Effect of Sm-A short-range order on the activation energies of translational and rotational viscosities of nematic liquid crystals with highly polar molecules

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(Received 27 August 2018; revised manuscript received 31 October 2018; published 19 December 2018)

We report experimental studies on the temperature-dependent translational and rotational viscosities of a few nematic liquid crystals made of highly polar molecules. Cyanobiphenyl (nCB) with longitudinal and cyanobicyclohexane molecules (CCN-mn) with transverse dipole moments were chosen and the measurements were made in the nematic phase. The translational viscosity (shear viscosity) is measured by using a rheometer and the rotational viscosity is measured from the dynamics of the Freedericksz transition by measuring the optical phase-retardation decay of the sample. The associated activation energies are obtained from the fitting of the appropriate equation in the nematic phase. Only 8CB and CCN-47 exhibits N to Sm-A phase transition and their activation energies of translational and rotational viscosities are larger compared to the shortest homologs in the respective series. Both activation energies of 8CB are significantly larger than that of CCN-47. The temperature-dependent steady states of the director distribution under shear are comprehensibly reflected in the rheodielectric measurements of 8CB than that of CCN-47. The results are explained based on the differences in the Sm-A short-range orders and the critical slowing down of the order parameter fluctuations. We present a simple physical model of molecular association that gives rise to different Sm-A short-range orders in both classes of compounds.

DOI: 10.1103/PhysRevE.98.062701

I. INTRODUCTION

The flow properties of nematic liquid crystals made of elongated molecules are very complex compared to their isotropic counterparts because in most cases the flow disturbs the alignment and conversely the change in alignment may induce flow in the nematic [1]. The translational (shear) viscosity due to flow depends on the orientation angle of the director (\hat{n}) with respect to the shear and the velocity gradient directions. Miesowicz first defined and measured three flow viscosities, namely [2,3] η_1 ($\hat{n} || \nabla v$), η_2 ($\hat{n} \perp \nabla v$), and η_3 $(\hat{n} \perp v \text{ and } \nabla v)$. Figure 1 schematically represents mutual orientation of the director, velocity (v), and the velocity gradient (∇v) directions, leading to three viscosities. These viscosities can be expressed in terms of six Leslie coefficients α_i [4–6]. There are several studies on the effect of molecular structure on the viscosities and their temperature dependencies [7-15]. The flow alignment angle of the director with respect to the shear direction is given by $\theta = \tan^{-1}(\sqrt{\alpha_3/\alpha_2})$ [16]. In the vicinity of the nematic-isotropic (N-I) transition, usually both are negative and the director is aligned along the flow direction with a small angle ($\theta \leq 5^{\circ}$).

Safinya *et al.* reported an interesting effect of critical slowing down of the Sm-A order fluctuations on the dynamics of nematic director of the liquid crystals exhibiting N-Sm-A phase transition [16,17]. They showed that near the N-Sm-A transition, renormalized α_3^R becomes positive due to the divergence of correlation length ξ_{\parallel} and the nematic director evolves through a precessional motion along the neutral direction, *z*

(perpendicular to both the velocity and velocity gradient directions) which can be described by an equation of ellipse [16]: $n_x^2(t)/n_{x0}^2 + n_y^2(t)/n_{y0}^2 = 1$, where $n_x(t) = n_{x0}\cos(\omega_0 t)$ and $n_y(t) = n_{y0}\sin(\omega_0 t)$. The precessional frequency ω_0 depends on the shear rate $\dot{\gamma}$ and the Leslie coefficients α_2 and α_3^R . Consequently, several steady states with different director distributions are observed as the N-Sm-A transition is approached depending on the relative amplitudes of the projected director components along x and y directions, respectively. A schematic representation of different distribution types of \hat{n} is shown with shaded areas covering the unit spheres in Fig. 1(e). They are denoted as a_m , a_s , a(b), and a_c [16]. In a_m type, $n_{x0} > n_{y0}$; in a_s type, $n_{x0} \simeq n_{y0}$; in a(b) type, $n_{x0} < n_{v0}$ [not shown in Fig. 1(e)]; and in a_c type, $n_{x0} \ll n_{v0}$. The director dynamics presented in Fig. 1 has been captured by three-dimensional nonuniform orientation simulations using Leslie-Ericksen equations by Han et al. [18,19]. The effect of such distribution of director has also been investigated experimentally by nonequilibrium rheodielectric studies [20–22]. Rotational viscosity (γ_1) is another important property, which is directly related to the electrooptical response time of the liquid crystal displays. There are several experimental studies on the measurement of rotational viscosity [14,15]. There are also some reports in which attempts were made to correlate these two viscosities [10,11].

In this paper we report experimental studies on the temperature dependence of shear and rotational viscosities of a homologous series of cyanobiphenyl with longitudinal and cyanobicyclohexane liquid crystals with transversely polar molecules. We show that the activation energies in the nematic phase of both shear and rotational viscosities of compounds having N-Sm-A phase transition are much higher than that

2470-0045/2018/98(6)/062701(7)

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FIG. 1. [(a)–(c)] Schematic diagrams showing three different director orientations with respect to shear and corresponding Miesowicz viscosities. Schematic representation of different types of distribution of \hat{n} on the unit sphere [16]. The first sphere from the right-hand side represents the "b" orientation corresponding to the viscosity η_2 . The shaded regions on the subsequent unit spheres show the excursion of the director under shear in different distribution types.

of compounds having no N-Sm-A phase transition in the homologous series. We discuss the effect of Sm-A short-range order on the rotational viscosity and the critical slowing down of the Sm-A order parameter fluctuations on the shear viscosity of cyanobicyclohexane and cyanobiphenyl compounds exhibiting N-Sm-A phase transition. Both the effects are much stronger in liquid crystals with longitudinal dipole moments than that of transversely polar molecules.

II. EXPERIMENTAL

We studied a few compounds from the homologous series of cyanobiphenyl (nCB) and cyanobicyclohexane (CCN-mn) liquid crystals. The cyano group (-CN) is oriented along the longitudinal and transverse directions for nCB and CCN-mn molecules, respectively. The phase-transition temperatures and molecular structures of the compounds are shown in Table I and in Fig. 2, respectively. The CCN-mn compounds have bicyclohexane core hence exhibits very low birefringence ($\Delta n \simeq 0.03$) [23]. CCN-35 exhibits only nematicisotropic (N-I) phase transition. CCN-47 exhibits both N-I and N-Sm-A phase transitions. CCN-73 and CCN-55 exhibits both N-I and N-Sm-B phase transitions. The dielectric anisotropy of the compounds are largely negative ($\Delta \epsilon < 0$) due to the presence of transverse dipole moments (see Fig. 2) [23-26]. The nCB compounds are well known. They exhibit large positive dielectric anisotropy and large birefringence.

TABLE I. Phase-transition temperatures of CCN-35, CCN-73, CCN-47, and CCN-55 compounds.

Sample	Phase transitions (°C)	Nematic range (°C)
CCN35	Cry 38.4 N 49.3 I	10.9
CCN73	Cry 38.6 Sm-B 38 N 50.2 I	12.2
CCN47	Cry 25.6 Sm-A 28.2 N 57.3 I	29.1
CCN55	Cry 25 Sm-B 30 N 66.4 I	30.4



FIG. 2. Chemical structure of cyanobiphenyl (nCB) and cyano bicyclohexane (CCN-mn) compounds. The red arrows show the directions of permanent dipole moments of $-C \equiv N$ group.

Shear viscosity was measured by using a rheometer (Anton Paar MCR-501) in cone-plate geometry with a plate diameter of 25 mm and cone angle of 1°. For measuring the dielectric constant under shear, we used a parallel plate configuration with a gap of 75 μ m. The dielectric constant was measured as a function of temperature with the help of an LCR meter (Agilent E4980A) at an applied voltage of 0.5 V and frequency 4.11 kHz. The details of the rheodielectric setup is presented in our previous reports [21,22,27–30]. The temperature of the sample was controlled with an accuracy of 0.1°C. All the measurements were made on cooling the samples from the isotropic phase.

Rotational viscosity of the CCN-mn compounds was measured in homeotropic cells by using a phase-decay time measurement technique [31]. The experimental setup consists of two Glan-Thompson polarizers, a He-Ne laser, and a photomultiplier tube (Hamamatsu). The nematic director was deformed by applying a small voltage just above the Freedericksz threshold value. The director relaxes when the voltage is switched off at t = 0. The corresponding decay in the phase retardation is approximately expressed as $\delta(t) =$ $\delta_0 \exp(-2t/\tau_0)$, where δ_0 is the total phase change of the cell and τ_0 is the relaxation time. The rotational viscosity is given by $\gamma_1 = \tau_0 K_{33} \pi^2/d^2$, where *d* is the cell gap and K_{33} is the bend elastic constant. In case δ_0 is close to $n\pi$, the retardation decays as $\delta(t) = \delta_0 \exp(-4t/\tau_0)$. τ_0 is obtained from the slope of the linear plot of $\ln[\delta_0/\delta(t)]$ with time, t [13,31].

III. RESULTS AND DISCUSSION

First we performed rheodielectric measurements of nCB liquid crystals at a fixed shear rate ($\dot{\gamma} = 100 \text{ s}^{-1}$) and the results are shown in Fig. 3(a). The effective shear viscosity (η_{eff}) of both 5CB and 7CB decreases discontinuously below the N-I phase transition and then continue to increase as the temperature is reduced. The corresponding rheodielectric data suggest that in the nematic phase $\varepsilon_{\text{eff}} \simeq \varepsilon_{\perp}$. Hence the director gets "b" orientation in the nematic phase as described in Fig. 1(b) and, consequently, $\eta_{\text{eff}} \simeq \eta_2$. The rheodielectric



FIG. 3. Temperature dependence of effective viscosity (η_{eff}) and the dielectric constant (ε_{eff}) as a function of temperature measured at a fixed shear rate $\dot{\gamma} = 100 \text{ s}^{-1}$ for (a) 5CB and 7CB and for (b) 8CB. Solid and open symbols represent the viscosity and dielectric constant, respectively. The steady states with director distribution types "*a*," "*a* – *b*" (intermediate regime of "*a*" and "*b*"), "*a_m*," "*a_s*," and "*a_c*" are labeled in correlation to the shear induced distributions reported by Safinya *et al.* [16]. Red arrow in the bottom figure indicates N-Sm-*A* phase-transition temperature.

data of 8CB looks very different in comparison to 5CB and 7CB, especially near the N-Sm-A phase transition [Fig. 3(b)]. A small discontinuity around $T_{\rm NI} - T = 2.2^{\circ} \rm C$ indicates a change of director orientation from "b" to an intermediate regime, labeled "a - b." Corresponding change is also reflected in the temperature variation of $\varepsilon_{\rm eff}$. Below $T_{\rm NI} - T =$ 5°C, the average director orientation is changed along the neutral direction (z direction). The temperature variation of dielectric constant reflects the effective orientation of the director with respect to the applied electric field under shear. While decreasing the temperature from the isotropic phase at a few temperatures both the values and slopes of $\eta_{\rm eff}$ and $\epsilon_{\rm eff}$ simultaneously changes indicating changes in the director distribution. These temperatures are marked by vertically dotted line in Fig. 3(b). Both $\eta_{\rm eff}$ and $\epsilon_{\rm eff}$ increase discontinuously at the N-Sm-A phase transition $(T_{\rm NI} - T \simeq 7.5^{\circ} {\rm C})$, which is marked by an upward arrow in Fig. 3(b). This is because of the weak first-order N-Sm-A phase transition of 8CB. The steady states with different director distributions, namely a_m , a_c , and a_s , are identified from the change of slope in $\varepsilon_{\rm eff}$ and in $\eta_{\rm eff}$ and they are consistent with the results of synchrotron x-ray studies reported by Safinya et al. [16]. They showed that there is an interplay of frictional and flow-induced fluctuation forces on the nematic director as the N-Sm-A transition is approached. Consequently, several steady states as mentioned emerge due to the critical slowing

down of the Sm-A order parameter fluctuations. This effect is clearly revealed in the rheodielectric data. Although Negita *et al.* reported rheodielectric measurements on 8CB [20] using a homemade concentric double cylinder-type viscometer, our rheodielectric measurements using a cone-plate and parallel plate geometries of MCR 501 rheometer are able to capture the fine structure of director distributions associated with different steady states. It may be mentioned that the transition temperatures of different steady states weakly depend on the applied shear rates. To avoid this, we kept the low shear, i.e., $\dot{\gamma} = 100 \text{ s}^{-1}$, in our experiments.

There are several experimental studies on the anchoring transition of CCN-47 [32-34]. It was proposed that there exists a smectic short-range order in the nematic phase [35–37]. Inspired by this, we studied the rheodielectric properties of CCN-47 and also a few compounds of the homologous series. Figure 4 shows the temperature dependence of effective shear viscosity (η_{eff}) and effective dielectric constant ($\varepsilon_{\rm eff}$). For all the compounds, $\eta_{\rm eff}$ decreases below the N-I phase transition and then increases as the temperature is decreased. It is observed that $\eta_{\text{eff}}^{\text{CCN}-47}$ increases more rapidly in the nematic phase compared to the other homologs as the N-Sm-A transition is approached. For example, there is a small slope change at a temperature of $T_{\rm NI} - T = 7^{\circ}$ C, and we identify this as a change of orientation from steady state "b" to an intermediate regime "a - b" type [Fig. 4(a)]. It has been shown that there is a Sm-A short-range order in the nematic phase of CCN-47 liquid crystal [35]. Hence it is legitimate to expect the occurrence of steady states due to the critical slowing down of the Sm-A order parameter fluctuations similar to that of 8CB. However, we do not see any distinct variation of effective viscosity (like we see in case of 8CB) as the N-Sm-A transition is approached except another small slope change in the η_{eff} at $T_{\text{NI}} - T = 24^{\circ}\text{C}$. This change is an indication of the change of director orientation and attributed to the onset of appearance of other steady states " a_m ," " a_s ," "a(b)," and " a_c ." Unlike 8CB, the steady states are not distinguishable in CCN-47.

The effective dielectric constant $\varepsilon_{\rm eff}$ measured at the same shear rate are shown in Fig. 4(b). ε_{eff} increases discontinuously for all the compounds below the N-I phase-transition temperature. This confirms that the steady state form is "b" type since the dielectric anisotropy of all the compounds is negative. Above $T_{\rm NI} - T = 24^{\circ}$ C, $\varepsilon_{\rm eff}$ tends to increase as indicated by a small vertical arrow in Fig. 4(b). This is consistent with the viscosity data and is associated to the onset of subsequent steady states. However, they cannot be distinguished as clearly as we see in case of 8CB (see Fig. 3). This means that the Sm-A order parameter fluctuations in CCN-47 are not as strong as that of 8CB. In other words, ξ_{\parallel} is much larger in 8CB than that of CCN-47, i.e., $\xi_{\parallel}^{8CB} >$ ξ_{II}^{CCN-47} . A schematic diagram of the fluctuating Sm-A cluster with correlation length $\xi_{||}$ is shown in Fig. 5 when the Deborah number $D = \dot{\gamma} \tau \simeq 1$, where $\dot{\gamma}$ is the shear rate and τ is the longest characteristic structural relaxation time [17]. These clusters are anisotropic and tend to get distorted due to shear flow and this is energetically costly.

The effect of Sm-A short-range order fluctuations can be seen on the temperature dependence of $\xi_{||}$ and hence we looked at the critical exponents in both these compounds,



FIG. 4. (a) Temperature variation of effective shear viscosity (η_{eff}) and (b) effective dielectric constant (ε_{eff}) of CCN-mn compounds measured under a fixed shear rate $\dot{\gamma} = 100 \text{ s}^{-1}$. The vertical solid lines and upward arrows in the viscosity data in the top figure indicates the viscosity increases discontinuously at the N-Sm-A or N-Sm-B phase transitions. The temperature range of steady states, "b" and "a - b," " a_m ," " a_s ", "a(b)," and " a_c " are labeled under the viscosity data of CCN-47 with dotted arrows. The vertical solid lines and downward arrows in the viscosity data in the bottom figure indicates the dielectric constant decreases discontinuously at the N-Sm-A or N-Sm-B phase transitions. The upward arrow below the dielectric data of CCN-47 indicates a small slope change due to the occurrence of steady states.

which can be obtained easily from the temperature dependence of bend elastic constant K_{33} . According to the meanfield theory, the renormalized bend elastic constant varies as $K_{33}^R \propto \xi_{\parallel}(T)$. The correlation length diverges as $\xi_{\parallel}(T) \sim t^{-\nu}$, where $t = (T - T_{N-\text{Sm}A})/T_{N-\text{Sm}A}$ is the reduced temperature and ν is the critical exponent [17,38]. From the temperaturedependent measurement of bend elastic constant near the N-Sm-*A* phase transition it is found that in case of 8CB, $\nu \simeq 1$ [39], whereas for CCN-47, $\nu \simeq 0.3$, which is much smaller than that of 8CB [40]. The lower critical exponent of CCN-47



FIG. 5. Schematics of a cluster with the nematic director along the horizontal direction (a) at rest and (b) under shear flow. The dotted ellipse indicates Sm-A-type order with correlation length $\xi_{||}$ along the director.

is an indicator of weaker Sm-A short-range order. Another substantial difference in the physical properties of these two categories of compounds is that the bend elastic constant of CCN-47 is much smaller than splay elastic constant, i.e., $K_{33} < K_{11}$, whereas in case of 8CB, $K_{33} > K_{11}$ [23,40].

The temperature-dependent linear part of the shear viscosity in the N phase of all the compounds are fitted to the Arrhenius equation, $\eta_{\rm eff}(T) = \eta_0 \exp(E_S/kT)$, to get the activation energy of the translational viscosity. The fittings for CCN-mn compounds are shown in Fig. 6. For nCB the fittings are performed on the data shown in Fig. 3 but not shown here. The activation energies of shear viscosity in the nematic phase (E_S) of all the compounds are summarized in Table II. This table brings out some interesting features of the activation energies of the nematic liquid crystals made of highly polar molecules with transverse and longitudinal dipole orientations. It is noticed that E_S of CCN-47 which exhibits N-Sm-A transition is much larger than that of other homologs. For example, E_S of CCN-47 is about 66% larger than that of CCN-35 (shortest homolog). Similarly in nCB compounds, 8CB has much larger E_S than 5CB or 7CB. For example, E_S of 8CB is 185% larger than that of the shortest homolog 5CB. Hence the activation energy of translational viscosity in the



FIG. 6. Estimation of activation energy of shear viscosity from the Arrhenius equation, $\eta_{\text{eff}}(T) = \eta_0 \exp(E_S/kT)$. Variation of $\ln(\eta_{\text{eff}})$ with 1000/T. Solid lines represent the least square fits to the data. Due to shorter temperature range, CCN-35 and CCN-73 are shown separately in the inset.

TABLE II. $E_S \rightarrow$ Activation energy of shear viscosity in the nematic phase. $E_R \rightarrow$ Activation energy of the rotational viscosity in the nematic phase. E_R of 5CB, 7CB, and 8CB were obtained from Ref. [13], Ref. [42], and Ref. [41], respectively.

Samples	E_S (N-phase, kJ/mole]	E_R (N-phase, kJ/mole]
CCN-35	27	42
CCN-73	26	39
CCN-47	45	48
CCN-55	31	39
5CB	20	27 [13]
7CB	30	37 [42]
8CB	57	71 [41]

nematic phase is significantly larger in polar compounds with longitudinal and transverse dipole moments which also have a Sm-*A* phase.

We measured the rotational viscosity (γ_1) of the CCNmn compounds as a function of temperature and they are presented in Fig. 7(a). We notice that except for very close to N-I, the γ_1 of CCN-47 is relatively larger than other homologs



FIG. 7. (a) Temperature dependence of rotational viscosity (γ_1) of CCN-mn compounds. (Inset) Birefringence (Δn) of the samples adapted from Ref. [23]. (b) Inverse temperature dependence of $\ln(\gamma_1/\Delta n)$. Solid line represents the least-squares fits to the data.

and it increases rapidly as the N-Sm-A phase transition is approached. This is expected, as the smectic correlation length increases with decreasing temperature, i.e., $\gamma_1 \propto \sqrt{\xi}$, where $\xi \sim [T/(T - T_{NA})]^{0.33}$ [43]. The rotational viscosity of the nematic is related to the Leslie coefficients and is given by $\gamma_1 = \alpha_3 - \alpha_2$ [10,44]. The renormalized α_3^R due to the Sm-A short-range order fluctuations is proportional to η_2 ($\alpha_3^R \propto$ η_2). Thus Sm-A short-range order is reflected in both the translational and rotational viscosities. The temperature dependence of rotational viscosity can be expressed as $\gamma_1(T) \sim$ $Sexp(E_R/kT)$ [15], where S is the orientational order parameter and is proportional to the birefringence Δn , and E_R is the activation energy of the rotational viscosity. The temperature variation of Δn of the compounds are shown in the inset of Fig. 7(a). In the nematic phase it is almost the same for all the compounds. Figure 7(b) shows a linear variation of $\ln(\gamma_1/\Delta n)$ with 1/T. The activation energies obtained from the fitting are also presented in Table II. The activation energies of rotational viscosities of nCB compounds were obtained from several references [13,41,42]. E_R of CCN-47, which has Sm-A phase, is also comparatively larger than that of other homologs. For example, E_R of CCN-47 is about 15% larger than the shortest homolog CCN-35. Similarly, in the nCB homologous series, 8CB has a much larger E_R than 5CB or 7CB. For example, the E_R of 8CB is 163% larger compared to the shortest homolog, 5CB. Hence the activation energy of rotational viscosity in the nematic phase is significantly larger in longitudinally polar compounds which have a Sm-A phase. This clearly suggests that both CCN-47 and 8CB have Sm-A short-range order but it is comparatively weaker in CCN-47.

We present a simple physical model of molecular association that accounts for the smaller Sm-A short-range order and activation energies in the nematic phase of CCN-47 than that of 8CB. It is known that liquid crystal molecules with strong permanent dipole moments exhibit antiparallel association between pairs of molecules. The interaction becomes strongest when the dispersion energy between the aromatic cores having high polarizabilities [45,46]. The induced dipole moment by the cyano group of 8CB of a neighbor is parallel to the permanent dipole of the cyano group of the given dipole; consequently, the effective dipole moment of each molecule is enhanced as shown in Fig. 8(a). The chain-chain dispersion interaction energy is negligible in this case. Compounds with such a strong antiparallel correlation are found to exhibit strong Sm-A short-range order even if there is no long-range Sm-A order such as in 5CB or 7CB. In fact, in the case of nCB the effective molecular length is enhanced due to antiparallel correlation. CCN-47 has a strong transverse dipole moment and a possible molecular association is shown in Fig. 8(b), although in this case the effective transverse dipole moment is enhanced but the interaction is not strong as the core is made of bicyclohexane, which has very low polarizability $[\Delta n \simeq 0.03$ for CCN-47, see inset of Fig. 7(a)] compared to the biphenyl moiety. The effective molecular length is also not enhanced. In this configuration the Sm-A correlation length and hence the short-range order is expected to be much smaller than that of 8CB. The antiparallel correlation of dipoles is usually reflected in the dielectric data across the N-I phase transition. It is known that the average dielectric constant $\overline{\varepsilon} = (\varepsilon_{||} + 2\varepsilon_{\perp})/3$ of nCB is reduced in the nematic



FIG. 8. Schematic diagram showing the antiparallel configuration of (a) two 8CB molecules and (b) two CCN-47 molecules. The arrow with the solid red line represents the direction of permanent dipole moment and the one with dotted line the induced one. The polar cyano group (-C \equiv N) is parallel and perpendicular to the long axes of the 8CB and CCN-47 molecules, respectively.

phase below the N-I phase transition in highly polar (longitudinal) compounds due to the strong antiparallel correlation of dipoles [46,47]. For CCN-47 and its homologous series, it has been found that $\overline{\epsilon}$ remains unchanged across the N-I transition [24,48]. This confirms that antiparallel association of molecules and short-range order is smaller in CCN-47 than 8CB.

IV. CONCLUSION

The short-range smectic order in the nematic phase enhances the activation energies of translational and rotational viscosities of highly polar compounds with both longitudinal

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and transverse dipole moments in compared to the other homologs in the respective series. The enhancement is significant in the case of 8CB than CCN-47. Although both 8CB and CCN-47 compounds have the same dipolar group, the activation energies of the rotational and translational viscosities of 8CB are much larger than those of CCN-47 due to stronger Sm-A short-range order in the nematic phase. Using a simple physical model we showed that the Sm-A short-range order due to strong antiparallel correlation of longitudinal dipole moments of 8CB molecules which enhances both the activation energies is expected to be larger in 8CB than in CCN-47. The director excursion due to the critical slowing down of the Sm-A order parameter fluctuations in CCN-47 is smaller compared to the 8CB liquid crystal; consequently, the steady states are not observed. Computer simulations on nematic liquid crystals made of highly polar molecules in the framework of Leslie-Ericksen formalism can shed more light on the proposed mechanism. We emphasize that, as far as we know, ours is the first among a few rheodielectric experiments to probe the effect of smectic short-range order and critical slowing down of the Sm-A order parameter fluctuation as the N-Sm-A transition is approached in highly polar compounds with both longitudinal and transverse dipole moments. Such studies also have important relevancy on our understanding of the phase transitions in liquid crystals away from equilibrium.

ACKNOWLEDGMENTS

M.P.K. acknowledges UGC for CSIR-UGC fellowship (Ref No: 21/06/2015(i)EU-V). S.D. gratefully acknowledges the support from the DST (DST/SJF/PSA-02/2014-2015). We thank N. V. Madhusudana from Raman Research Institute, Bangalore, for useful discussion.

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