This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Dynamics of the two-dimensional melting transition of a liquid crystal confined in Anopore membranes

K. L. Sandhya; Geetha G. Nair; S. Krishna Prasad; Anjuli Khandelwal

Online publication date: 06 August 2010

To cite this Article Sandhya, K. L. , Nair, Geetha G. , Prasad, S. Krishna and Khandelwal, Anjuli(2001) 'Dynamics of the two-dimensional melting transition of a liquid crystal confined in Anopore membranes', Liquid Crystals, 28: 12, 1847 — 1853

To link to this Article: DOI: 10.1080/02678290110082374

URL: http://dx.doi.org/10.1080/02678290110082374

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 2001, VOL. 28, NO. 12, 1847–1853

Dynamics of the two-dimensional melting transition of a liquid crystal confined in Anopore membranes

K. L. SANDHYA, GEETHA G. NAIR, S. KRISHNA PRASAD*
and ANJULI KHANDELWAL†
Centre for Liquid Crystal Research, Jalahalli, Bangalore 560 013, India

(*Received 28 April 2001; in final form 13 June 2001; accepted 21 June 2001*)

Dielectric measurements on a liquid crystal exhibiting the smectic A–crystal B transition and confined to Anopore membranes having 20 and 200 nm pore sizes are reported. The studies reveal that compared with the bulk, the confined material shows a decrease in transition temperature. More importantly, the confinement leads to a slowing of the relaxation mechanism by about three orders of magnitude.

1. Introduction

The behaviour of liquids and solids confined in porous media is of considerable current interest from both fundamental and technological points of view [1–4]. The interest arises from the fact that finite size constraints can lead to significant effects on the bulk properties. Among the well studied phenomena are crystal melting, and transitions in binary liquid mixtures, in superfluid systems and between different solid forms. In comparison with these studies, investigations on liquid crystalline materials in confined geometries are relatively recent [5]. Various types of porous materials have been used to confine liquid crystals. They are (i) polymer matrices (polymer dispersed liquid crystals) having well defined spherical or ellipsoidal cavities, (ii) porous glasses with narrow pore size distributions, but randomly oriented and interconnected pore, (iii) silica gels and aerosil with broad pore size distributions and irregular shapes of the cavities, and (iv) porous filters like Millipore, Nucleopore and Anopore membranes. Of these, the Anopore membranes are quite attractive as they have highly parallel cylindrical pores with narrow size distributions and a smoother cavity surface.

Most of the work reported in this field has been devoted to the isotropic–nematic (I–N) transition [6–10], although nematic–smectic A (N–SmA) [11, 12], smectic A–chiral smectic C (SmA–SmC*) [13, 14] and nematic–smectic B (N–SmB) [15] transitions have also been studied. An important influence of confinement is that it affects the nature of the transition. In the case of the I–N transition, for example, a weakening of the first order character and also a broadening of the two-phase region associated with the transition have been observed. In fact, for sufficiently small pore diameters, the high temperature phase is not truly isotropic as a small degree of residual orientational order persists well above the transition; in such a case the isotropic phase is referred to as the paranematic phase. These effects can be so strong that the I–N transition is completely absent and a gradual increase in the local orientational order is seen as the temperature is lowered. Another, but related, feature observed is the depression in the transition temperature when the material is confined in porous media. Although a number of studies have been made in the effort to understand various properties of liquid crystals confined in porous environments, only a few reports exist on the dynamic behaviour. Dielectric spectroscopy as a tool to study the dynamics associated with different liquid crystalline phases and the transitions between them, has been quite successful. The few reports on dielectric studies in this area are on the I–N transition [9, 10] and on the smectic C* phase [13]; only very recently [15] has the nematic–smectic B transition been studied. In this paper we present the first report on the effect of confinement on the dielectric behaviour of a liquid crystal exhibiting a smectic A–crystal B (SmA–CrB) transition.

The smectic A phase possesses, in addition to the orientational order, a one-dimensional positional order. The rod-like molecules are stacked to form layers, with their average orientation direction (the director) lying parallel to the layer normal. The order within the layer is short range or liquid-like [16]. Thus one can describe the SmA phase as a 'one-D solid and two-D liquid'. In contrast, the CrB is a three-D solid with some degree of orientational freedom for the molecules. Hence the transition from CrB to SmA can be regarded as a two-dimensional melting process and consequently the

---

*Author for correspondence, e-mail: clcr@vsnl.com

†Permanent address: Physics Department, S.D. (P.G) College, Muzaffarnagar, India

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290110082374

dynamics associated with the director modes should show appreciable change, as has indeed been seen experimentally for bulk systems [17–19]. In this paper we report on the behaviour of the dielectric constant and its dynamics across the SmA–CrB transition when the material is confined in Anopore membranes of 200 and 20 nm pore size, and compare the results obtained with those for the bulk state.

2. Experimental

Measurements have been carried out on *N*-(4-*n*-butyloxybenzylidene)-4′-*n*-octylaniline (4O.8), having the following phase sequence: I 348 K N 332.6 K SmA 318.4 K CrB. For experiments on bulk samples, the material was sandwiched between two ITO-coated glass plates treated with silane to promote homeotropic orientation of the molecules. For measurements in confined geometry, the sample was introduced into Anopore membranes (Whatman, USA). These membranes are made from aluminium oxide and have parallel cylindrical pores penetrating the 60 μm thickness normally. Two types of membrane with pore sizes 200 and 20 nm and having 50 and 25% mean porosities, respectively, were used. The cylindrical pores being strictly parallel and lying normal to the surface are the main advantage of Anopore membranes over other types of confining media. Such a disposition allows the measuring electric field, in a dielectric experiment, to be applied along a predetermined direction with respect to the nematic director **n**. As our interest was to study the dielectric behaviour along **n**, we used the membranes without treating them with any surfactant, as it is well known [5] that untreated membranes align the molecules such that **n** is parallel to the axes of the pores. Before filling with the liquid crystal, the membranes were heated to 300°C for 4 h to remove residual gas. After this, the LC sample was placed on the top surface of the membrane and the temperature was maintained a few °C above the clearing point for ~24 h to ensure complete filling. The excess of liquid crystal left on the surface of the membrane was then removed by pressing the membrane between filter papers. The membrane, which was opaque before filling with the sample, became quite transparent after this procedure. This shows that a substantial number of the liquid crystal molecules inside the pores are oriented such that the nematic director is along the axes of the pores and, due to matching of the refractive indices of the membrane and the liquid crystal, the medium appears transparent. For an ideal alignment where the molecules are along the pore axes, the conoscopic view in the polarizing microscope should show a Maltese cross. On the other hand if the molecules lie in the plane of the membrane there would be strong scattering of light. As we did not find either of these features, we believe that in our case, the alignment was homeotropic, but imperfect. A second factor that must be kept in mind is that a calculation of the precise amount of sample inside the membrane is not trivial. Although, the mass change before and after filling the sample can be used to estimate the amount of sample inside the pores, a proper estimation on this basis requires accurate values of the density of pores. However, the pore density data available from the manufacturer are correct to only an order of magnitude. For these reasons, we represent the dielectric data in terms of the measured capacitance C' and loss $C'' = C''{*}G/(2\pi f)$, where G is the conductance and f the measuring frequency.

The membrane containing the sample was sandwiched between two ITO-coated glass plates serving as electrodes. With the nematic director nearly parallel to the membrane normal, this geometry allowed us to study the behaviour corresponding to $\varepsilon_{\|}$, the dielectric constant parallel to the director. A wide frequency range impedance analyser (Solatron model 1260) along with a broadband dielectric converter (BDC-N, Novocontrol) controlled by WinDeta software (Novocontrol) was used to carry out the dielectric experiments. The sample temperature was varied using a Mettler hot stage. Measurements at a constant frequency were made by continuously ramping the temperature at the uniform rate of 1°C min^{-1}, and the dispersion data were collected by stabilizing the temperature during the period of the scan. Hereafter, for brevity we refer to the membranes filled with the liquid crystal and having 200 and 20 nm pores as An-200 and An-20, respectively.

3. Results and discussion

Figure 1 shows the temperature variation of the sample capacitance at a fixed frequency of 0.1 kHz for the bulk and for An-200 and An-20. The bulk measurements were made with the sample contained in a 56 μm thick ITO-coated glass cell with the substrate surfaces treated for homeotropic alignment of the molecules. (Experiments on the bulk sample were made on cells whose thickness ranged from 3.5 to 125 μm; no systematic differences were observed as a function of the cell thickness.) In this geometry the measured capacitance would correspond to $\varepsilon_{\|}$ and as expected for a compound with negative dielectric anisotropy, the value shows a decrease across the I–N transition. A marked decrease in the capacitance was also seen at the N–SmA and SmA–CrB transitions, but the changes are much larger compared with that across the I–N transition. For An-200 and An-20, only the SmA–CrB transition is very clearly seen, with an abrupt drop in the capacitance value. It is known that transitions become broadened and weaker when samples are confined in Anopore

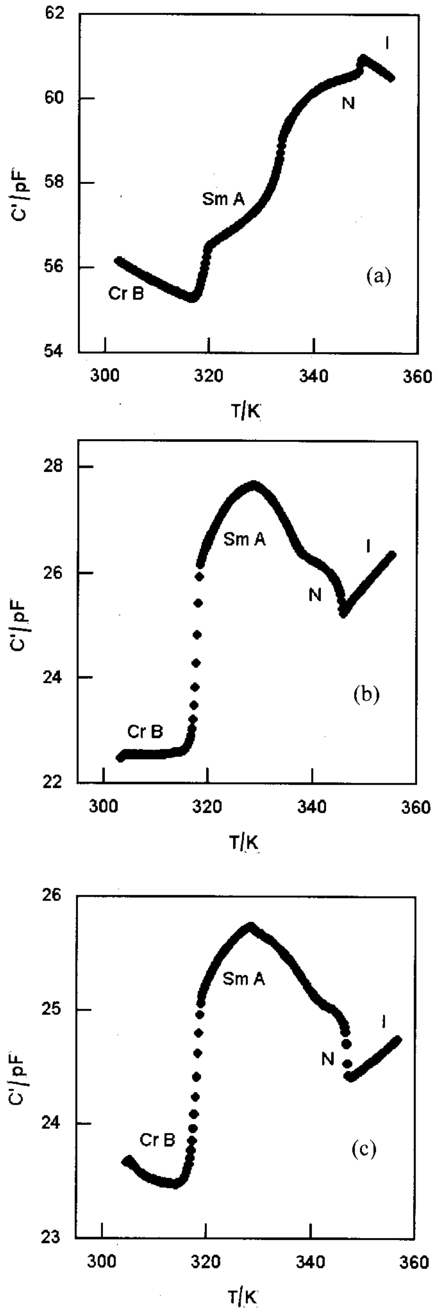

Figure 1. Temperature dependence of the sample capacitance at 1 kHz in (*a*) the bulk and in the confined geometries with (*b*) 200 nm and (*c*) 20 nm Anopore membranes. While the bulk sample shows clear changes at all three transitions, the N–SmA transition is not detectable for the samples in the membranes.

membranes [12]. Thus the I–N transition, which has a quite weak signature even for the bulk sample, is hardly noticeable for An-200 and An-20. Another feature to be noted is the shift in the transition temperature upon confinement. While the I–N transition temperature decreases by ~3.6 K, the SmA–CrB transition shifts by only ~1 K. These features are in the range generally observed for materials confined in porous matrices [5].

As the main purpose of the study was to investigate the effect of confinement on the dynamics of the two-dimensional melting process, the dispersion measurements were restricted to the vicinity of the SmA–CrB transition. Figures 2, 3 and 4 show representative dielectric

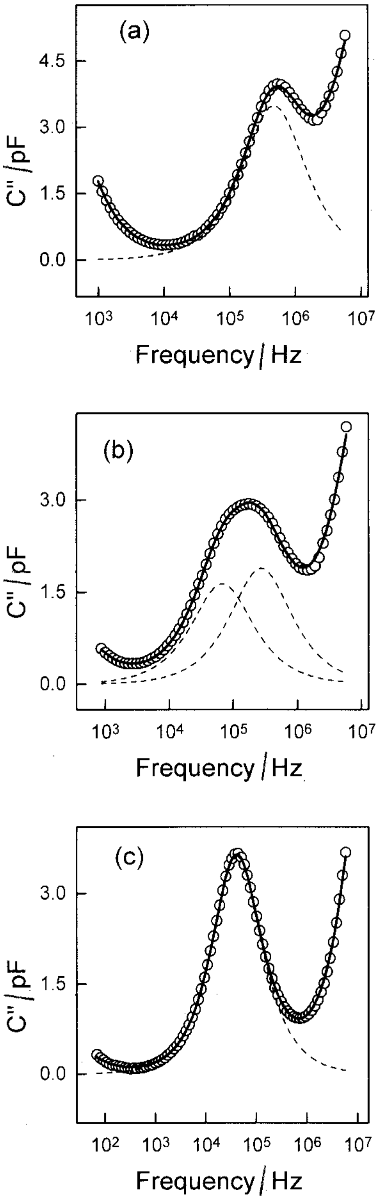

Figure 2. Representative loss (C'') curves for the bulk sample in (*a*) the SmA phase, (*b*) the two phase region and (*c*) the CrB phase. The circles show the experimental data and the thick solid line in the fit to equation (1) including the conductivity term. The thin line represents the extracted profile for the relevant relaxation mechanism. Note that in (*b*) the data can be represented by two coexisting loss curves contributed to by the coexisting SmA and CrB phases.

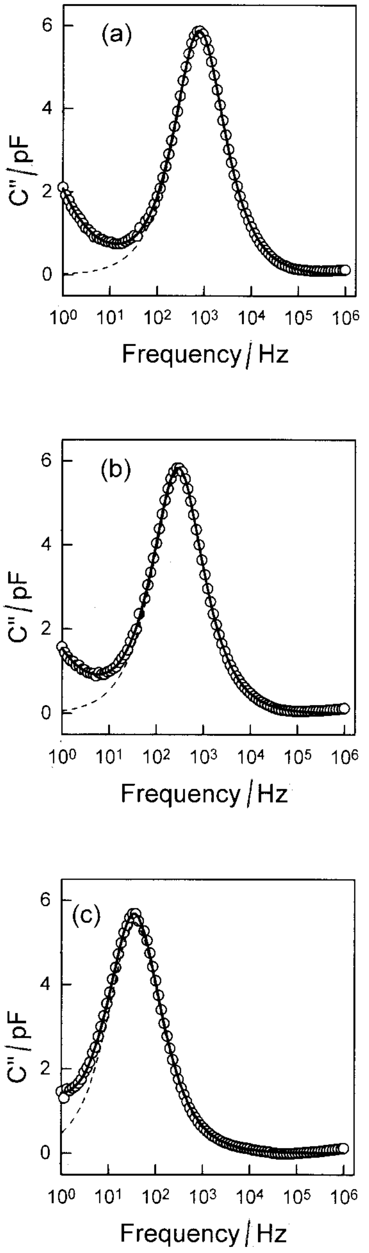

Figure 3. Loss (C'') curves for An-200 in the (*a*) SmA phase. (*b*) SmA–CrB transition region and (*c*) CrB phase. The circles and the lines carry the same meaning as for figure 2. Notice that the data in the transition region are also well described by a single loss curve, unlike for the bulk sample.

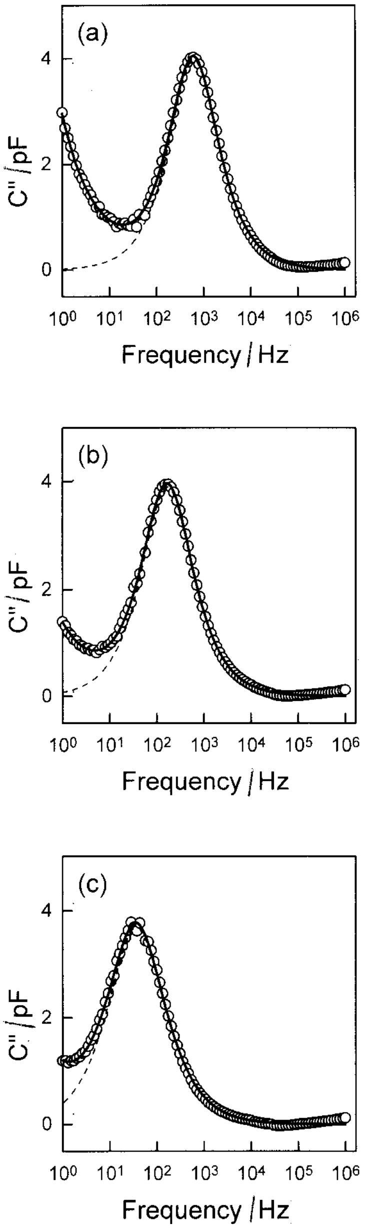

Figure 4. Loss (C'') curves for An-20 in the (*a*) SmA phase. (*b*) SmA–CrB transition region and (*c*) CrB phase. The circles and the lines carry the same meaning as for figure 2.

spectra for the bulk and confined geometries in the SmA and CrB phases, as well as for the transition region. For the bulk sample (figure 2), in each of the two phases a sharp peak is seen, but in the transition region, the peak is much broader. This is to be expected for the following reason. It is known that the SmA–CrB transition is strongly first order and is associated with a two-phase coexistence region [20]. Further, as we shall see later, the relaxation frequency changes appreciably just across the transition for the bulk sample. These factors enable one to observe the coexistence of the loss curves due to both phases in the transition region, resulting in the peak becoming broader. In fact, such features have been seen in X-ray scattering [20, 21], spontaneous polarization [22] and dielectric [23] experiments on materials exhibiting first order phase transitions. To determine the relaxation parameters, data collected outside the transition region were analysed using a single Havriliak–Negami (HN) function [24]; in the two-phase region two HN functions were used. The HN function is written as

$$\varepsilon(f) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{[1 + (\mathrm{i}f/f_{\mathrm{R}})^{\alpha}]^{\beta}} \tag{1}$$

where f is the measuring frequency, and ε_{∞} is the sum of the dielectric strengths of all the high frequency modes other than the one under consideration. $\Delta\varepsilon$ is the difference between low and high frequency dielectric constants and is a measure of the dielectric strength of the mode of interest, and f_{R} is the characteristic relaxation frequency. The parameters α and β describe the width and asymmetric broadening of the relaxation curve. To account for the d.c. conductivity (σ) contribution to the imaginary part of the dielectric constant, the term $-\mathrm{i}(\sigma/2\pi\varepsilon_{\mathrm{o}}f)^{N}$ was added to the right hand side of equation (1). Here ε_{o} is the permittivity of free space; for all the samples studied here N was found to be equal to 1, indicating pure ohmic conductivity. Solid lines in figures 2–4 result from the best fit of the data to equation (1). The fitting clearly brings out (figure 2) the presence of coexisting peaks in the case of the bulk sample. In contrast, An-200 and An-20 exhibit (figures 3 and 4, respectively) a single relaxation in the transition region.† Differential scanning calorimetry scans show that although the coexistence region becomes widened, the enthalpy associated with the SmA–CrB transition decreases by 38% and 57% when the material is confined in An-200 and An-20, respectively. It may be remarked that reduction in the strength of first order transitions when the sample is in confined geometry environments is well known. The combination of the increase in the width of the two-phase region and the reduced enthalpy change perhaps prevents the observation of co-existing loss curves in the transition region.

For the bulk sample, the two distribution parameters α and β were equal to 1 (within the errors) for scans taken at all temperatures. This indicates that the relaxation is pure Debye in type with a single relaxation frequency. For An-200 and An-20, only β remains equal to 1 over the entire temperature range: α decreases from a value of ~0.94 in the SmA phase to ~0.90 and ~0.86 in the CrB phase of An-200 and An-20, respectively. This feature suggests that confinement of the sample in the Anopore membranes causes the relaxation frequency to be distributed over a few values.

The temperature dependence of f_{R} in the vicinity of the SmA–CrB transition for the bulk, for An-200 and for An-20 are presented in figures 5(*a*), 5(*b*) and 5(*c*), respectively. The observed dependences are very different for the samples confined in Anopore membranes, in comparison with the bulk sample. For the bulk sample, the decrease in the value of f_{R} at the transition is abrupt and, as mentioned earlier, is accompanied by a coexistence of f_{R} values corresponding to the SmA and CrB phases. The magnitude of the decrease, a factor of 4, is quite large, but is typical for the bulk SmA–CrB transition [17–19]. The inset of figure 5(*a*) shows the data for the two-phase region; the values in this region just continue the trend shown in the respective phases, without any pre- or post-transitional behaviour. This is to be expected as the transition is strongly first order in character.

For the samples in the Anopore membranes, figures 5(*b*) and 5(*c*), the decrease in the value of f_{R} across the SmA–CrB transition is still appreciable, but the change is gradual unlike that for the bulk sample. This is perhaps related to the widening of the transition as seen in the DSC scans. But the most important feature to be noted is that the absolute values of f_{R} have decreased by about three orders of magnitude when compared with the values for the bulk sample. The magnitude of the slowing of the relaxation frequency is about the same for both An-200 and An-20. Further, the effect is about the same in both the SmA and CrB phases. Also, unlike the bulk sample, the data for the membranes show more temperature dependence in the CrB phase than in the SmA phase.

In order to characterize the temperature dependence of f_{R}, the data for the bulk, An-200 and An-20 have been plotted on a semi-logarithmic scale in figure 6. For the bulk sample, Arrhenius type behaviour is seen throughout the two mesophases. In contrast, for An-200 and An-20, such a trend is observed in the entire range of the SmA phase, but only well away from the transition in the CrB phase. The activation energy values calculated from the linear portion of the data lying away from the transition are listed in the table. It is only in the SmA phase that we see a drastic difference in the values between the bulk and both the Anopore samples. In contrast, in the CrB phase, confining the sample to a 200 nm dimension hardly alters the value of the activation energy, while reducing the pore size to 20 nm results in a 3-fold decrease in the value. There are some similarities between our observations and those seen for a material confined in a porous glass matrix with 86 nm pore size and showing a nematic–smectic B sequence [15]. It was

---

† It may be tempting to ascribe the dispersion seen for the Anopore samples to the Maxwell–Wagner (MW) mechanism, which arises in heterogeneous materials—here the Anopore matrix and the liquid crystal. We attempted to find out whether this mechanism could account for the relaxation seen. For this purpose we used an expression quoted in [5], to estimate the relaxation time for a MW process. With the conductivity values in the range 10^{-8}–10^{-11} S m^{-1} in the SmA and CrB phases, we get relaxation times which are 2–3 orders of magnitude slower than those experimentally observed. Therefore we do not wish to attribute the observed relaxation to the MW relaxation mechanism.

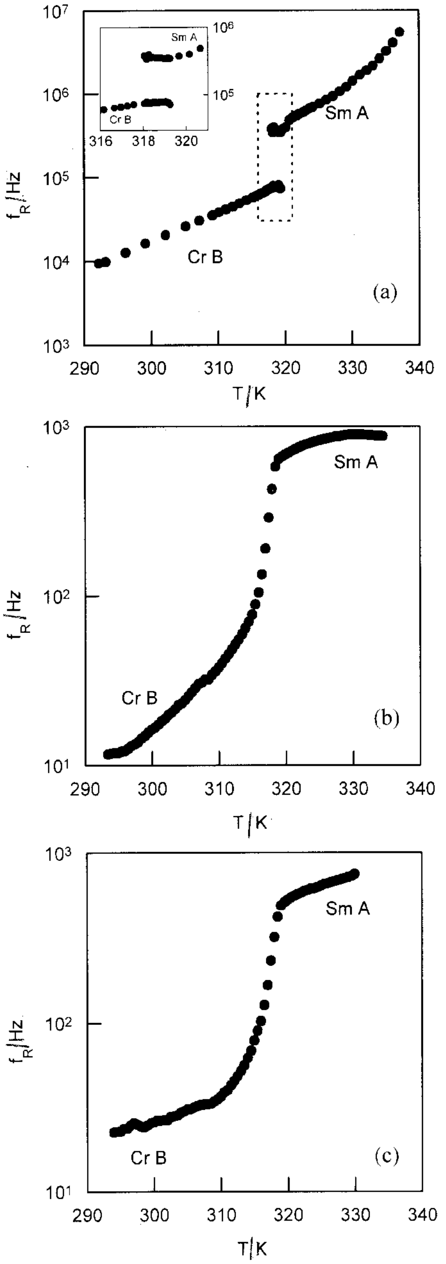

Figure 5. Plots showing the thermal variation of the relaxation frequency f_R for (*a*) the bulk, (*b*) An-200 and (*c*) An-20 samples. The value of f_R decreases by a factor of 4 across the SmA–CrB transition; the change is abrupt for the bulk sample, but more gradual for the two samples in the Anopore membranes. The abrupt change for the bulk sample enables separation of the individual contributions in the two-phase region. The data in this region are shown on an enlarged scale in the inset of (*a*). Notice that the absolute value of f_R decreases by about three orders of magnitude upon confinement in the membranes.

found that on confinement, while the activation energy values in the nematic phase decrease substantially, the values in the smectic B phase are hardly affected.

Table. Calculated activation energies.

	Activation energy/kJ mol^{-1}	
Sample	SmA phase	CrB phase
Bulk	117.4 ± 3.8	61.6 ± 0.4
An-200	28.1 ± 1.3	61.1 ± 0.9
An-20	27.6 ± 0.4	20.2 ± 0.2

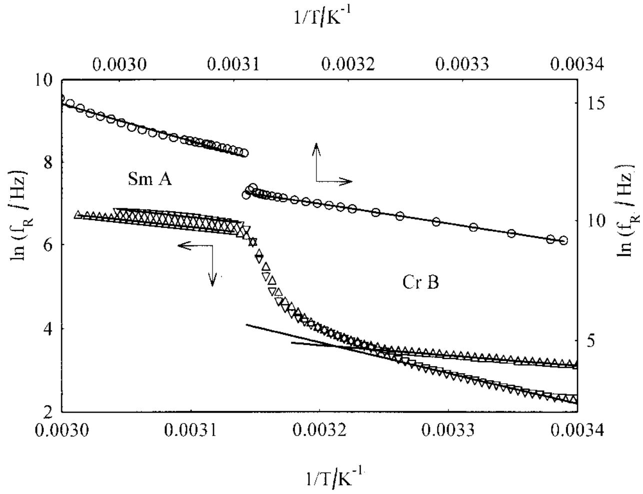

Figure 6. Semi-logarithmic plots of f_R versus inverse temperature for the bulk (○), An-200 (▽) and An-20 (△) samples. The lines drawn represent fits to an Arrhenius equation by considering data outside the two-phase region. The activation energy values obtained from such fits are listed in the table. The axes on the top and the right are for the bulk sample and those on the left and bottom are for An-200 and An-20.

In summary we have studied the dielectric behaviour across the smectic A–crystal B transition in the bulk, as well as in a confined geometry by having the sample contained in Anopore membranes of 20 and 200 nm pore sizes. Upon confinement, apart from the shift in the transition temperature, we observe substantial reductions in the relaxation frequency in both the smectic A and crystal B phases.

We are grateful to Prof. S. Chandrasekhar for many useful discussions. A research grant from the U.S. Office of Naval Research (ONR Grant No. N00014-97-1-0904) is acknowledged with thanks.

References

[1] Patrick, W. A., and Kemper, W. A., 1938, *J. phys. Chem.*, **42,** 369.

[2] Krauth, W., Trivedi, N., and Ceperley, D., 1991, *Phys. Rev. Lett.*, **67,** 2307.

[3] Drake, J. M., Klafter, J., Kopelman, R., and Awschalom, D. D. (editors), 1993, *Dynamics of small confining systems*, Materials Research Society Proceedings, Vol. 290 (Pittsburg: Materials Research Society).

[4] Klein, J., and Kumacheva, E., 1998, *J. chem. Phys.*, **108,** 6996.

[5] For an excellent collection of review articles in this field, see Crawford, G. P., and Zumer, S. (editors), 1996, *Liquid Crystals in Complex Geometries* (London: Taylor & Francis).

[6] Kuzma, M., and Labes, M. M., 1983, *Mol. Cryst. liq. Cryst.*, **100,** 103.

[7] Crawford, G. P., Stannarius, R., and Doane, J. W., 1991, *Phys. Rev. A*, **44,** 2558.

[8] Dadmun, M. D., and Muthukumar, M., 1993, *J. chem. Phys.*, **98,** 4850.

[9] Rozanski, S. A., Stannarius, R., Groothues, H., and Kremer, F., 1996, *Liq. Cryst.*, **20,** 59.

[10] Sinha, G. P., and Aliev, F. M., 1998, *Phys. Rev. A*, **58,** 2001.

[11] Bellini, T., Clark, N. A., and Schaefer, D. W., 1995, *Phys. Rev. Lett.*, **74,** 2740.

[12] Finotello, D., Iannacchione, G. S., and Qian, S., 1996, in *Liquid Crystals in Complex Geometries* (London: Taylor & Francis), 325.

[13] See e.g., Aliev, F. M., 1996, in *Liquid Crystals in Complex Geometries* (London: Taylor & Francis), 345.

[14] Skarabot, M., Kralj, S., Blinc, R., and Musevic, I., 1999, *Liq. Cryst.*, **26,** 723.

[15] Werner, J., Otto, K., Enke, D., Pelzl, G., Janowski, F., and Kresse, H., 2000, *Liq. Cryst.*, **27,** 1295.

[16] See e.g., Chandrasekhar, S., 1992, *Liquid Crystals* (Cambridge: Cambridge University Press).

[17] Benguigui, L., 1983, *Phys. Rev. A*, **28,** 1852.

[18] Bata, L., and Buka, A., 1981, *Mol. Cryst. liq. Cryst.*, **63,** 307.

[19] Nagabhushan, C., Nair, G. G., Ratna, B. R., Shashidhar, R., and Goodby, J. W., 1988, *Liq. Cryst.*, **3,** 175.

[20] Pershan, P. S., Aeppli, G., Litster, J. D., and Birgeneau, R. J., 1981, *Mol. Cryst. liq. Cryst.*, **67,** 205.

[21] Prasad, S. K., Rao, D. S. S., Chandrasekhar, S., Neubert, M. E., and Goodby, J. W., 1995, *Phys. Rev. Lett.*, **74,** 270.

[22] Prasad, S. K., Nair, G. G., and Chandrasekhar, S., 1995, *J. matr. Chem.*, **5,** 2253.

[23] Nair, G. G., Prasad, S. K., Kumar, S., and Manickam, M., 1998, *Mol. Cryst. liq. Cryst.*, **319,** 89.

[24] Havriliak, S., and Negami, S., 1966, *J. polym. Sci.*, **C14,** 99.