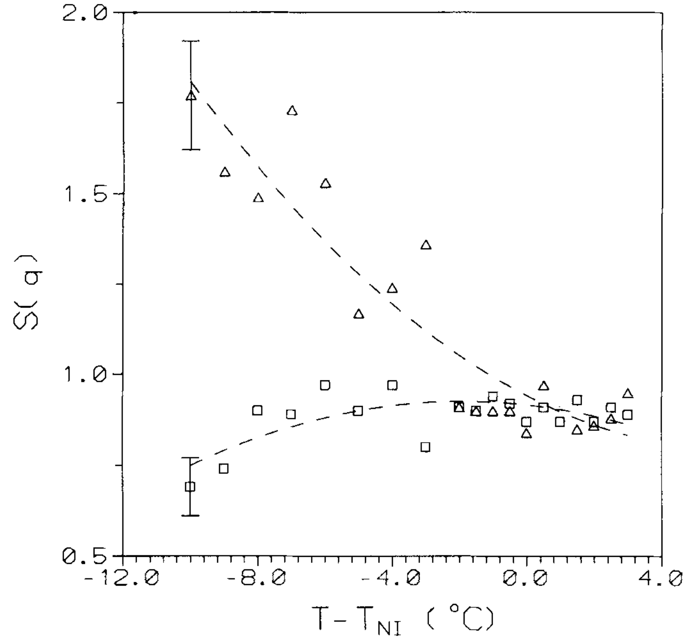

FIGURE 3 The variation of S(q) with temperature obtained from the DLS data for $q = 2.6\times 10^{-3}$ Å^{-1} (squares) and $q = 7.0\times 10^{-4}$ Å^{-1} (triangles). Particle concentration: 0.5 wt%, Surfactant concentration: 46 wt%. The dashed lines are guides for the eye.

The temperature dependence of S(q) obtained from the DLS studies is consistent with that expected from the sticky hard sphere model [8]. Fig.4 shows the variation of S(q) with qa, a being the well diameter, for a few values of the well depth. As can be seen from this figure, the short-range attraction results in the increase of S(q) with increasing magnitude of the interaction only at very small values of q. There is a range of q below q_m (corresponding to the maximum in S(q)), where S(q) decreases with increasing magnitude of the attractive potential. This trend can be clearly seen in Fig.2. It is also reflected in the preliminary results of our static light scattering studies, shown in Fig.5. In the isotropic phase, I(q) monotonically increases as q is decreased. On the other hand, at lower temperatures in the nematic phase, it has a shallow minimum at $q \approx \times 10^{-3}$ Å^{-1}.

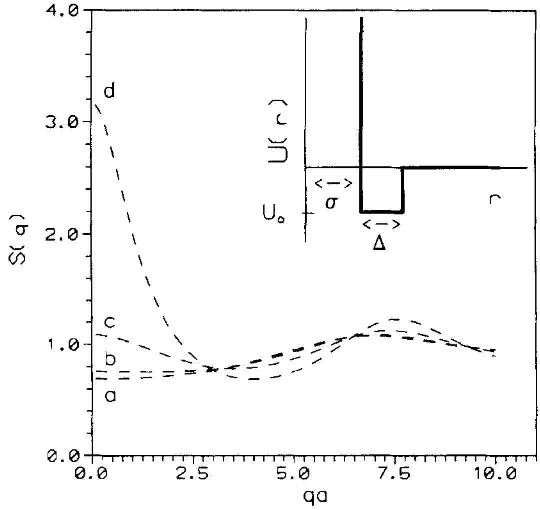

FIGURE 4 The structure factor of the sticky hard sphere model for a few values of the well depth u_o (after ref. 8). $-u_o/kT = 0.09$ (a), 1.5 (b), 2.0 (c) and 2.1 (d). The inset gives the definitons of the different parameters involved in the model. $\Delta/\sigma = 0.1$, Volume fraction = 0.07.

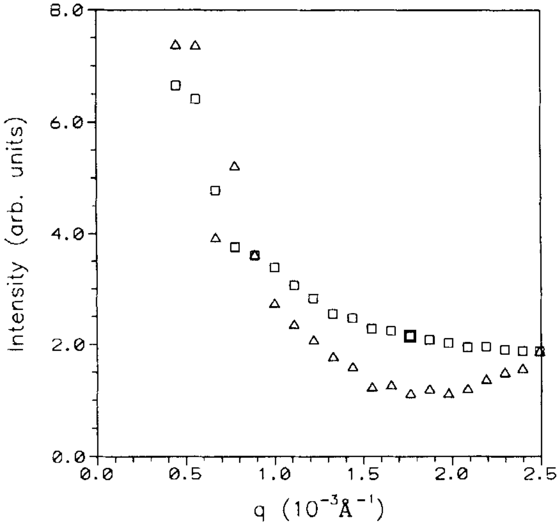

FIGURE 5 The intensity of the scattered light as a function of q, obtained from static light scattering studies. The squares correspond to the isotropic phase with $T=T_{NI}+2.8$ °C and the triangles to the lamellar phase with $T=T_{NI}-9.6$ °C. The two curves have been normalized at the maximum value of q.

In conclusion, we have observed phase transitions driven by an attractive interparticle potential in a colloidal suspension in a liquid crystalline solvent. Both the liquid and solid phases of the particles are found to be anisotropic. Further experiments are necessary to ascertain the origin of the attractive interactions responsible for the observed behaviour of this system.

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