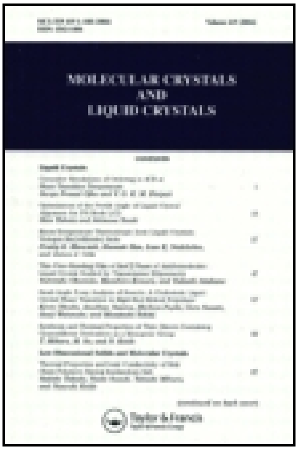

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# Liquid Crystal Wetting in Cylindrical Pores

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# Liquid Crystal Wetting in Cylindrical Pores

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We have performed a calorimetry and deuterium nuclear magnetic resonance study for a member of the liquid crystal homologous series, $\bar{n}.O.\bar{m}$ , in bulk and confined to the 0.2 µm cylindrical pores of aluminum oxide Anopore membranes. It was shown in an ellipsometry study by Lucht and coworkers that this material shows a prewetting nematic transition at an air interface. Thermodynamically, at the Anopore solid pore walls these liquid crystals also exhibit unique wetting properties: a distinct signature in the specific heat, a "bump" at a temperature approximately 0.5 K above $T_{NI}$ is found. We believe that such signature is related to the manner that the nematic liquid crystal wets the solid surfaces.

*Keywords:* wetting; confinement; specific heat

## I. INTRODUCTION.

There is a wealth of phenomena that thermotropic liquid crystals exhibit when at a liquid crystal-solid wall or a liquid crystal-vapor interfaces. Several investigations employing a variety of experimental techniques have been aimed at understanding the wetting behavior of surfaces by liquid crystals, specifically focusing on the manner in which a given liquid crystal phase grows at an interface.

At liquid crystals-solid interfaces, for example, for cyanobiphenyl liquid crystals and in particular, for nematic 5CB confined to aluminum oxide Anopore membranes whose pores were previously treated with a variable length aliphatic acid chain surfactant, an orientational order wetting transition from partial to quasi-complete was found with increasing aliphatic chain length[1]. This effect was manifest in deuterium nuclear magnetic resonance (DNMR) study as the pretransitional temperature dependence of the adsorption parameter changed from weak to strong, but remained non-divergent.

Also, in aliphatic acid treated Anopore but imbedding smectic 12CB that lacks the nematic phase, complementary specific heat and x-ray scattering studies showed the existence of surface-induced discrete smectic order in the isotropic phase[2]. The signature in the specific heat consisted of small peaks that were present at temperature above the bulk smectic-A to isotropic transition temperature. In the complementary x-ray scattering studies, the scattered peak intensity increased in a stepwise, discrete manner. These effects were not seen on the bare Anopore surface nor when the pores were treated with other surfactants like lecithin. Such wetting features were neither present when the imbedded liquid crystal also possessed the nematic phase (e.g. 5CB or 8CB). Thus, the 12CB in Anopore results were understood in terms of a surface-induced bilayer-by-bilayer growth of the smectic phase at the solid wall.

Using an ellipsometric technique, measurements were performed to study the wetting behavior at the free surface of the isotropic phase for a variety of liquid crystal compounds[3]. It was observed, for the first time, that a prewetting transition occurred above the bulk nematic to isotropic phase transition. For the liquid crystal compound $\overline{10}.O.\overline{8}$, this was manifest as a sharp rise in the ellipsometry coefficient at a temperature 0.3 K above the nematic to isotropic transition temperature $T_{NI}$.

Motivated by those studies, here, we report on DNMR and calorimetry results for the liquid crystal compound used in Ref. [3] at an air interface, but most importantly, while confined to Anopore membranes. Its behavior is contrasted to that of 8CB also in Anopore[4] suggesting that $\overline{10}.O.\overline{8}$ exhibits unique wetting properties at a solid wall.

## II. EXPERIMENTAL DETAILS.

For the specific heat studies we used the liquid crystal compound $\overline{10}.O.\overline{8}$ which exhibits the nematic to isotropic phase transition at about 365 K. Its nematic phase of ~ 3 K width, is preceded by a smectic-A (and a lower temperature) smectic-C phases; therefore, the phase sequence is similar to that in 8CB. For the DNMR studies, the $\overline{1}\overline{0}.O.\overline{8}$ liquid crystal material was deuterated at the alfa position; for specific heat studies, the non-deuterated compound was investigated.

Anopore membranes are commercially available as 47 mm diameter disks that can be easily cut to any desired size or shape. Produced through an electrochemical anodizing process, they are made from a high purity alumina matrix with the 0.2 *μm* diameter pores extending through the membrane's 60 *μm* thickness. The pores are cylindrical, non-interconnected, and withstand a variety of chemical surfactant treatments. The Anopore porosity is approximately 40 %.

Nuclear magnetic resonance (NMR) is an extremely valuable tool in liquid crystal studies as it probes the orientational order, director configurations, and molecular dynamics. Deuterium NMR has been extensively and successfully applied to the study of liquid crystals in bulk or confined to several porous materials[5]. The spectrometer used consists of a 4.7 Tesla (200 MHz for protons, 30.8 MHz for deuterium) superconducting magnet fitted with a homemade probe and electronics. The probe head is inserted in an oven housed in the magnet bore, through which a mixture of ethylene glycohol and water circulates from an external temperature controlled bath. The probe head is provided with a calibrated 100 $\Omega$ platinum thermometer that is read after each DNMR pulse sequence and averaged over the accumulated scans. The temperature stability over the entire DNMR spectra acquisition time is better than ± 0.05 K with a resolution of ± 0.005 K.

The deuterated liquid crystal bulk sample partially fills a cylindrical tube, ~ 5 *mm* in diameter and 15 *mm* long. The tube axis is perpendicular to the filed; the half filling of the tube with the liquid crystal ensures the presence of an air interface of approximate dimension 3.5 x 15 *mm*. Measurements used a quadrupole-echo pulse sequence ($90^{\circ}_{x}$- $\tau$ - $90^{\circ}_{y}$- $\tau$ - acquisition) with full phase cycling: $\tau \cong$ 100 *μs*, $90^{\circ} \cong 3$ μs, a 1024 to 2048 point acquisition, and a last delay of 300 *ms*. The sequence is accumulated for up to 50000 scans over a 2 hours period. The final spectrum is obtained by a complex Fourier transform of the single zero-filled free induction decay. In the nematic phase, the presence of orientational order splits the quadrupolar resonance line by[6]:

$$\delta\nu = \tfrac{1}{2}\,\delta\nu_0\, S\,(3\cos^2\theta_B - 1) \qquad (1)$$

where $\delta\nu_0$ is the maximum possible splitting observable for completely aligned bulk nematic sample, $S$ is the scalar order parameter, and $\theta_B$ is the angle that the nematic director (**n**) makes with the static NMR field ($\mathbf{B_0}$). For bulk, $\theta_B = 0^o$ due to the uniform $\mathbf{B_0}$ field alignment of **n**. For a typical bulk nematic liquid crystal sample, the DNMR spectral pattern consists of two sharp absorption lines, typically 200-400 Hz full-width-half-maximum (*fwhm*), separated by an amount $\delta\nu_{bulk} = \delta\nu_0 S_0$, the quadrupolar splitting.

The specific heat was measured using an *ac* calorimetry technique that permits accurate measurements for small samples near a phase transition[4]. Measurements take place under near equilibrium conditions since the sample is set into very small temperature oscillations about a precisely determined average temperature. The amplitude of the resulting temperature oscillations is inversely proportional to the heat capacity, $C$, of the sample. This amplitude, $T_{AC}$, can be written as:

$$T_{AC} = (Q_0 / 2\,\omega C)\,(\,1 + (\omega\tau_i)^2 + (1/\,\omega\tau_e)^2\,)^{-\frac{1}{2}} \qquad (2)$$

where the thermal relaxation times are defined as $\tau_e = C/K_b$ (external) and $\tau_i^2 = \tau_\theta^2 + \tau_h^2 + \tau_s^2$ (internal). The individual relaxation times are $\tau_\theta = C_\theta/K_\theta$, $\tau_h = C_h/K_h$, and $\tau_s = C_S/K_S$ corresponding to the thermometer, heater, and sample respectively. Qualitatively, the internal time constant is the time required for the entire assembly to reach equilibrium with the applied heat while the external time constant is the time required to achieve equilibrium with the surrounding bath.

The calorimeter has an internal time constant of about 1.26 seconds (0.79 Hz high frequency roll off) and an external time constant of about 31.4 seconds (0.032 Hz low frequency roll off). The addendum heat capacity is 42 mJ/K at 303 K, increasing linearly with temperature at a rate of 0.286 mJ/K$^2$. The voltage frequency was 76 mHz and the induced temperature oscillations were kept on the order ~ 3 mK peak-to-peak. Data, spaced at roughly 10-15 mK intervals, is averaged at every temperature for 8 to 10 minutes. The sample for the specific heat studies consisted of a single Anopore membrane cut to a disk of 9 *mm* diameter, containing about 2.5 *mg* of $\overline{1}\,\overline{0}.O.\overline{8}$ liquid crystal.

## III. RESULTS.

The nematic prewetting transition[3] arises from the formation at the free air interface of a surface layer of nematic material a few nanometers thick, resting above the isotropic fluid. Since a nematic layer is orientationally ordered, it may be detectable by DNMR. This is difficult given that the number of (deuterated) molecules forming the nematic layer may be below the DNMR required sensitivity level of at least $10^{17}$ molecules. Nevertheless, encouraged by the recent success of the technique[5] to detect the molecular order in a thin liquid crystal layer coating a porous media., we attempted the experiment.

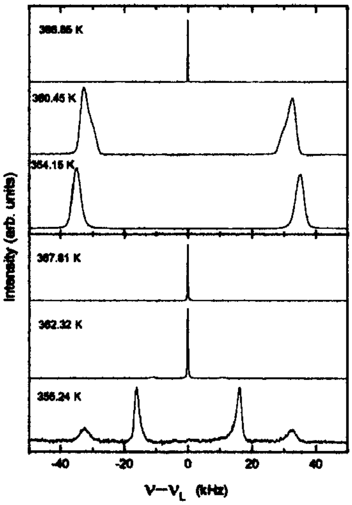

FIGURE 1. DNMR patterns for bulk (top three panels) and confined to Anopore (bottom three) $\overline{1}\,\overline{0}.O.\overline{8}$ as a function of temperature. The peaks intensity and the horizontal frequency axis have been rescaled for clarity purposes.

The bulk DNMR results are seen in the top three panels of Fig. 1. There is a high temperature central absorption peak typical of the isotropic phase. Decreasing temperature there is a transition to an orientationally ordered phase as characterized by two distinct absorption peaks, the quadrupole splitting. These peaks are unusually broad (second panel from top in Fig. 1), but become sharper at lower temperature. A wetting signature would consist of the coexistence of a prominent central peak with a much less intense quadrupole splitting at a temperature above $T_{NI}$. Due to the small air interface surface area, this was not detectable.

To increase the surface area considerably, liquid crystals are often confined to a porous media. Thus, we imbedded $\overline{1}\overline{0}.O.\overline{8}$ in Anopore membranes. Although under confinement the air interface is not present, a liquid crystal-solid interface exists and is of considerable surface area. Since we suspected that wetting phenomena may also arise under these conditions, we performed DNMR studies for Anopore confined $\overline{1}\overline{0}.O.\overline{8}$, which are shown in the bottom three panels of Fig. 1.

The liquid crystal confined DNMR results with decreasing temperature show the evolution from an isotropic peak to the coexistence of the isotropic peak with a less intense quadrupole splitting. Although this could be taken as a wetting signature, due to the nature of DNMR measurements, we are unable to unambiguously determine if the spectrum shown in the second panel from the bottom corresponds to a temperature above $T_{NI}$. What can be concluded, however, is that since this quadrupole splitting is half that of bulk, the molecular alignment at the pore walls is homeotropic, namely, molecules perpendicular to the pores' axes. With an additional temperature decrease into the smectic-C phase, the isotropic peak disappears; the quadrupole splitting grows in intensity and is accompanied by a second splitting at a higher frequency separation suggesting a molecular configuration with molecules perpendicular to the cylindrical axes and some parallel to it. The study of smectic-C materials under confinement needs to be pursued further.

Undaunted by the results of the DNMR study, we proceeded with complementary calorimetry measurements. For the bulk specific heat studies, the liquid crystal material was placed on a small, uncovered aluminum cup thermally anchored to a thin sapphire disk provided with heater and thermometer. In this manner, the liquid crystal sample possesses an air interface, but again of rather small surface area.

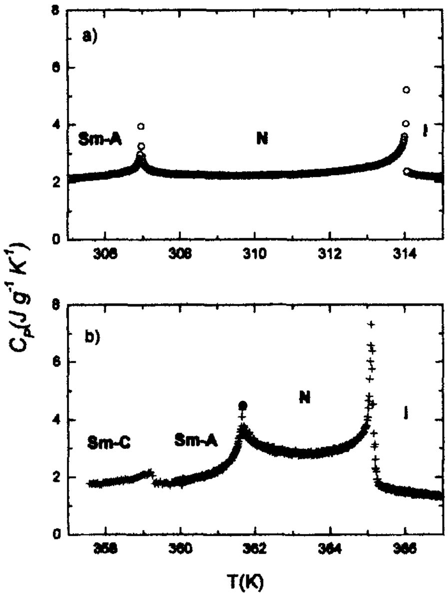

FIGURE 2. (a) Specific heat for bulk 8CB and b) for 10.O.8 showing the weakly first order nematic to isotropic and the second order smectic-A to nematic phase transitions. Also, the smectic-C to smectic-A transition is seen for $\overline{1}\overline{0}.O.\overline{8}$.

The specific heat results for bulk $\overline{1}\overline{0}.O.\overline{8}$ are shown in Fig. 2b where the weakly first order NI, the second order Sm-A-N and the Sm-C-Sm-A transitions are evident; the specific heat signature for the two high temperature transitions is like that of the better-known 8CB shown in Fig. 2a for comparative purposes. Again, given the small surface area and the large heat capacity background, no evidence of interface-induced orientational order in the isotropic phase was found.

As mentioned earlier, porous media are ideal to increase a signal since they possess large surface-to-volume ratios. We benefited from this aspect and thus imbedded $\overline{1}\overline{0}.O.\overline{8}$ to Anopore membranes. Although under confinement we are unable to probe properties at the air interface, we searched for wetting phenomena that might occur at the solid walls. The measurements were then performed, and the specific heat results for Anopore confined $\overline{1}\overline{0}.O.\overline{8}$ and 8CB samples prepared are detailed in the experimental detail section are illustrated in Fig. 3 where we concentrate on the Sm-A-N and NI transitions.

For 8CB in Anopore, Fig. 3a, the confinement effects on the weakly first order NI transition consist of suppressing, rounding, and broadening the specific heat On the nematic side of the transition pretransitional effects are manifest through the data curvature that is similar to bulk's. Once the specific heat peak maximum is reached, the specific heat decreases quite sharply in bulk, but slightly less sharply in Anopore. Similar effects occur at $T_{Sm\text{-}A\text{-}N}$ except that they are more pronounced with more noticeable specific heat peak suppression. Both transitions temperatures are downshifted by approximately the same amount, thus the nematic range is unchanged from bulk's.

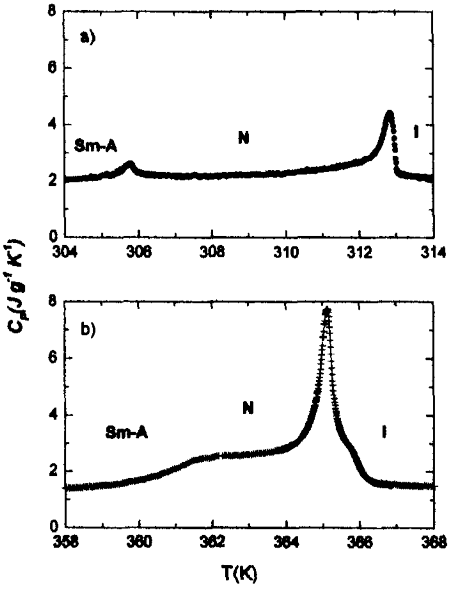

FIGURE 3. Specific heat results for (a) 8CB and (b) $\overline{1}\overline{0}.O.\overline{8}$ confined to the 0.2 μm cylindrical pores of Anopore membranes.

Confinement affects the specific heat of $\overline{10}.O.\overline{8}$ in distinct and more interesting ways than 8CB. The transition temperatures are only mildly affected by the confinement and the nematic range is unaffected from bulk. The smectic-A to nematic phase transition is strongly suppressed and highly broadened; it is in fact reminiscent of what occurs for 8CB but under the more restrictive and interconnected confinement found in by aerogel porous glass[6]. Near $T_{NI}$, the curvature on the nematic side is bulk-like; the sharp decrease into the isotropic phase, a characteristic of a weakly first order phase transition is however not present with the data exhibiting a curvature similar to that below the transition. Effectively, the specific heat peak near $T_{NI}$ seems symmetric, which is more the characteristic of a second order phase transition (e.g. the Sm-A-N peak in bulk 8CB, Fig. 2a). In addition, at T ~ $T_{NI}$ + 0.5 K, Fig. 3b, the $\overline{10}.O.\overline{8}$ specific heat exhibits what could be termed a "bump". No such feature is seen for 8CB, Fig. 3a, nor in any of our many other confined specific heat studies[7].

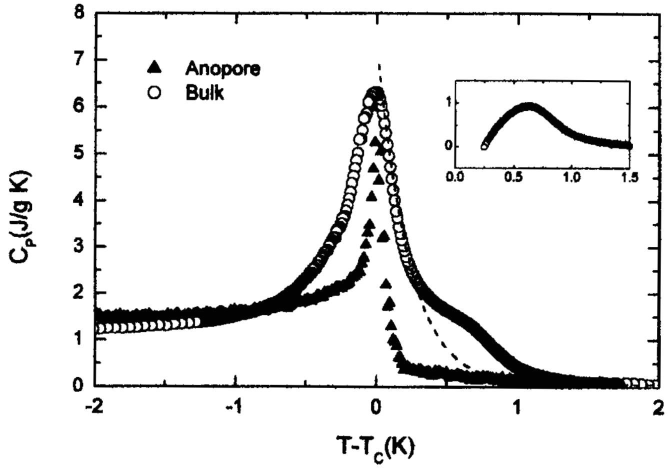

FIGURE 4. Specific heat results near the nematic-isotropic transition Inset shows the bump after an arbitrary background subtraction indicated by the solid line.

By analogy with the work in Ref. [2], we believe that this specific heat bump is a thermodynamic signature indicating the manner that the $\overline{10}.O.\overline{8}$ nematic liquid crystal wets the solid surfaces. This is the first time that we have seen any thermodynamic signature above $T_{NI}$ for a confined nematic liquid crystal. Quantitatively, we arbitrarily choose a regular background, indicated by the solid line in Fig. 4, and subtract it from the actual data. Then, the bump turns into a visible small peak shown in the inset to Fig. 4. From the ratio of the area under this peak to the total area, we estimate that at most 10 % of the molecules are ordered by the surface in the isotropic phase. Due to the strong surface influence and its orientational wetting by the liquid crystal, a nematic layer at most 10 *nm* thick is formed at the solid wall on the isotropic side of the transition. Note that the temperature location of the wetting signature and the ordered layer thickness as estimated here, are of the same order of magnitude as found at the air interface[3].

## IV. CONCLUSIONS.

Motivated by the wetting studies of Lucht, Bahr, and coworkers studies at an air interface for several liquid crystal compounds, we performed DNMR and specific heat measurement for bulk and Anopore confined $\overline{10}.O.\overline{8}$. Bulk measurements included a small area air interface while a considerably larger liquid crystal-solid wall area is present under confinement.

Bulk studies did not reveal any wetting phenomena, however, under confinement in the cylindrical pores of Anopore membranes, the specific heat peak at the weakly first order bulk NI transition became more symmetric suggesting that the confinement affects the order of the transition. In addition, at a temperature 0.5 K above the NI transition temperature, a specific heat "bump" was found and has been interpreted as a signature of nematic wetting of a solid surface. From DNMR it was concluded that the molecular configuration in the pores is homeotropic and studies with confined smectic-C materials should be interesting. It would also be interesting to partially fill the pores thus also leaving an air interface. $\overline{10}.O.\overline{8}$ is a very suitable liquid crystal material to study wetting at interfaces. We are extending these studies to include other members of the homologous series like $\overline{9}.O.\overline{8}$ as well as other confining morphologies.

## V. ACKNOWLEDGEMENTS

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### *References*

[1] G.P. Crawford, R.J. Ondris-Crawford, J.W. Doane, and S. Zumer, *Phys. Rev.* **E 53**, 3647 (1996).

[2] G.S. Iannacchione, J.T. Mang, S. Kumar, and D. Finotello, *Phys. Rev. Lett.* **73**, 2708 (1994).

[3] R. Lucht, Ch. Bahr, G. Heppke, and J.W. Goodby, *J. Chem. Phys.* **108**, 3716 (1998); R. Lucht and Ch. Bahr, *Phys. Rev. Lett.* **78**, 3487 (1997).

[4] G.S. Iannacchione and D. Finotello, *Phys. Rev.* **E 50**, 4780 (1994); *Phys. Rev. Lett.* **69**, 2094 (1992).

[5] B. Zalar, S. Zumer, and D. Finotello, *Phys. Rev. Lett.* **84**, 4866 (2000).

[6] L. Wu, B. Zhou, C.W. Garland, T. Bellini, and D.W. Schaefer, *Phys. Rev.* **E 51**, 2157 (1995).

[7] D. Finotello, G.S. Iannacchione, and S. Qian, in *"Liquid Crystals in Complex Geometries Formed by Polymer and Porous Networks"*,edited by G.P. Crawford and S. Zumer (Taylor & Francis, London 1996).