Effect of high pressure on the nematic–isotropic transition in aerosil–liquid crystal composites

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ABSTRACT

We report the first high pressure investigations of the nematic–isotropic transition in the composites of a liquid crystal compound with hydrophilic aerosil particles. The low concentrations of the aerosil particles used create soft gels of the composites. As expected $T_{N–Iso}$, the nematic–isotropic transition at room pressure exhibits a non-monotonic variation with increasing aerosil concentration. This non-monotonic behaviour is seen in the isobaric scans over the wide range of pressures studied, and its "magnitude" is dependent on the pressure applied. The surprising result of the present investigations on these nanocolloidal systems is that the slope of the pressure–temperature boundary also exhibits a non-monotonic dependence with the aerosil concentration, which qualitatively is similar to that of the transition temperature variation. Employing the transition enthalpy values determined at room pressure using differential scanning calorimetric scans collected at low heating rates, we calculate the transition volume dependence on the aerosil concentration. The study adds a new dimension, namely, the influence of pressure on liquid crystalline transitions in restricted geometries.

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1. Introduction

Investigations on liquid crystals confined in restricted geometries have been attracting significant attention in the past few years [1]. The restricted geometry can be realized by using prefabricated confining matrix such as Anopore and Nuclepore in which the voids are highly regular with well defined pore dimensions or an irregular network like aerogels. The geometrically enforced disorder observed in these situations can also be obtained by having the liquid crystal in a network termed as aerosils formed with silica spheres of ~7 nm diameter whose surfaces are decorated to achieve hydrophilic or hydrophobic interactions [2]. The advantage of the aerosil network is that the random disorder can be controlled and fine tuned by simply varying the concentration of the silica particles. The fragile hydrogen bond network that results from the interactions between the particles permits the disorder to be created *in situ*, allowing the influence of the quenched randomness on various phase transitions in LC materials to be examined. Despite the fact that a variety of probes have been used [3–12] to understand the behaviour of LC–aerosil dispersions, there has been no report on the effect of high pressure. This article describes the results of such an investigation.

2. Experimental

The liquid crystalline compound is 8CB (4-n-octyl cyanobiphenyl, from E-Merck) exhibiting in the cooling mode the isotropic–nematic–smectic A sequence. This compound does not crystallize at room temperature, a feature that was a necessary criterion, since the aerosil network formed by the aerosil–LC system is a fragile one and crystallization of the material may seriously disrupt the network. For these investigations we used hydrophilic aerosil particles (Aerosil 300) with a diameter of ~7 nm obtained from Degussa Corporation [13]. Before the preparation of the mixtures, the aerosil particles were degassed and dried at a temperature of ~200 °C for 12 h. The mixtures of aerosil and 8CB were prepared by the generally employed solvent mixing process. The details of the procedure, in which high purity acetone was used as the solvent, are described in an earlier report [11]. Aerosil mixtures are usually characterized in terms of the aerosil density defined as $\rho_a = m_a/V_{LC}$, where m_a is the mass of aerosol and V_{LC} is the volume of 8CB (as the density of the LC is ~1 g cm^{-3}, ρ_a can be taken to be m_a/m_{8CB}). We have carried out studies on composites with $\rho_a = 0.03$, 0.05 and 0.10 g cm^{-3} (the unit is dropped hereafter) as well as on pure 8CB.

The details of the high pressure apparatus used have already been described in earlier articles [14,15]. It essentially consists of the sample sandwiched between two optically polished sapphire rods enclosed in an elastomeric tube, serving not only as a container but also to isolate the sample from the liquid pressure-transmitting

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medium. The phase transition is detected by monitoring the intensity of a He–Ne laser beam transmitted through the sample. The sample pressure was measured using a precision Heise gauge. The experiments were always conducted along isobars and in the cooling mode, i.e. keeping the pressure constant at any desired value and decreasing the sample temperature at a constant rate of ∼1 °C/min from the isotropic phase.

3. Results and discussion

3.1. Phase diagram

Fig. 1 shows the raw trace of the temperature variation of the transmitted intensity obtained for the pure and $\rho_a = 0.03$ composite samples at two different pressures, viz., 31 and 227 MPa for 8CB, and 68 and 192 MPa for $\rho_a = 0.03$. The abrupt variation in the transmitted intensity in an otherwise smooth background signifies the occurrence of Iso–N phase transition. Notice that the signature of the transition is very clear for the composite case as well. Similar traces were obtained for the other two composites also. The pressure–temperature phase diagram for all the four materials – pure compound and the three composites – are shown in Fig. 2(a)–(d). The most important point to be noticed, from an experimental point of view, is that the data appears smooth over the entire range of pressure studied for the composites, a clear indication that the network remains intact even at elevated pressures and therefore suitable for quantitative analysis. Fig. 3 displays the T_{Iso-N} value at a few selected pressures as a function of ρ_a. The non-monotonic change in T_{Iso-N} with increasing ρ_a, characteristic
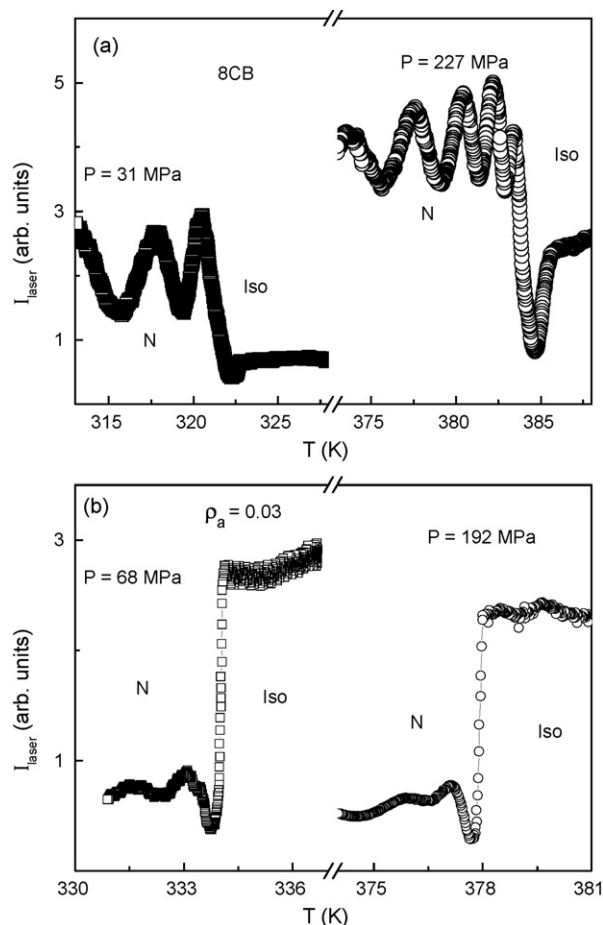

Fig. 1. Raw intensity vs. temperature scans for (a) the pure compound 8CB and (b) an aerosil–LC composite with $\rho_a = 0.03$ at two representative pressures.

of the aerosil–LC composites is seen at elevated pressures also. Further, the "amplitude" of this feature, as quantified by the difference between the values for $\rho_a = 0.05$ and 0.1, increases with increasing pressure: while at room pressure there is a small difference of ∼0.03 K, it increases to 2.7, 5.5 and 7.8 K at 40, 140 and 220 MPa, respectively, and can be described by a linear expression with the difference increasing at a rate of 0.028 K/MPa.

The thermal behaviour of the LC–aerosil systems has been analysed in terms of different theoretical models [16–18]. Two theories to consider for dealing with the density dependence of the first-order N–Iso transition are a pinned-boundary-layer (PBL) and a random-field (RF) model. In both the models, one assumes that a fraction p of the LC material is quenched and does not participate in any ordering transition. In effect, this partitions the LC material into ordering and nonordering masses. For the PBL model, the orientational anchoring at the silica surface is so strong that the LC material in the boundary layer is quenched and the remaining LC behaves as pure bulk material. For the RF model, the quenched LC is simply distributed randomly in space leading to an additional reduction of the average order in the remaining material affecting the latent heat of the N–Iso transition. The quenched fraction p may be related to the experimentally known quantity ρ_a as $p = l_b A \rho_a$, where A is the specific surface area of the aerosil and l_b is the boundary layer thickness [16]. Several predications of these models are not consistent with experimental observations and as an improvement, a model based on surface-induced order (SIO) that converts the isotropic phase into a paranematic phase at the aerosil interface, was proposed [16]. When SIO is taken into account the theory seems to predict the behaviour seen at least in low aerosil concentration regime. It has been suggested that at very low ρ_a the RF model is a viable approximation: the aerosil strains can move around in the sample and anneal elastic strains, thus achieving relatively large nematic domains randomly oriented by an aerosil strand within them, while at higher ρ_a this shift can be modelled through elastic-strain (ES) approach. However, for the cyanobiphenyl samples it has been found that even for very low aerosil fractions ($\rho_a = 0.005$) the transition temperature shift is already slower than that predicted by RF model [16,19]. Even the model by Caggioni et al. [17] which considers a crossover from a random-dilution regime to a random-field regime also does not fully reproduce the experimentally observed trend. Thus none of the existing models have satisfactorily reproduced the experimentally observed non-monotonic dependence of T_{N-Iso} on the aerosil concentration. In the background of this scenario, we just make a suggestion that application of pressure compacts the system and perhaps make the network move in the direction of a stiffer gel (all the three composites used here are expected to be in the soft gel regime [2]).

3.2. Quantitative analysis of the phase boundary

According to classical thermodynamics, the pressure-dependence of the transition temperature of a first order transition (as is the case for the Iso–N transition) can be described by the Clausius–Clapeyron equation:

$$\frac{dT}{dP} = T\frac{\Delta V}{\Delta H} \tag{1}$$

If the transition volume ΔV and the transition enthalpy ΔH are considered to be independent of pressure, and are given by their values at atmospheric pressure, then Eq. (1), which results in a linear relationship (with a slope, $m = dT/dP$) between the transition temperature and transition pressure, can be used to describe the phase boundary. In fact, to a first approximation this appears to be valid in the present situation also (blue-coloured lines in Fig. 2). The slope (m) values determined for 8CB as well as the three aerosil composites are shown in Table 1. The surprising feature is the alter-
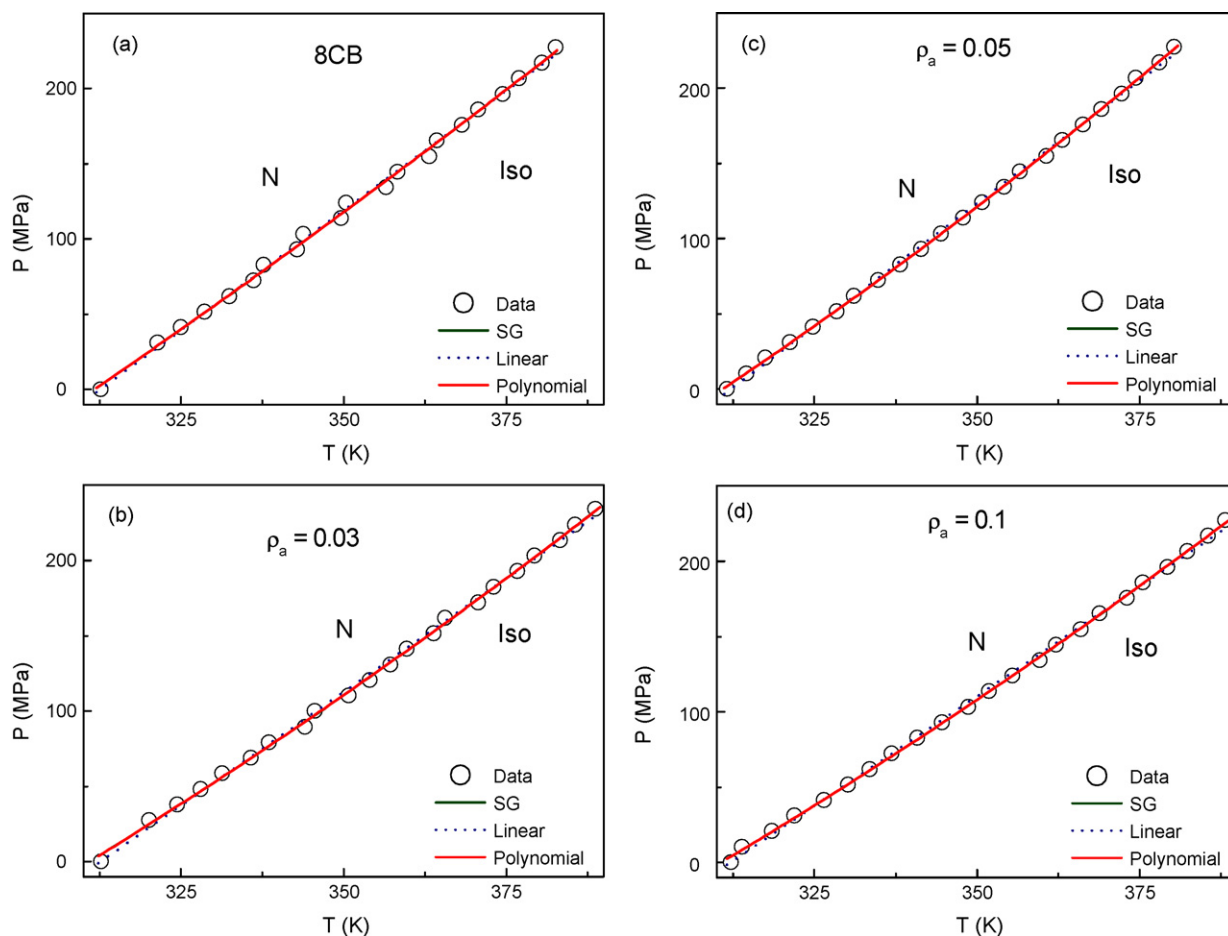
Fig. 2. The pressure–temperature phase diagrams obtained for (a) 8CB, and the aerosil–LC composites with (b) $\rho_a = 0.03$, (c) $\rho_a = 0.05$ and (d) $\rho_a = 0.10$. The circles represent the experimental data. The blue dashed curve represents the fitting to the straight line, the red solid line to a second degree polynomial Eq. (2) and the green solid line to the Simon–Glatzel equation (Eq. (3)). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

nation in the value of m with increasing ρ_a, mimicking the $T_{\text{Iso–N}}$ variation with aerosil concentration. We shall return to this point later.

Generally, phase boundaries in the $P–T$ plane are not straight lines and therefore have been described by different empirical relations: an obvious choice has been higher degree polynomial expressions. In fact, it has been shown by Horn [20] and Shashidhar [21] that for many compounds the $P–T$ boundary of the Iso–N transition can be described by a second degree polynomial,

$$T = a + bP + cP^2 \qquad (2)$$

The fitting to the data definitely improves with Eq. (2) in comparison to that for a straight line (red coloured lines in Fig. 2). For example, in the case of 8CB, the cumulative error reduces by 16% with Eq. (2). Van Hecke [22] has proposed that the data (reported by various authors) for as many as 53 different compounds, the N–Iso boundary in the $P–T$ plane can be described by a universal expression with the coefficients (in the range bracketed by the limits indicated by the $\pm$ sign) $b = (3.8 \pm 0.6) \times 10^{-3}$ K/bar

and $c = (-2.5 \pm 1) \times 10^{-6}$ (K/bar^2). Indeed the data for 8CB and the composites studied here agree with this universality concept (see Table 1). It should however be noted that despite the success of this polynomial expression, it remains a mathematical equation, with no physical background. It further has the drawback that while interpolations within the data limits are acceptable, extrapolations can be dangerous, owing to the increasing curvature with increasing pressure. Another expression, especially successful in describing melting transition in a variety of materials (including liquid crystals), is the Simon–Glatzel equation [23]

$$\frac{P}{A} = \left(\frac{T}{T_0}\right)^n - 1 \qquad (3)$$

implying the law of corresponding states and containing only two material-dependent constants, A and n (In the form used here the reference pressure P_0 is taken as room pressure and therefore T_0 corresponds to $T_{\text{N–Iso}}$ at room pressure). In addition, this equation is obtained using the Clausius–Clapeyron equation in the linear approximation of the pressure dependence of the volume change

Table 1
Parameters extracted from the fit of the $P–T$ phase diagram data for materials with different aerosil concentrations (ρ_a) to linear (m), second degree polynomial (b and c) and the Simon–Glatzel (A and n) equations (see text for details).

ρ_a	m ($\times 10^{-2}$ K/MPa)	b ($\times 10^{-2}$ K/MPa)	c ($\times 10^{-4}$ K/MPa^2)	A (MPa)	Exponent n
0	31.4 ± 0.3	33.5 ± 1.2	−0.88 ± 0.5	567 ± 154	1.6 ± 0.4
0.03	33.1 ± 0.3	36.7 ± 1	−1.48 ± 0.4	415 ± 69	2.0 ± 0.3
0.05	30.6 ± 0.2	34.0 ± 0.4	−1.5 ± 0.15	427 ± 30	2.1 ± 0.1
0.1	34.2 ± 0.3	38.0 ± 0.6	−1.67 ± .25	397 ± 37	2.0 ± 0.2

at the melting point. It may be mentioned that the N–Iso transition, although quite different from a crystal melting transformation, is actually the point at which the orientational order melts. Notice that when n takes a value of 1, Eq. (3) leads to a linear relationship between pressure and temperature. The coefficients A and n determined by fitting the data for all the materials studied here is shown in Table 1 (The quality of fitting is nearly the same as that with Eq. (2)). While it is not difficult to get these coefficients from such a fit, a proper determination of the errors associated is not trivial since Eq. (3) is transcendental in nature. Therefore, we followed the method suggested by Babb [24] in which the errors on A and n are determined by performing the fitting while one of them is held fixed. The exponent n obtained shows a non-monotonic behaviour, although the values are much higher for the composites. The parameter nA/T_0 represents the slope of the phase boundary at T_0; the calculated values of this parameter are quite close to the slope obtained from the linear fit (Eq. (1)). As seen from Eq. (1), the volume change at the transition can be calculated using this slope, the transition temperature and transition enthalpy at room pressure. Employing ΔH values obtained from differential scanning calorimetric measurements (carried out at a slow heating rate of 0.3 °C/min), the transition volumes were determined. The dependences of ΔH and ΔV (normalized with respect to ΔV for pure 8CB) on ρ_a are shown in Fig. 4(a) and (b); the variations of both appear to be mirror reflections of the dT/dP dependence on ρ_a (Fig. 4(c)). Volumetric measurements for the aerosil composites are necessary

Fig. 4. The dependences of (a) ΔH and (b) ΔV and (c) the slope dT/dP on ρ_a. In panels (b) and (c), the error bars are smaller than the size of the data marker used.

to test the non-monotonicity of ΔV with aerosil composition. The values seen for $\rho_a = 0.1$ composite seems to suggest that the N–Iso transition which is weakly first order even for the bulk, gets further weakened at least by an order of magnitude in transition enthalpy and transition volume.

In summary we have performed the first high pressure measurements on a nanocolloidal system comprising a nematic liquid crystal and its composites with aerosil particles in the soft gel regime. Application of pressure keeps the gel structures intact but appears to push the system towards a stiffer regime. Quantitative analysis of the pressure–temperature phase diagrams using a simple linear, a second degree polynomial and the Simon–Glatzel equation have been performed which reveal interesting behaviour of parameters such as the transition temperature, slope of the phase boundary and the transition volume. High pressure experiments on such composites exhibiting different phase sequences, including the nematic–smectic A transition are being planned and are expected to yield valuable information regarding the influence of pressure on the random disorder imparted by the aerosil particles.

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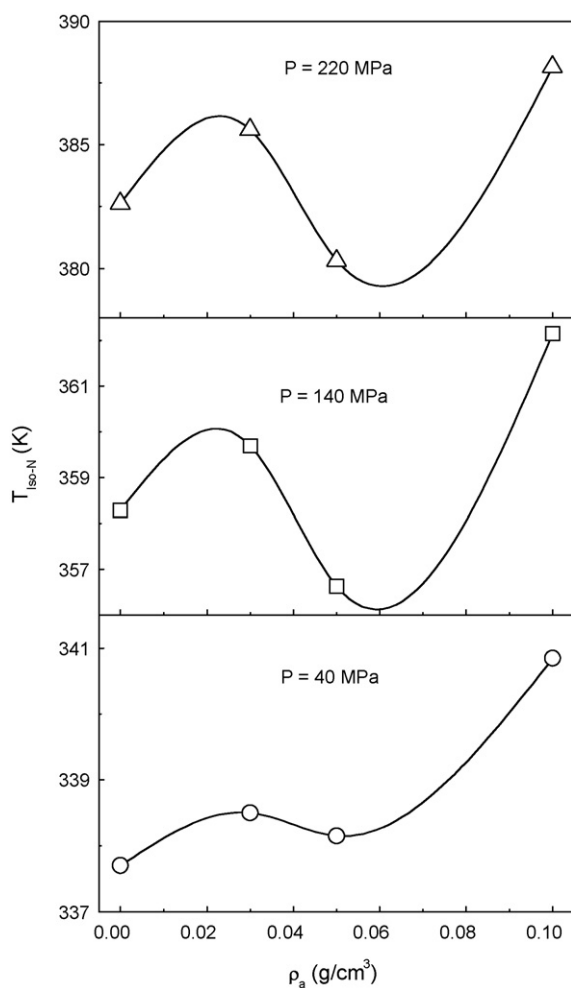[3] R. Eidenschink, W.H. de Jeu, Electron. Lett. 27 (1991) 1195.

Fig. 3. The dependence of the nematic–isotropic transition temperature $T_{Iso–N}$ on the aerosil concentration in the composite, for three different pressures. The lines are only a guide to the eye.
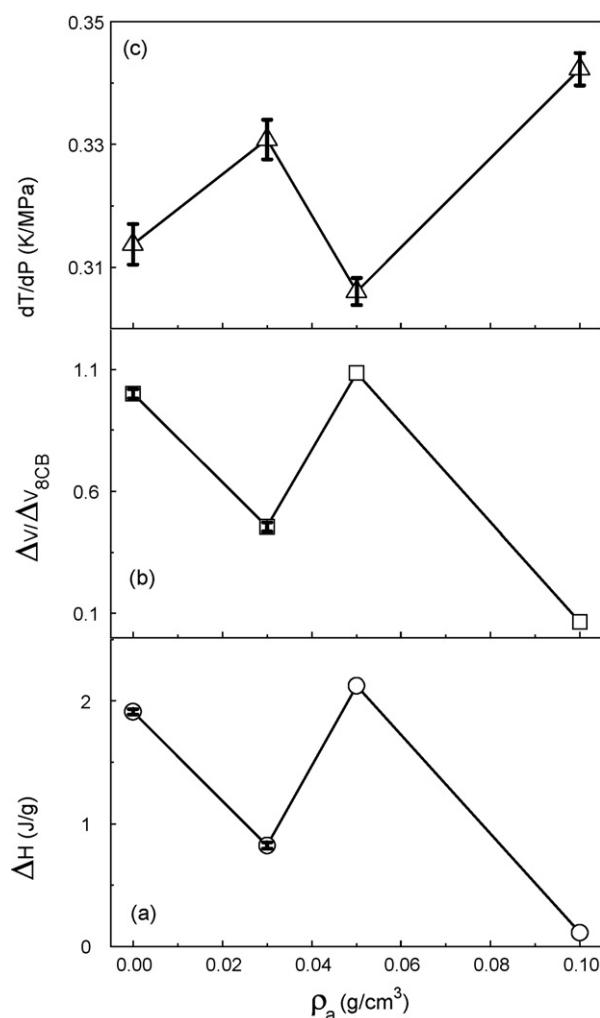
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