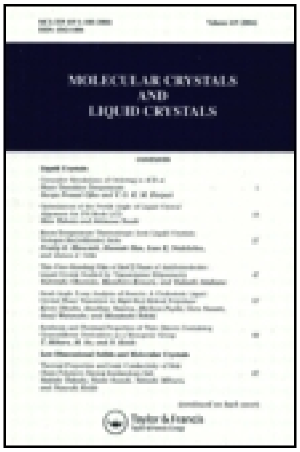

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Orientational Effects on Confined 5CB

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Abstract We report measurements of the heat capacity at the N-I transition for 5CB confined in submicron size cavities. A radically different behavior is observed depending on the orientation of the liquid crystal molecules within the cavities. A comparison with bulk measurements is also made.

INTRODUCTION

A great amount of theoretical and experimental attention has been devoted to studies of the physical properties of liquids confined in geometries more restrictive than bulk[1]. The relevance of studying confinement properties is in that they provide tests for finite-size scaling ideas and can also probe bulk critical behavior. Clearly, finite-size effects are strongly related to surface effects and properties. In addition, in the liquid crystal case and given the confining geometry studied here, it is also possible to probe effects due to orientation of the nematic director relative to the symmetry axis of the confining geometry. Nematic liquid crystal are an ideal candidate to perform these studies because they represent the simplest symmetry change.

Although much of the earlier work was performed on superfluid helium, films and confined bulk[2], very recently, a large amount of work has been devoted to studies of nematic liquid crystals confined in submicron-size nearly cylindrical cavities[3]. In particular, NMR studies[4] on 5CB confined in Nuclepore membranes provided information upon the surface-induced nematic ordering over a very broad temperature range. The surface order parameter was found to be temperature independent so that partial wetting was realized. Further[5], it was found that the director pattern within the cylindrical cavities was dependent on the surface elastic constant K_{24}. The NMR work led to the first experimental determination of K_{24}. Building on the success of the NMR studies, we decided to perform heat capacity studies on 5CB confined on Anopore membranes[6] and investigate the effects on the first order nematic-isotropic (N-I) phase transition. The study of first order phase transition has seen little progress and a complete real understanding does not exist. The main reason is that even in the infinite system, the correlation length is finite at the transition. There is no theory that predicts, for example, how the latent heat is affected by making the system finite.

This work was performed in parallel to similar NMR studies which have been published elsewhere[7]. Our heat capacity work on confined 8CB at the N-I and smectic A-to-nematic phase transitions will appear separately.[8]

EXPERIMENTAL DETAILS

Our experimental studies were carried out in the 2000 Å, capillary-like cylindrical cavities of Anopore membranes filled with the liquid crystal material 4'-n-pentyl-4-cyanobiphenyl (5CB). We chose Anopore over Nuclepore membranes because of their larger surface-to-volume ratio. A scanning electron microscope (SEM) photograph of an Anopore membrane is shown in Fig. 1.

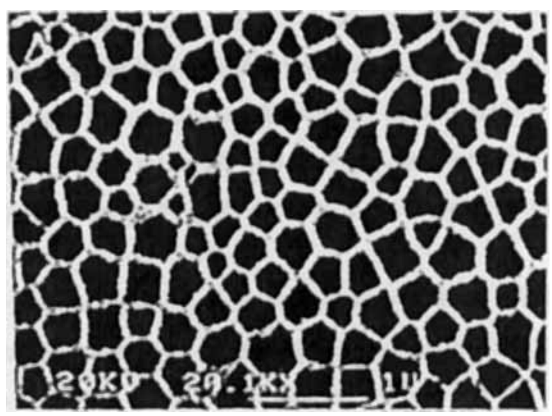

FIGURE 1 Scanning electron microscope photograph of an Anopore membrane

The membranes, produced from an electrochemical anodizing process, are made from a high purity alumina matrix with the cavities oriented perpendicular to the membranes' surface and extending through its 0.06 mm thickness. These rather flat membranes were dipped in nematic material and heated above the N-I transition to homeotropic surface alignment of liquid crystals[9], was used in this work to treat the cavities. The amount of Lecithin left in the cavities was estimated to be less than 3% by weight of the liquid crystal introduced.

The deuterium nuclear magnetic resonance (^{2}H-NMR) technique is ideally suited to probe the director alignment[5] and orientational order parameter[4,7] of liquid crystals in confined systems as illustrated in Fig. 2.

The ^{2}H-NMR spectral patterns for the untreated and macroscopically aligned bulk samples are identical revealing that axial alignment is present in the untreated cavities. However, the lecithin treated sample yields a quadrupole splitting that is

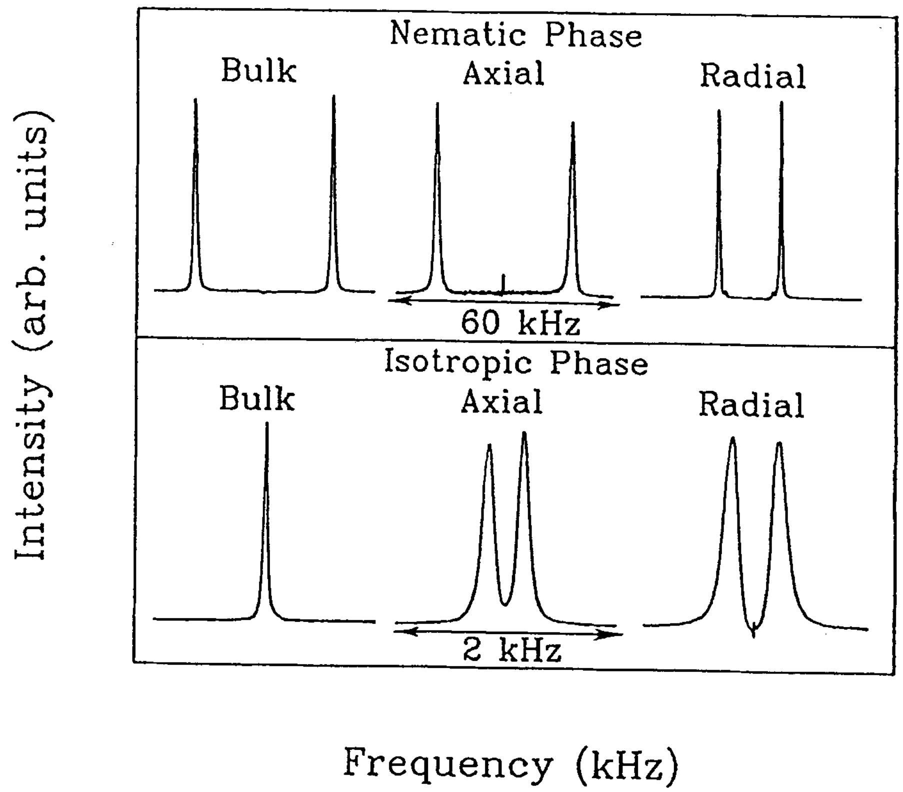

FIGURE 2 ^{2}H-NMR spectral patterns of the untreated (axial) and lecithin treated (radial) Anopore membranes filled with 5CB-βd_2 compared with the macroscopically aligned bulk as modified from Ref.7. The spectrum were recorded at T_{NI}-T=11 K (nematic phase) and T-T_{NI}= 2.3 K (isotropic phase) with the cavity axis parallel to the magnetic field.

insure complete wetting of the cavities. The excess liquid crystal outside the cavities was completely removed by pressing the Anopore membranes between Whathan filtration paper.

One membrane, containing about 3 mg. of 5CB, 0.9 cm. in diameter and 0.006 cm. thick, was placed on top of a 1 cm. by 0.013 cm. thick sapphire disk. Sapphire was chosen as the substrate because of its good thermal properties, rigidity and flatness. An evanohm heater wire (0.005 cm. diameter) and a thermistor flake (0.013 cm. square cross-section) were attached to the sapphire disk with a small amount of Stycast 1266 epoxy. The experimental cell (disk plus Anopore) was completely enclosed and thermally anchored to a brass ring. The brass ring was weakly anchored to an evacuated copper chamber sitting on top of a water bath.

For our measurements, we used an A.C. heat capacity technique. Sinusoidal heating at 0.11 Hz. was applied to the evanohm heater. The operating frequency was chosen based on frequency scans performed at several temperatures. The internal and external time constants of the calorimeter, as determined from the frequency scans, were independent of whether the Anopore membrane was simply rested on top of the sapphire disk, or, whether it was tied to the sapphire with dental floss or fine silk thread. Only a marginal increase in the addendum heat capacity due to the dental floss was detected. The temperature oscillations were detected with the previously D.C. biased thermistor flake using lock-in amplification. The temperature oscillations of the experimental cell were kept at 3.5 mK, while, the temperature of the cell was typically 60 mK higher than the regulated brass ring provided with a commercially calibrated platinum thermometer. The heat capacity was obtained by monitoring the temperature and temperature oscillations of the cell as the temperature of the brass ring was changed. Data was averaged at each temperature for nearly 20 min. The heat capacity of the addendum materials (sapphire disk, heater, thermistor and membrane) was first determined. This was later subtracted from the total heat capacity measured with liquid crystal present.

RESULTS

Anopore membranes are chemically compatible with many solvents, allowing the surface to be treated with different surfactants. Lecithin, known to produce one-half that of the aligned bulk. This indicates that the directors are constrained in a plane perpendicular to the magnetic field in a radial-type alignment which is expected since lecithin is known to introduce perpendicular anchoring conditions[9]. For a truly isotropic sample, there is no quadrupole interaction resulting in a single absorption line. The presence of surface-induced orientational order above the nematic-isotropic transition temperature is responsible for the quadrupole splitting in both the axial and radial configured systems. Analysis of the quadrupole splitting as a function of temperature reveals rather different temperature dependence behaviors of the orientational order parameter at the surface, S_0, and substantially larger values of S_0 in the radially aligned sample (S_0=0.11) than in the axially aligned sample (S_0=0.021) 80 mK above the nematic-isotropic transition temperature.

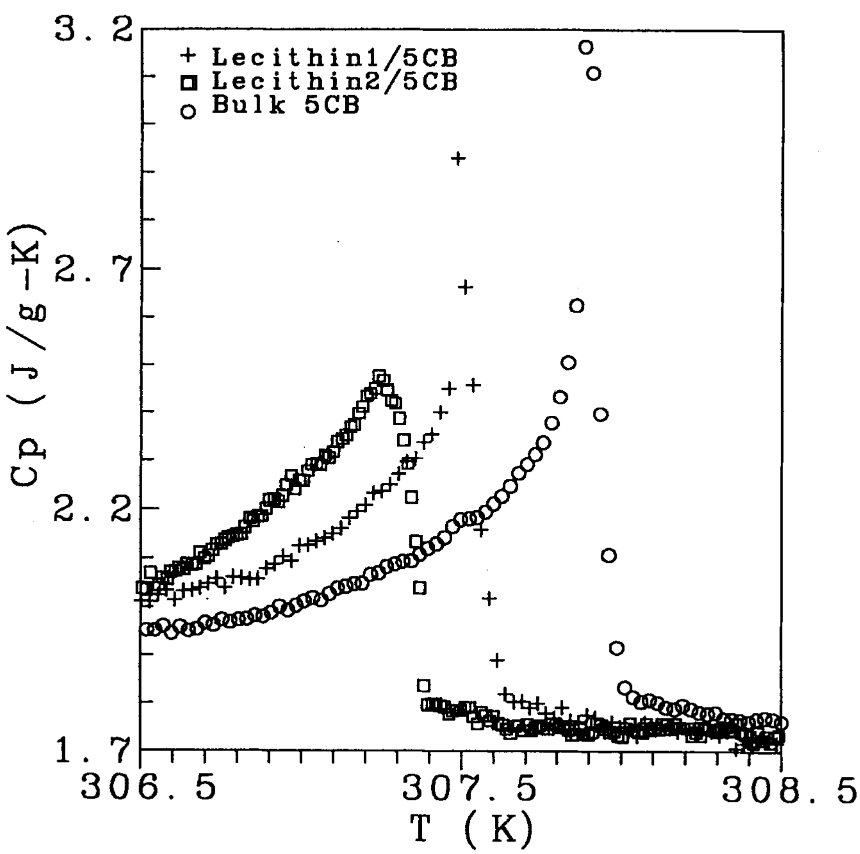

FIGURE 3 Specific heat results for bulk 5CB and two 5CB-Lecithin mixtures. The lecithin content is 20% (+) and 50% (□) approximately.

In order to establish the character of the nematic-isotropic phase transition we have also measured the heat capacity of 5CB confined in untreated and Lecithin-treated cavities. Also, and in order to facilitate data comparison, we performed heat capacity measurements on a bulk sample of 5CB and two 5CB-lecithin mixtures. The results for bulk 5CB as well as for the two different mixtures of 5CB and Lecithin are shown in Fig. 3.

Our bulk heat capacity results are very similar to those found in the literature[10], exhibiting all the features characteristic of a weakly first order phase transition. The addition of Lecithin up to about a 20% mixture (+) does not appear to introduce major changes in the overall shape of the heat capacity peak. A slight heat capacity peak suppression and a shift in the transition temperature are observed. These effects are further enhanced by increasing the Lecithin content present in the sample to nearly a 50% mixture (□). A minor broadening of the nematic-isotropic phase transition is also seen. However, the sharp decrease in the heat capacity at the transition temperature is retained in all cases.

The results of our heat capacity measurements for 5CB confined in the 2000 Å Anopore membranes treated and untreated cavities are plotted as a function of temperature in Fig. 4. Bulk data is also included for comparison.

Several features of the data emerge from Fig. 4. In the untreated cavities, where the liquid crystal molecules are aligned along the cavities axis what is observed is a suppression of the specific heat peak, a broadening of the transition, but most importantly, the dramatic decrease in specific heat at the N-I phase transition is retained. This is to be contrasted with the Lecithin treated cavities where there is a larger suppression of the peak, further broadening of the phase transition and, as the N-I temperature is approached, a more gentle decrease of the specific heat on the isotropic side. This is unlike the Lecithin added bulk samples where the sharp heat capacity decrease at the phase transition was unaffected. A broader and more rounded phase transition is also seen for liquid helium confined in Nuclepore membranes[2].

The transition temperatures, consistent with the observations in Ref. 3, are shifted to lower temperature by 0.66 and 1.37 K for the untreated and treated cases respectively. The temperature shift in the treated cavities case far exceeds that observed in the heavily Lecithin-contaminated samples shown in Fig. 3. Impurities are present in these measurements and can certainly contribute to transition temperatures shifts and rounding of phase transitions. The magnitude of the effects we observe are too large to be accounted for by the presence of impurities. Thus, we believe that the different orientation of the liquid crystal molecules within the cavities is the major ingredient in these results.

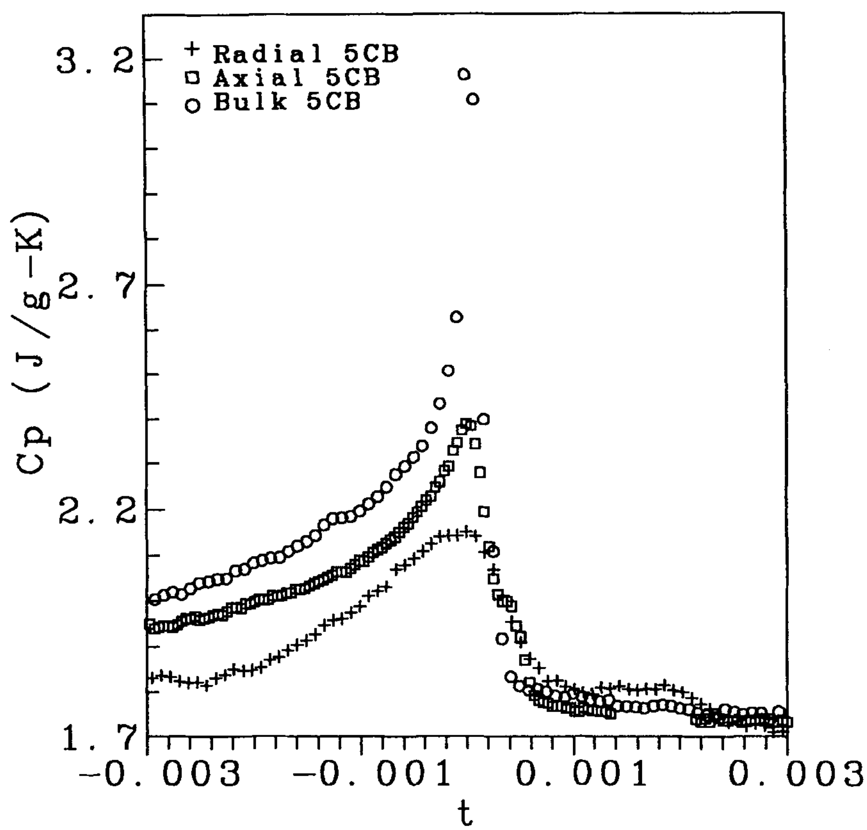

FIGURE 4 Specific heat as a function of reduced temperature for 5CB confined in untreated and treated cavities. Bulk data is also shown.

To emphasize the differences in specific heat, we have replotted the data from Fig.3, as a function of reduced temperature. This is shown in Fig. 5. Comparing with the Lecithin mixtures of Fig. 4, it is clear that the confined specific heat results are quite different from the Lecithin added bulk samples results.

Finally, we note from Fig. 3, that although the specific heat on the isotropic side of the transition is of nearly the same magnitude, on the nematic side is quite different and it is much lower for the radially aligned treated cavity case. This is in contrast to the bulk samples of Fig. 5, where the specific heat is the same in the isotropic as well as nematic side of the transition. The good match on the isotropic side of the transition for the data of Fig. 3 is also an indication of a good thermal contact between sapphire substrate and Anopore membrane.

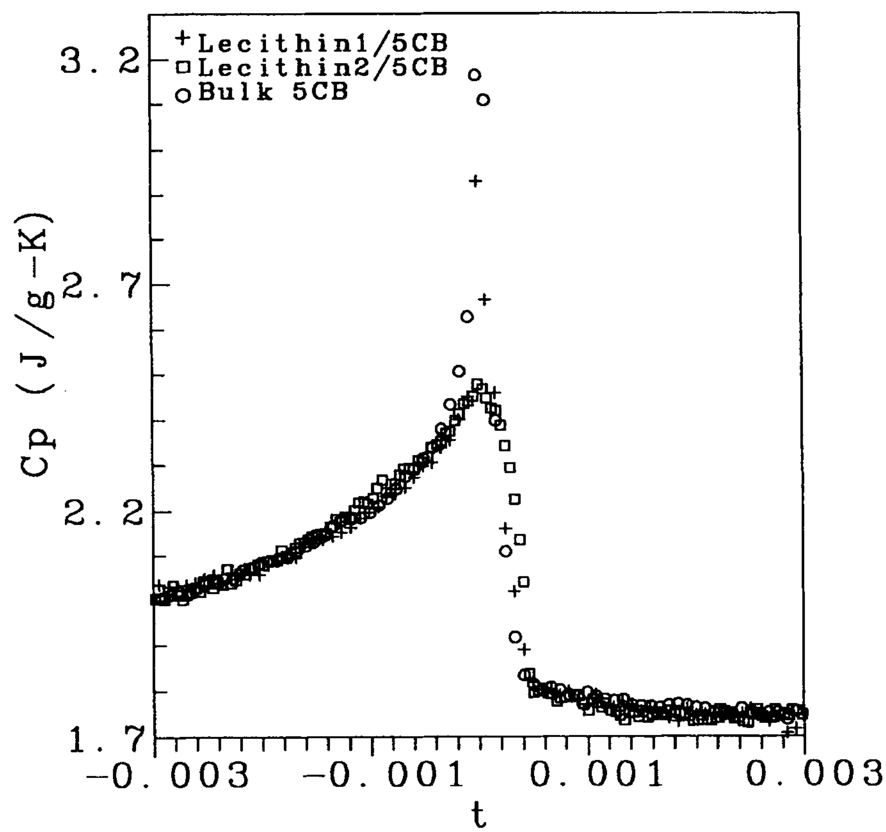

FIGURE 5 Specific heat as a function of reduced temperature for data of Fig. 3. Note the perfect matching in the nematic and isotropic sides.

We should also note that the area under the peaks in Fig. 5, which represents part of the latent heat of the transition and pretransitional effects, is marginally affected by the added lecithin[11]. This is in contrast to the confined data where the area under the peak, as compared to the bulk data, decreases by 20% and 50% for the axial and radial cases respectively.

In order to understand the above observations, we are presently analyzing our data starting from the Ginzburg-Landau free energy and incorporating the magnitude and temperature dependence on the order parameter as obtained from the NMR work discussed above and in Ref. 7. We are also continuing our measurements with a higher temperature resolution and as a function of chain, pore size and surface treatment in order to understand the nature of the observed effects.

In conclusion, several interesting features are emerging from the study of confined liquid crystals. The nematic to isotropic phase transition appears to be strongly sensitive to the director orientation within the nearly cylindrical cavities. Different magnitudes of specific heat peaks, temperature shifts, broadening and rounding of the N-I phase transition are found as a function of director orientation. Further work to understand these effects is in progress.

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11. Note that the AC technique is not suitable to detect the latent heat at a first-order phase transition. In our case, since broadening is present, some of the latent heat is included by the area under the curve.