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Nematic liquid crystalline structures in dilute surfactant solutions

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Nematic liquid crystalline structures in dilute surfactant solutions

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The nematic phase and the viscous isotropic (VI) phase formed by solutions of CTAB and SHNC are investigated using light scattering and viscosity techniques. It is argued that the turbidity in the nematic phase is due to orientational fluctuations in the director and therefore the intensity scales as Q^{-2}. It is shown that with dilution of the nematic phase with water the turbidity disappears with a simultaneous increase of viscosity.

1. Introduction

Formation of liquid crystalline (LC) phases in surfactant solutions at concentrations of about 10 per cent and above by weight is quite well known and the structures have been investigated in considerable detail [1]. But such observations for dilute solutions are rare [2–5]. In recent years there has been a considerable interest in so-called worm-like micelles or living polymers. A typical example is provided by a solution of a cationic surfactant-like cetyltrimethylammonium bromide (CTAB) mixed with sodium salicylate (SS) which forms very strongly viscoelastic solutions. An excellent review of these systems has been given by Rehage and Hoffmann [6], and the industrial importance of such systems has been pointed out by Peiffer in his papers and patents [7]. In the last few months it has become evident, both on experimental and theoretical grounds, that these worm-like micellar systems can produce nematic liquid crystalline structures [8–10]. The first such indication came from CTAB + sodium 3-hydroxynaphthalene-2-carboxylate (SHNC) solutions [8] for which it was shown that, by controlling the relative ratio of the components, one can obtain either viscoelastic solutions or nematic liquid crystals. It was observed that the nematic liquid crystal samples were turbid, while the VI samples were isotropic and clear.

This observation raised the natural question as to whether the turbidity observed arose from orientational fluctuations, just as in thermotropic nematic liquid crystals [11], and whether the VI phase is really the isotropic phase of the nematic phase.

In the present paper we address these questions, and the approach we have chosen is the following. In thermotropic liquid crystals, the turbidity observed has been shown to have a dependence of Q^{-2} as predicted by de Gennes and confirmed by experiments [11]. Therefore we have carried out light scattering experiments to check this for both the VI phase and the nematic phase. Secondly, we argued that the nematic solutions, on dilution with water, should go to the isotropic phase and hence the turbidity should disappear, but the viscosity should increase. In the present work we confirm both these expectations.

2. Materials and methods

CTAB was purchased from Sigma Chemicals and SHNC was a gift from M/S Atul Products. The latter was purified using methods mentioned earlier [8]. Light scattering experiments were performed using the BI-2000 equipment marketed by Brookhaven Instruments, USA. The viscosity measurements were performed using a Brookfield cone and plate viscometer, employing a shear rate of $1\ \mathrm{s}^{-1}$.

3. Results and discussions

The light scattering intensity at various angles was measured for two samples as a function of the wavevector $Q = (4\pi n/\lambda)\sin(\theta/2)$, where n is the refractive index of

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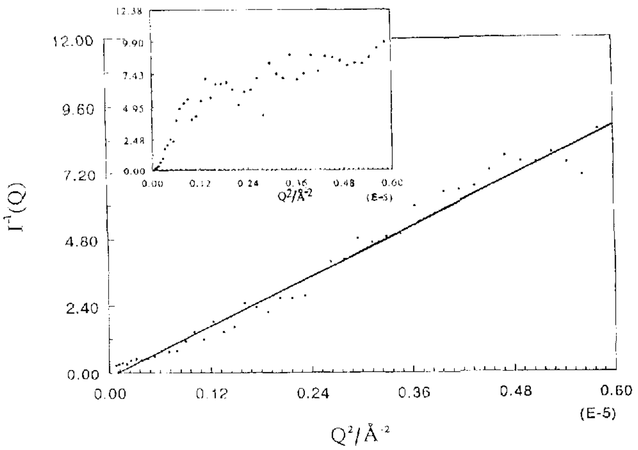

Figure 1. Inverse light scattering intensity as a function of Q^2 for CTAB = 60 mM, SHNC = 40 mM. The plot is linear, with the line passing through the origin, consistent with the turbidity arising from orientational fluctuations in the nematic director. The inset shows the results for the VI sample (CTAB = 60 mM, SHNC = 30 mM) indicating the absence of orientational fluctuations.

water and θ is the scattering angle. The first sample was liquid crystalline, containing CTAB = 60 mM and SHNC = 40 mM, and the second was a VI sample with CTAB = 60 mM and SHNC = 30 mM. The scattering intensities were an order of magnitude higher in the nematic phase than in the VI phase. The corresponding ratios for conventional thermotropic liquid crystals are much higher, but this difference is to be expected in view of the dilute nature of the samples in the present case. Figure 1 shows the results, with the inverse intensity $I^{-1}(Q)$ plotted as a function of Q^2. It is clearly seen that in the nematic phase, the plot is linear throughout the Q range, in accordance with the de Gennes prediction for thermotropic liquid crystals [11], while it is not linear for the VI sample (see inset of figure 1).

Next we wanted to confirm further whether the turbidity was due to orientational fluctuations. We have argued that the liquid crystalline sample should become isotropic on dilution with distilled water and the scattered intensity should reduce drastically in the isotropic phase. Further, we argued that if the VI phase is the isotropic phase of the nematic state, then the viscosity should increase with the disappearance of the turbidity. Figure 2 shows the intensity of the light scattered at 90° as the sample is diluted from the nematic phase. The viscosity at a shear rate of 1 s^{-1} was also measured as the sample was diluted. Figure 2 conclusively shows that as the scattered intensity decreases, the viscosity increases. It should be pointed out that Doi and Edwards have predicted such an increase in viscosity in the isotropic phase for rigid cylindrical molecules [12].

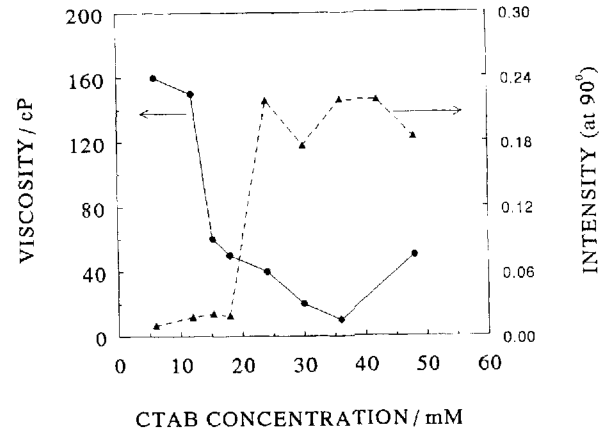

Figure 2. The viscosity and the turbidity are compared as the nematic sample with CTAB = 60 mM and SHNC = 40 mM is diluted. The viscosity is measured at a shear rate of 0·1 s^{-1} and the scattered intensity is measured at a 90 degree angle. (CTAB/SHNC = 1·5).

4. Conclusions

The main conclusions of this work are the following. (i) The turbidity of the dilute nematic phases observed for CTAB-SHNC systems is a result of orientational fluctuations, (ii) the scattered intensity scales as $1/Q^2$ in accordance with the predictions of de Gennes for thermotropic liquid crystals and (iii) the nematic phase becomes isotropic on dilution and the turbidity disappears, but the viscosity increases.

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