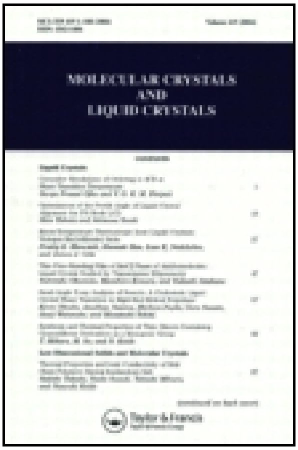

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Dielectric Relaxation in Liquid Crystal Confined to Cylindrical Pores: Effect of Different Layer Thicknesses and Boundary Conditions

Manuel Bengoechea [a] , Sarmistha Basu [a] & Fouad Aliev* [a]

[a] Department of Physics, University of Puerto Rico, PR, USA

To cite this article: Manuel Bengoechea, Sarmistha Basu & Fouad Aliev* (2004): Dielectric Relaxation in Liquid Crystal Confined to Cylindrical Pores: Effect of Different Layer Thicknesses and Boundary Conditions, Molecular Crystals and Liquid Crystals, 421:1, 187-196

To link to this article: http://dx.doi.org/10.1080/15421400490501789

Mol. Cryst. Liq. Cryst., Vol. 421, pp. 187–196, 2004
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490501789

Taylor & Francis
Taylor & Francis Group

DIELECTRIC RELAXATION IN LIQUID CRYSTAL CONFINED TO CYLINDRICAL PORES: EFFECT OF DIFFERENT LAYER THICKNESSES AND BOUNDARY CONDITIONS

---

*Manuel Rivera Bengoechea, Sarmistha Basu, and Fouad M. Aliev**
Department of Physics, P.O. BOX 23343, University of Puerto Rico, PR 00931, USA

Broadband dielectric spectroscopy was applied to study influence of the boundary conditions and layer thickness of liquid crystal confined to cylindrical pores on low frequency and high frequency relaxation processes. The low frequency measurements provide information on the relaxation of surface polarization that arises at liquid crystal–pore wall interface. The information about reorientational dynamics of molecular origin is obtained in high frequency experiments. The homeotropic alignment of molecules facilitates the investigation of the librational mode. The behavior of this mode is different from the behavior observed in investigations of relaxation due to reorientation of molecules around their short axis.

Keywords: confinement; dielectric spectroscopy; relaxation

INTRODUCTION

Dielectric spectroscopy applied to bulk nematic and smectic-A LCs studies relaxation processes of molecular origin. In the bulk phases of these LCs there are no dielectric relaxation processes associated with the order parameter since there is no polar ordering and therefore dynamics of order parameter is not involved. Alkylcyanobiphenyls such as 5CB and 8CB are liquid crystals, which have been deeply investigated in the past and whose dielectric bulk properties have been quite clearly understood [1–5]. Their molecules have a large dipole moment ≈ 5D oriented along the molecular long axis, which significantly simplifies the understanding of the dielectric

This work was supported by American Chemical Society Petroleum Research Fund grant 36418-AC7 and NASA grant # NCC3-1034.

*Corresponding author. Tel.: 1 (787) 764-0000, ext. 7554, Fax: 1 (787) 756-7717, E-mail: faliev@rrpac.upr.clu.edu

behavior. In the nematic phase in a geometry in which the electric field **E** is parallel to the director **n**, the real ε' and imaginary ε'' parts of the dielectric permittivity have a dispersion region with a characteristic frequency at about 5 MHz. This dispersion is of relaxation origin due to the restricted rotation of the molecules about their short axis and is of Debye type, i.e., it has a single relaxation time. For the geometry in which the electric field **E** is perpendicular to the director **n**, the most prominent relaxation process with characteristic frequency about 70 MHz due to librational motion of the molecules was observed. The available information on dynamics of librational mode even for bulk liquid crystals, to our best knowledge, is scarce.

Dielectric spectroscopy can be applied [6–9] to investigate multiple aspects of the influence of confinement on dynamic properties of liquid crystals impregnating porous matrices. We report in this paper on the investigations of the influence of different boundary conditions (planar-axial and homeotropic-radial) and the surface layer thickness of liquid crystal, confined in cylindrical pores matrices, on dielectric relaxation. To obtain information on relaxation of the librational mode, we apply dielectric spectroscopy to investigate relaxation properties of 8CB confined in 200 nm cylindrical pores of Anopore membranes treated with lecithin. This treatment provides homeotropic boundary conditions (the molecules are oriented perpendicularly to the pore walls) for confined 8CB. Since the pore axis is parallel to the probing electric field and the molecular dipole moment is oriented perpendicularly to its direction, such a configuration makes it possible to investigate the dynamics of librational (tumbling) mode by dielectric method. Detection of relaxation process due to librational motion of molecules in samples with axial symmetry is principally impossible and the use of treated sample is the most effective way to investigate dynamics of this mode. In addition, using dielectric spectroscopy we have investigated the influence of layer thickness on the dynamics of reorientational motion of 8CB molecules – partially filling cylindrical pores.

EXPERIMENTAL

Measurements of the real (ε') and imaginary (ε'') parts of the complex dielectric permittivity (ε^*) in the frequency range 3 MHz–10^6 Hz, were carried out using a Schlumberger Technologies 1260 Impedance/Gain-Phase Analyzer in combination with a Novocontrol Broad Band Dielectric Converter and an active sample cell (BDC-S). The BDC-S containing the sample holder, the sample capacitor, high precision reference capacitors and active electronics optimizes the overall performance and reduces the typical noise in the measurements, particularly at low frequencies. For measurements in the frequency range 1 MHz–1.5 GHz we used Hewlett-Packard 4291A RF Impedance Analyzer in combination with the high frequency Novocontrol cell. In this frequency range measurements were performed at two hundred different frequencies with averaging done over three hundred times at each frequency. The sample temperature was varied using filtered airflow through the sample cell and was controlled to within 0.02°C using a Novocontrol Temperature Controller. Computer software WinFit provided with the dielectric spectrometer was used in the analysis of the data. The quantities measured directly by the spectrometer were the real and imaginary parts of the dielectric permittivity of the material under investigation as a whole. The porous membrane we used has negligible electrical conductivity, and its dielectric permittivities are practically independent of frequency and temperature. For this reason for the confined LC we discuss below the temperature and frequency dependencies of the measured dielectric permittivities of the composition membrane + liquid crystal. In the experiments performed with LC confined in Anapore membranes the probing electric field was parallel to the axis of the cylindrical pores.

The dielectric spectra were analyzed using the Havriliak-Negami function [10] shown below

$$\varepsilon^*(\omega) = -i\frac{\sigma_o}{2\pi\varepsilon_o f^n} + \frac{\Delta\varepsilon}{(1+(i2\pi f\tau)^\alpha)^\beta} + \varepsilon_\infty \tag{1}$$

where the first term on the right represents contributions from the dc conductivity, ε_0 represents the permittivity of free space and ε_∞ represents the high frequency limit of the real part of the dielectric permittivity, $\Delta\varepsilon$ represents the dielectric strength, τ is the relaxation time and f is the frequency of the probing electric field. The parameter α represents the width of the distribution while β describes the skewness of this distribution. Both parameters can take on values in the range from 0 to 1. The case $\alpha = 1$ and $\beta = 1$ represents the single frequency Debye relaxation process. The term $i\sigma_o/2\pi\varepsilon_o f^n$ accounts for the contribution of a.c. conductivity. For ohmic conductivity n = 1. The decrease of n, i.e., n < 1 could be observed, as a rule, if additionally to the contribution to ε'' from conductivity, if there is an influence of electrode polarization.

We used Anopore membranes with both untreated and lecithin treated pores. Porous matrices were impregnated with liquid crystal 8CB at temperatures corresponding to isotropic phase. The bulk 8CB has a smectic A phase in the temperature range of 294.2–306.8 K in addition to the nematic range of 306.8–314.4 K. The interaction between 8CB molecules and non-treated pore walls of Anapore membrane provides planar (axial) orientation of the molecules. To obtain homeotropic orientation we treated the pore walls with lecithin molecules.

For treatment of cylindrical pores with lecithin a porous Anopore membrane was dipped inside a 2% mass concentration solution of lecithin in hexane for one hour. The matrix was dried until complete evaporation of hexane from the pores.

Layers of different thickness are formed on the pore walls as a result of controlled impregnation [9] of porous matrices with 8CB from solutions of different liquid crystal concentration. When the matrix dried up, the hexane molecules evaporated leaving relatively long and heavy liquid crystal molecules at the surface of the pore wall. In this way, by varying the liquid crystal concentration in the hexane solution, we were able to obtain variable thickness of the surface layers of LC formed on the pore walls. It is natural to assume, at least qualitatively, that the lower the concentration of LC in solution the thinner the LC layer thickness on the surface of the pore wall.

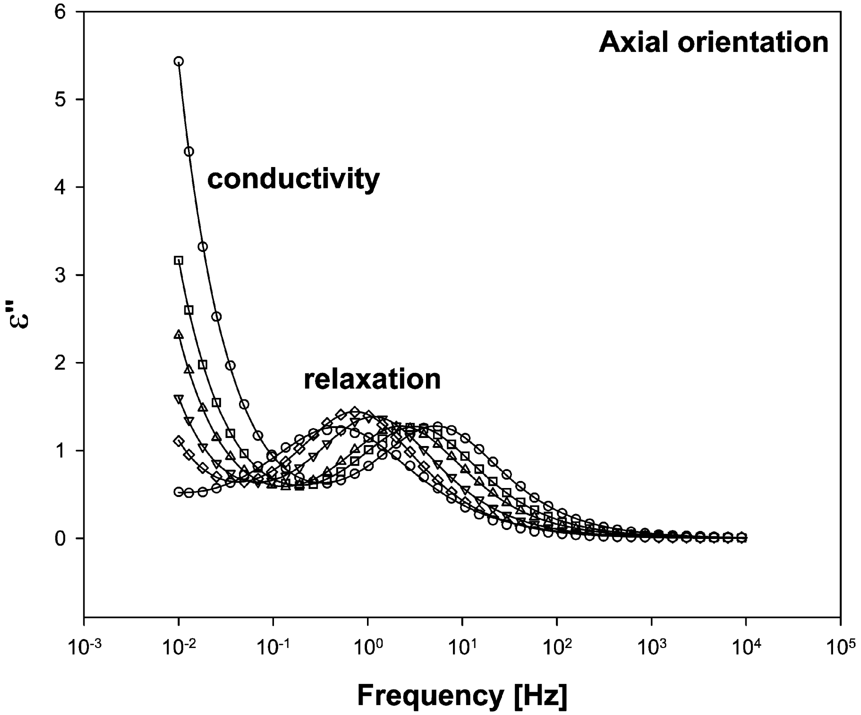

FIGURE 1 Frequency dependence of ε'' at different temperatures for 8CB confined in 200 nm cylindrical pores: axial orientation. Symbols – experiment, solid lines – fitting. o-T = 327.15 K, – T = 321.15 K, Δ-T = 317.15 K, ∇-T = 313.75 K, ◇-T = 312.15 K, ●-T = 300.15 K.

RESULTS AND DISCUSSION

The results of the low frequency measurements (f < 1 MHz) are presented in Figures 1–3. Application of formula (1) for data analysis shows that the strong frequency dependence of ε'' at f < 0.1 Hz (axial orientation) and f < 1 Hz (radial orientation) is due to ohmic conductivity and the contribution from the electrode polarization is negligibly small. The low frequency relaxation process observed for both samples with axial and radial orientation of molecules on pore walls is the relaxation of the interfacial polarization arising at the pore wall-liquid crystal interface. The structure of the thin surface layer of LC on solid surface, in our case the pore wall, could be very different from the structure of the liquid crystal in bulk. For example, at the interface a layer with surface induced polar ordering may exist. In this case cooperative and slow process may arise

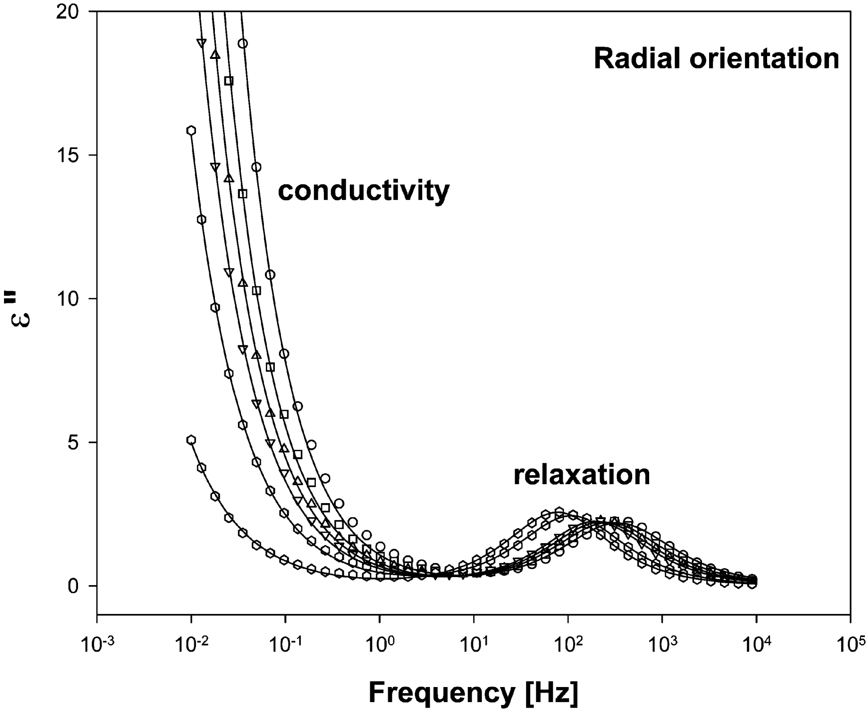

FIGURE 2 Frequency dependence of ε'' at different temperatures for 8CB confined in 200 nm cylindrical pores: radial orientation. Symbols – experiment, solid lines – fitting. o-T = 327.15 K, $-$T = 321.15 K, Δ-T = 317.15 K, ∇-T = 313.75 K, ◇-T = 312.15 K, ●-T = 300.15 K

as it is observed in our experiments. The rate of this relaxation depends on boundary conditions of liquid crystal at the pore wall. The relaxation process is slower for the axial orientation than for the radial one as it is illustrated in Figure 3, which represent temperature dependence of relaxation times of the slow process for both samples. This temperature dependence suggests that the viscosity of surface layers of on the pore walls is greater for layers with axial orientation of molecules than for radial one. Therefore the relaxation of the surface induced polarization is slower for layers with axial orientation than for radial one.

By varying boundary conditions of LC in pores we can investigate at high frequencies relaxations of molecular-reorientation around short axis (for axial orientation) and libration (for radial orientation) separately in these pores. Figure 4 illustrates the difference in relaxation observed at high frequencies in bulk 8CB and 8CB confined in cylindrical pores with axial (par-

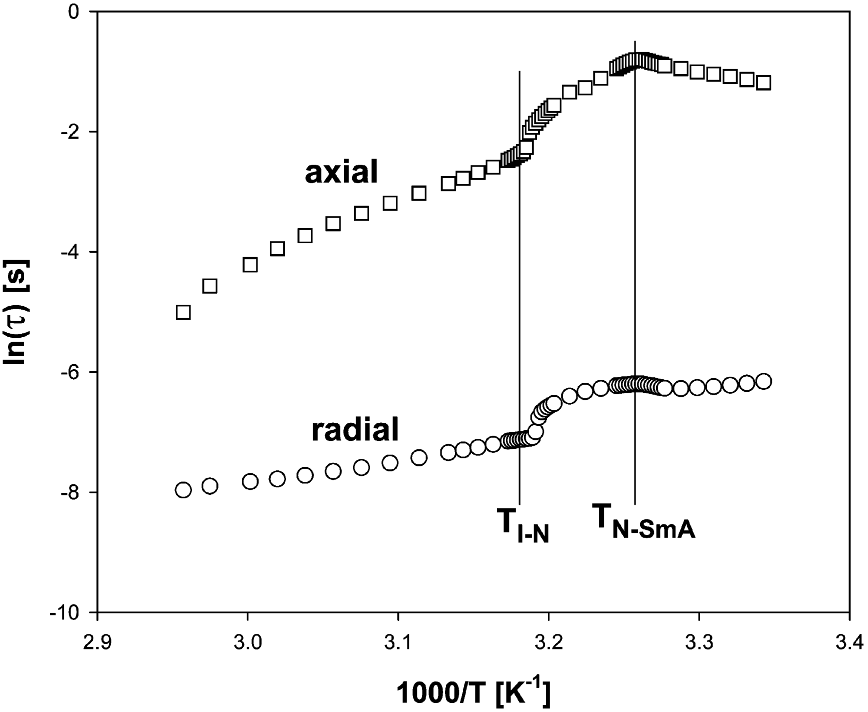

FIGURE 3 Temperature dependence of the relaxation time of the slow (low frequency) process for 8CB confined in 200 nm cylindrical pores: -axial orientation, o-radial orientation. Vertical lines indicate bulk phase transitions temperatures of 8CB.

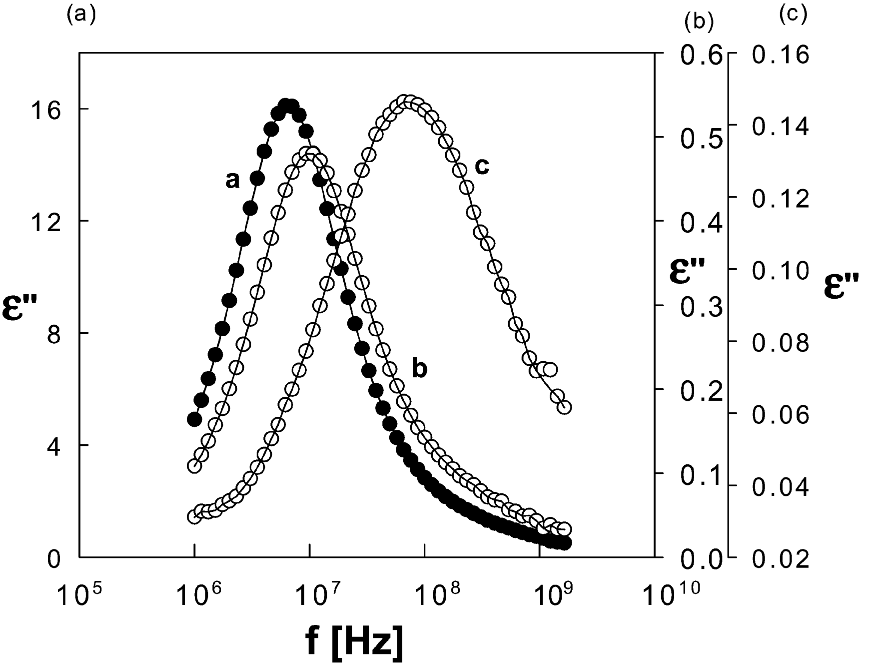

FIGURE 4 Frequency dependence of ε'' at 310.15 K for 8CB. Symbols – experiment, solid lines – fitting. a-bulk, b-confined: axial orientation, c-confined: radial orientation.

allel to the probing electric field) and radial (perpendicular to the electric field) orientations. The relaxation in bulk 8CB, as well as in the sample with axial orientation of molecules represented in Figure 4, is due to reorientation of molecules around their short axis. It is clear that the relaxation process in lecithin treated matrices (radial orientation) is observed at much higher frequencies than in the bulk sample and therefore, cannot be assigned to the same mechanism. Since the molecules of 8CB do not have any component of dipole moment perpendicular to the long axis, the only explanation to the observed high frequency relaxation in the treated sample is to associate it with librational motion of molecules. This mode should be observed in 8CB if the probing electric field is perpendicular to the director, as it takes place in the treated sample. The lines in Figure 4 represent the use of fitting analysis according to relation formula (1). For the bulk LC the fitting line corresponds to Debye relaxation function ($\alpha = 1$, $\beta = 1$). The process for the librational mode observed in lecithin treated porous matrix is of non-Debye type with the parameter $\alpha = 0.75$. The spectra are wider and the asymmetry in the spectra is greater for the sample with the homeotropic alignment than in the sample with axial orientation. It should be noted that the process due to the rotation of the molecules around the short axis is faster in confined LC than in bulk, as it is shown in Figure 5 representing temperature dependence of relaxation times for all phases. This effect could be due to surface and pore curvature induced disorder important in anisotropic phases, as well as due to a possible reduction in the density of confined LC.

The temperature dependence of the relaxation times the librational mode obtained for 8CB confined in lecithin treated cylindrical pores is illustrated in Figure 6. This temperature dependence is totally different from the behavior observed in investigations of relaxation due to reorientation of

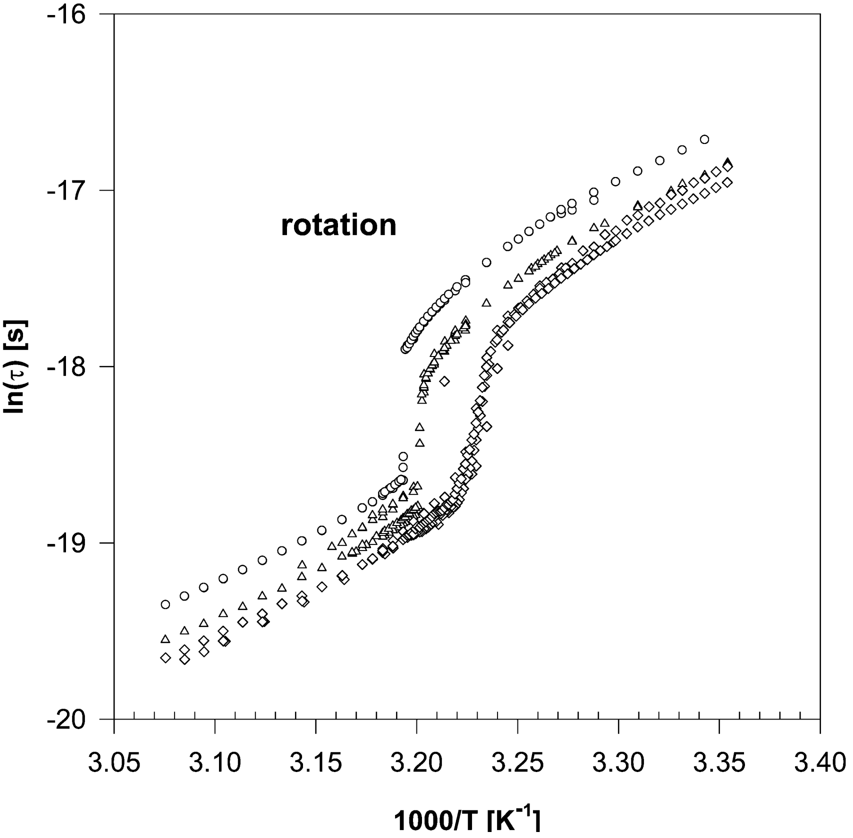

FIGURE 5 Temperature dependence of high frequency relaxation time of the process due to rotation of molecules around their short axis: bulk 8CB-(o); 8CB partially filling 200 nm cylindrical pores: axial orientation (Δ-50%, ◇-13%).

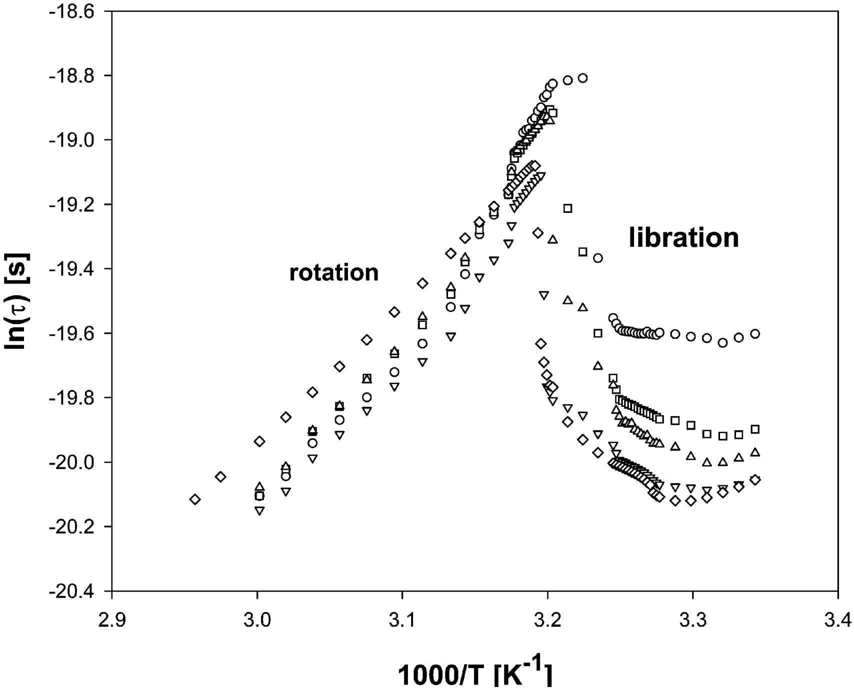

FIGURE 6 Temperature dependence of high frequency relaxation time for 8CB confined in 200 nm cylindrical pores – radial orientation. Concentrations: o-8%, −15%, Δ-30%, ∇-50%, ◇-100%.

molecules around their short axis. In isotropic phase the relaxation times correspond to the process due to the rotation of molecules around their short axis. The relaxation time of librational mode in the temperature range corresponding to the nematic phase increases upon increasing the temperature towards the nematic-isotropic transition temperature. In contrast, the temperature dependence of the relaxation times of the process due to reorientation of molecules around the short axis decreases upon increasing the temperature in the same temperature range (see Fig. 5). The interpretation of the results obtained in nematic phase needs the involvement of the temperature dependence of the orientational order parameter. The decrease of relaxation time in the temperature range corresponding to the nematic phase of 8CB could be due to an acceleration of the process with increasing the order parameter. In the sample with homeotropic boundary conditions, in the case of perfect order ($S = 1$) and taking into account that the dipole moment of the molecule is parallel to its long axis, the projection of the dipole moment on the direction of the electric field, which is along the pore axis, is minimal because the fluctuations of the molecular orientations with respect to the radial direction are very small. These fluctuations of the dipole moment (or molecular long axis) correspond to the librational motion of the molecule and the amplitude of the fluctuations determines the relaxation rate of the dipole in the viscous media. At higher temperatures, these deviations (fluctuations) are of greater amplitude (the order parameter is smaller) and this requires longer time to complete one librational cycle. As a result, the relaxation rate is smaller for fluctuations of greater amplitude and vice versa. Such a behavior has resulted in the particular temperature dependence of relaxation times observed for the librational mode in the nematic phase temperature range. In the smectic-A phase the temperature dependence of relaxation times is mainly determined by the variations of viscosity.

CONCLUSION

The relaxation of surface induced polarization on liquid crystal–solid pore wall interface has been observed for confined 8CB. This relaxation is slower for confined liquid crystal with axial boundary conditions than for radial orientation suggesting that the mobility of molecules in surface layers is strongly affected by boundary conditions. The relaxation of librational mode in lecithin-treated samples is observed in dielectric spectroscopy experiment. This is a proof of homeotropic orientation of liquid crystal in these samples. The dynamics of the librational mode is totally different from the behavior observed in investigations of relaxation due to reorientation of molecules around their short axis.

REFERENCES

[1] Cummins, P. G., Danmur, D. A., & Laidler, D. A. (1975). *Mol. Cryst. Liq. Cryst.*, *30*, 109.
[2] Lippens, D., Parneix, J. P., & Chapoton, A. (1977). *J. de Phys.*, *38*, 1465.
[3] Wacrenier, J. M., Druon, C., & Lippens, D. (1981). *Mol. Phys.*, *43*, 97.
[4] Bose, T. K., Chahine, R., Merabet, M., & Thoen, J. (1984). *J. de Phys.*, *45*, 11329.
[5] Bose, T. K., Campbell, B., Yagihara, S., & Thoen, J. (1987). *Phys. Rev. A*, *36*, 5767.
[6] Rozanski, S. R., Stanarius, R., Groothues, H., & Kremer, F. (1996). *Liq. Cryst.*, *20*, 59.
[7] Cramer, Ch., Cramer, Th., Arndt, M., Kremer, F., Naji, L., & Stannarius, R. (1997). *Mol. Cryst. Liq. Cryst.*, *304*, 209.
[8] Sinha, G. P. & Aliev, F. M. (1997). *Mol. Cryst. Liq. Cryst.*, *304*, 309.
[9] Sinha, G. P. & Aliev, F. M. (1998). *Phys. Rev. E*, *58*, 2001.
[10] Havriliak, S. & Negami, S. (1967). *Polymer*, *8*, 101.