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Chemical Physics Letters 398 (2004) 517–521
CHEMICAL PHYSICS LETTERS
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NMR measurement of smectic ordering and nematic–smectic-A coupling in a liquid crystal

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Received 23 June 2004; in final form 21 September 2004
Available online 18 October 2004

Abstract

The nuclear magnetic resonance (NMR) spectra of three substituted benzenes as solutes in the liquid crystal 8CB were investigated. The orientational order of all solutes was obtained in the nematic and smectic-A phases. A change in temperature dependence of orientational ordering was observed at the nematic to smectic-A phase transition. We analyzed these results via Kobayashi–McMillan theory applied to solutes, i.e. by incorporating smectic-A layering and nematic–smectic-A coupling into a mean-field orientational Hamiltonian. By fitting to experiment, we fully determined Hamiltonian prefactors. The nematic–smectic coupling, determined for the first time by NMR, appears solute independent. Solute smectic-A order parameters were self-consistently determined.

1. Introduction

The phase transition between the orientationally ordered nematic and smectic-A liquid crystalline phases [1,2] is a fertile testing ground for statistical mechanics because of the intrinsic coupling between an orientational order parameter (defined in both the nematic and smectic-A phases) and a smectic-A translational order parameter [1,3,4]. Experiments on the cyanobiphenyl liquid crystal 8CB are of particular interest, as the transition is expected to be second order or very weakly first order depending on the strength of the nematic–smectic-A coupling term. The situation is as yet unsettled, as different techniques have found the nematic–smectic-A transition in 8CB to be first [5–7] or second order [8,9] in nature, thus implying different strengths of the nematic–smectic-A coupling term. While the smectic order parameter and the nematic–smectic-A coupling have been described *phenomenologically* by a model Hamiltonian [3,6,10], a direct measure of the nematic–smectic-A coupling term in terms of molecular properties would be of interest.

The order parameter in ordered phases is a construct that depends on how it is experimentally measured. The description of macroscopic orientational order in terms of molecular properties of flexible molecules is of renewed interest in studies of macromolecular systems in biology [11] and polymer science [12] where molecular structure and macroscopic properties are intrinsically related. In studies of small molecules dissolved in nematic liquid crystals there are qualitative differences in temperature dependencies of the measured order parameters of different dissolved solutes. Nuclear magnetic resonance has been used extensively to study the effects of orientational order in nematic liquid crystals [13,14]. Investigations into this problem have used rigid and flexible solutes as probes of the anisotropic environment [14–16] as well as liquid crystal molecules themselves [13]. The dipolar

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0009-2614/$ - see front matter © 2004 Published by Elsevier B.V.
doi:10.1016/j.cplett.2004.09.108

interaction, which averages to zero when the solutes are free to tumble in an isotropic solvent, is non-zero in a liquid-crystalline (anisotropic) solvent giving rise to complex spectra even for simple molecules [17]. These dipolar coupling induced splittings present a wealth of information from which one may calculate the order matrix [14,18].

Extension of NMR studies to the smectic-A phase is particularly interesting because the smectic-A is uniaxial like the nematic but has in addition a periodic density modulation along the director. Previous work has demonstrated that orientational order in some smectic-A phases changes less rapidly as a function of temperature than in the nematic phase with no break at the phase transition [19–22]. Recent NMR experiments [23,24] have probed smectic-A domain reorientation dynamics.

In this Letter, we measure molecular order in the smectic-A phase via an NMR study of three aromatic solutes in the liquid crystal 8CB in order to quantify the subtle effects associated with layering in the smectic-A phase. Indeed, we not only test the applicability of a mean-field Hamiltonian that accounts for both nematic and smectic-A ordering, but also fully determine *the Hamiltonian prefactors*. The Kobayashi–McMillan potential contains a mean-field *smecticity* as well as a nematic–smectic-A *coupling* term in the smectic-A phase in addition to the Maier–Saupe orientational order term in both phases [2–4,10,13]. We modified this Hamiltonian for *dilute* non-uniaxial solutes. Using an order parameter asymmetry in two non-uniaxial aromatic solutes as a sensitive molecular probe of the liquid crystal environment, we then account for the difference in temperature dependence of the orientational order in the nematic and smectic-A phases by fitting to the smecticity and the nematic–smectic-A coupling terms.

2. Experimental

One mole percent each of solutes 1,4-dichlorobenzene (dcb), fluorobenzene (fb), 1,3,5-trichlorobenzene (tcb) and 4-pentyl-4′-cyanobiphenyl (‘5CB-d_4’, deuterated in the α and β positions) in the liquid crystal 4-octyl-4′-cyanobiphenyl (8CB) were placed into a 5-mm o.d. high-resolution NMR sample tube which was thoroughly mixed, degassed and sealed. The solutes tcb and 5CB-d_4 were orientational references. The substituted benzenes were purchased from various sources and used as supplied. The 8CB was purchased from B.D.H. The 5CB-d_4 was synthesized by Professor Gordon S. Bates. NMR experiments were performed on a Bruker WH-400 high-resolution nmr spectrometer with temperature control provided by the commercial air flow system. The $B_0 = 9.4$ T magnetic field ensures a homogeneous uniaxial nematic phase [25]. One half hour was allowed to achieve temperature equilibration before spectra were accumulated. The temperatures reported, measured via a thermocouple beneath the sample in the NMR probe, are accurate and stable to better than 1 K. To ensure equivalent conditions, proton and deuteron spectra were recorded without removing the sample from the probe. Only one sample tube was used so as to ensure that all solutes experience identical experimental conditions and the same average liquid-crystal orientational order. Three separate experimental runs were conducted with internally consistent results.

Proton NMR spectra were measured and analysed using the program LEQUOR [26] to obtain the dipolar couplings of tcb, dcb and fb as a function of temperature. The program SHAPE [27] was used to obtain the order matrix for these three solutes from the dipolar couplings. The geometrical parameters employed are as in [28,29]. In Fig. 1 we present the values of the non-zero

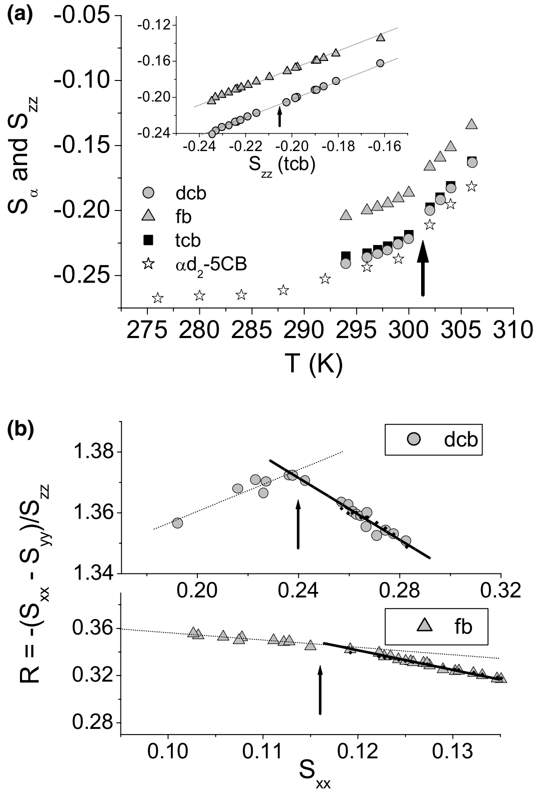

Fig. 1. (a) The element S_{zz} of the solute order parameter tensor plotted as a function of temperature for three solutes co-dissolved in the liquid crystal 8CB. Also plotted is S_α (5CB-d_4) which is taken as a measure of the 8CB liquid crystal order parameter. *Inset*: The temperature dependence of all solute order parameters is similar, as seen by the linearity of S_{zz} of solutes dichlorobenzene (dcb) and fluorobenzene (fb) against that of trichlorobenzene (tcb); (b) an order matrix ‘asymmetry’ parameter $R = -(S_{xx}-S_{yy})/S_{zz}$ is plotted against S_{xx} and is sensitive to the dissimilar environments experienced by solutes in the nematic and smectic-A phases. There is a change in slope on either side of the phase transition (denoted in all graphs by the arrow). The break is sharper for solute dcb than fb. Gray lines are a linear fit in the nematic phase. Solid black lines are asymmetry parameters calculated from a fit to smectic order: see text.

independent elements in the order matrix which is computed from the dipolar couplings for several temperatures in both nematic and smectic-A phases. We define axes systems in the substituted benzenes as follows: the direction perpendicular to the aromatic ring is the $\boldsymbol{z}$ direction, and the direction along the C-halogen bonds in dcb and fb is the $\boldsymbol{x}$-direction. The order parameter S_{zz} for solutes tcb, dcb and fb, and S_α are plotted in Fig. 1a. S_α is the order parameter of the CD bond corresponding to the α alkyl deuteron nucleus in 5CB-d_4 calculated from the quadrupolar splitting (assuming axial symmetry and using a value of 168 kHz for the quadrupolar coupling of a methylene deuteron [31]). The temperature dependencies of S_{zz} in dcb and fb are similar and linear with respect to S_{zz} (tcb) (Fig. 1a, inset).

A sensitive way to explore orientational mechanisms is to examine an order tensor asymmetry,

$$R = -(S_{xx} - S_{yy})/S_{zz}, \tag{1}$$

plotted against S_{xx} in Fig. 1b for solutes fb and dcb which have two independent elements of the order matrix (because of the D_{3h} symmetry, S_{xx} equals S_{yy} for tcb). This definition of asymmetry parameter is not unique but none of what follows depends on this choice. We used S_{xx} instead of thermocouple temperature as a precise internal thermometer that allowed results from three experimental runs to be overlaid. At the temperature resolution of the NMR experiment there is no observed discontinuity at the phase transition (reported in experiments at higher temperature resolution [7]), but there is a change of slope.

3. Results and discussion

For a homogeneous uniaxial nematic, the orientational Hamiltonian is

$$H_{\mathrm{N}}^{\mathrm{lc}} = -v_{\mathrm{lc}}\{S_{\mathrm{lc}} P_2 \cos(\theta)\}, \tag{2}$$

where v_{lc} is a scale parameter and $S_{\mathrm{lc}} = \langle P_2 \cos(\theta)\rangle$ is the nematic order parameter. Experimental observations of solutes in a given nematic liquid crystal can be modeled by a Hamiltonian involving a tensorial *solute* molecular property $\beta_{\gamma\delta}^{\mathrm{total}}$ whose anisotropic, traceless part $\beta_{\gamma\delta}$ interacts with an average *liquid crystal* field $F_{\gamma\delta}$:

$$H_{\mathrm{N}}^{\mathrm{sol}} = -1/2 F_{\gamma\delta}\beta_{\gamma\delta}. \tag{3}$$

$F_{\gamma\delta}$ and $\beta_{\gamma\delta}^{\mathrm{total}}$ have been identified physically as interactions such as that between a mean electric field (squared) and a dielectric polarizability or between a liquid crystal electric field gradient ('efg') and a solute quadrupole moment tensor [14]: for the purposes of this Letter the precise nature of the anisotropic intermolecular interactions is not important.

For a *solute* with C_{2V} symmetry in a uniaxial nematic phase, Eq. (3) becomes

$$H_{\mathrm{N}}^{\mathrm{sol}} = -3/4 F_{ZZ}\beta_{zz} P_{2,\mathrm{asymm}}, \tag{4}$$

where $P_{2,\mathrm{asymm}} = P_2(\cos(\theta)) - (b/2)\sin^2(\theta)\cos(2\phi)$. Here, we have defined the asymmetry in the solute molecular tensor

$$b = (\beta_{xx} - \beta_{yy})/\beta_{zz}, \tag{5}$$

and $\boldsymbol{x}$,$\boldsymbol{y}$ and $\boldsymbol{z}$ are chosen along the principal axis of the β tensor. The magnetic field and the nematic director are along $\mathbf{Z}$ and ($\mathbf{x}$,$\boldsymbol{y}$,$\boldsymbol{z}$) and ($\mathbf{X}$,$\mathbf{Y}$,$\mathbf{Z}$) are unit vectors along the molecule-fixed and lab-fixed coordinates ($\boldsymbol{z} \cdot \mathbf{Z} \equiv \cos\theta$ and $\boldsymbol{x} \cdot \mathbf{Z} \equiv \sin\theta \cos\phi$). Since the solutes are in dilute solution solute–solute interactions are unimportant, and the solute Hamiltonian H^{sol} has a form similar to H^{lc} but with solute-dependent prefactors [30]. One can also self-consistently obtain the solute nematic order parameter matrix

$$S_{ii} = \int \mathrm{d}\Omega P_{2ii} f_{\mathrm{N}}(\Omega), \tag{6}$$

where

$$f_{\mathrm{N}} = \frac{\exp(-H_{\mathrm{N}}^{\mathrm{sol}}/k_{\mathrm{B}}T)}{\int \mathrm{d}\Omega \exp(-H_{\mathrm{N}}^{\mathrm{sol}}/k_{\mathrm{B}}T)}, \tag{7}$$

is the distribution function, i is x, y, or z, $\int \mathrm{d}\Omega \equiv \int_0^{\pi}\int_0^{2\pi} \sin(\theta)\mathrm{d}\theta\, \mathrm{d}\phi$ and $P_{2ii} \equiv \frac{3}{2}(\mathbf{i}.\mathbf{Z})^2 - \frac{1}{2}$.

The NMR experiment gives us a (symmetric and traceless) experimental order matrix S_{E} (two independent values per experiment for solutes dcb and fb at a given temperature). The order matrix S_{C} (Eq. (6)) *calculated* from the solute Hamiltonian has only two adjustable parameters, β_{zz} and β_{xx}, because β is defined to be a traceless, symmetric tensor. This is because the isotropic part of the molecular tensor, having non-zero trace, has been subtracted out in our definition of β. This term adds only a constant to the Hamiltonian in the nematic phase (Eq. (4)) while in the smectic-A phase (Eq. (9)) it renormalizes the parameter τ'. Thus the solute molecular tensor is varied to obtain a good fit between S_{E} and S_{C}.

In Fig. 2 we plot b for solutes dcb and fb. In our calculations, we arbitrarily use a value of $F_{ZZ} = 16.1$ K × $k_{\mathrm{B}} \approx 1.39$ meV. Thus each element of the β matrix is unitless and the product $F_{ZZ}\beta_{xx}/k_{\mathrm{B}}T$ is a number of order unity. Solid symbols correspond to the β matrix calculated using the pure nematic potential (Eq. (4)). One would not expect b to depend on β_{xx} (or equivalently temperature) if there were only a single solute ordering mechanism. However, we do indeed observe a β_{xx} dependence that is linear in both phases but has different slopes in the nematic and smectic-A phase. The reason for the temperature dependence in the nematic phase is likely the presence of two (or more) competing mechanisms (such as one involving short-range effects and the other longer-range electrostatic effects) discussed elsewhere [14]. The difference in slope of the solute molecular

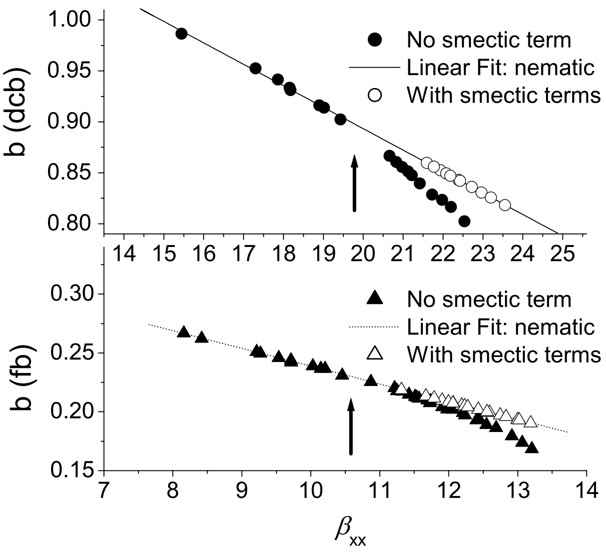

Fig. 2. The asymmetry b plotted against β_{xx} (solid symbols) exhibits a linear dependence in the nematic phase and is roughly linear but with different slope in the smectic-A phase. The nematic/smectic-A phase lie to the left/right of the arrow, which denotes the phase transition point. We introduce a *smecticity* and a nematic–smectic-A *coupling* term into the intermolecular potential (Eq. (9)) and re-fit the results (open symbols) requiring b in the smectic-A phase to fall on the extrapolation to the linear fit in the nematic phase. Both (a) dcb; (b) fb results are simultaneously fit *in the smectic phase* to five parameters (defined in Eq. (10)) representing the strengths of the coupling and smecticity. Note that $F_{ZZ} = 16.1\ \mathrm{K} \times k_B \approx 1.39$ meV in our calculations, so $F_{ZZ}\beta_{xx}/k_B$ T is of order unity.

tensor asymmetry b is less pronounced than that of the asymmetry R in the order parameter matrix (Fig. 1b).

We now account for the deviation in the smectic-A phase of b in Fig. 2 from the nematic linear dependence. In the smectic-A phase the liquid crystal field is periodically modulated along the Z-direction. The Kobayashi–McMillan model is mean field and includes both this periodic modulation as well as a term that accounts for the increase in nematic order arising from the coupling of the nematic and smectic-A order parameters. The *liquid crystal* Hamiltonian in the smectic-A phase is

$$\begin{aligned} H_A^{\mathrm{lc}} &= -v_{\mathrm{lc}}\{\delta_{\mathrm{lc}}\alpha\tau_{\mathrm{lc}}\cos(2\pi Z/d) \\ &\quad + [S_{\mathrm{lc}} + \alpha\kappa_{\mathrm{lc}}\cos(2\pi Z/d)]P_2(\cos(\theta))\} \\ &= -\tau'_{\mathrm{lc}}\cos(2\pi Z/d) + H_N^{\mathrm{lc}}(1 + \kappa'_{\mathrm{lc}}\cos(2\pi Z/d)), \end{aligned} \quad (8)$$

where $S_{\mathrm{lc}}, \tau_{\mathrm{lc}}, \kappa_{\mathrm{lc}}$ are the liquid-crystal order parameters, $\alpha = 2\exp[-(\pi r_0/d)^2]$, r_0 is of order the molecular length and d is the repeat distance of smectic-A translational periodicity (see [13, p.70] for more details). v_{lc} and δ_{lc} are scale parameters characterizing interaction strengths and $\kappa'_{\mathrm{lc}} \equiv \alpha\kappa_{\mathrm{lc}}/S_{\mathrm{lc}}$ and $\tau'_{\mathrm{lc}} \equiv v_{\mathrm{lc}}\delta_{\mathrm{lc}}\alpha\tau_{\mathrm{lc}}$.

We assume that the only change to H^{sol} in the smectic-A phase is a change in the liquid crystal molecular potential seen by the solutes. The *solute* smectic-A Hamiltonian can then be written

$$H_A^{\mathrm{sol}} = -\tau'\cos(2\pi Z/d) + H_N^{\mathrm{sol}}(1 + \kappa'\cos(2\pi Z/d)), \quad (9)$$

where H_N^{sol} is given by Eq. (4), and $\kappa' \equiv \alpha\kappa_{\mathrm{sol}}/S_{\mathrm{lc}}$ and $\tau' \equiv v_{\mathrm{sol}}\delta_{\mathrm{sol}}\alpha\tau_{\mathrm{lc}}$ are experimental *coupling* and *smecticity* parameters that will be varied in the smectic fit. The following five Hamiltonian prefactors for the two solutes are the smectic fit parameters:

$$\begin{aligned} \kappa'_{\mathrm{dcb/fb}} &= \kappa'_{0,\mathrm{dcb/fb}}, \\ \tau'_{\mathrm{dcb/fb}} &= \tau'_{0,\mathrm{dcb/fb}}(1 + \tau'_1 T/300\ \mathrm{K}). \end{aligned} \quad (10)$$

Note that while the 'bare' values κ'_0 and τ'_0 are allowed to be solute dependent, we require that the (dimensionless) temperature dependence of τ' be the same for both solutes (i.e. same τ'_1). κ' (being a ratio of two terms in the Hamiltonian) is left temperature independent.

From the Hamiltonian we can again calculate the self-consistent *solute* order parameters. In addition to the nematic order matrix ($S_{ii} \equiv S_E$ which is fit to S_C to obtain the Hamiltonian prefactors) we also calculate the smectic-A (τ) and coupling (κ_{ii}) order parameters:

$$\begin{aligned} S_{ii} &= \int \mathrm{d}\Omega \int_0^d P_{2ii} f_A(\Omega, z)\,\mathrm{d}z, \\ \tau &= \int \mathrm{d}\Omega \int_0^d \cos(2\pi Z/d) f_A(\Omega, z)\,\mathrm{d}z, \\ \kappa_{ii} &= \int \mathrm{d}\Omega \int_0^d \cos(2\pi Z/d) P_{2ii} f_A(\Omega, z)\,\mathrm{d}z \end{aligned} \quad (11)$$

where P_{2ii} is as previously defined and

$$f_A = \frac{\exp(-H_A^{\mathrm{sol}}/k_B T)}{\int \mathrm{d}\Omega \int_0^d \exp(-H_A^{\mathrm{sol}}/k_B T)\,\mathrm{d}z}, \quad (12)$$

is the smectic-A distribution function.

When smectic ordering is correctly accounted for in the model, b in the smectic-A phase should simply be an extrapolation of that in the nematic. The asymmetry b in the smectic-A phase is thus constrained to lie on the linear fit to the nematic b (open symbols in Fig. 2). Allowing the five Hamiltonian prefactors to vary, we then fit to the observed order matrix with the above constraint. We can only fit R, the observed asymmetry in order matrix for the two solutes (Fig. 1b), to different values of the τ'_0 parameter. This may be linked to a systematic difference in the position in the smectic-A layer preferred by each solute. The goodness of the fit is exemplified by the solid line in Fig. 1b. Another important result is that the nematic–smectic-A coupling is almost the same ($\kappa' \equiv \kappa'_0 \approx 0.9$) for two solutes with very different τ'_0; see Table 1(a).

The smectic and coupling order parameters given by Eq. (11) for solutes fb and dcb are shown in Fig. 3 (mean values shown in Table 1(b)). Note that neither τ nor κ_{ii} are the same for the two solutes. We do not currently understand why some of the order parameters are negative: this deserves further investigation.

Table 1
Hamiltonian prefactors (error in last digit, shown in parentheses, is the standard deviation obtained from the fit) (a) and (b) mean values of the temperature dependent self-consistent solute smectic order parameters calculated using Eq. (11) and plotted in Fig. 3

		dcb	fb
(a) Hamiltonian prefactors			
	κ'_0	0.92(1)	0.85(1)
	τ'_0 (eV)	0.120(3)	0.040(3)
	τ'_1	−0.64(1)	−0.64(1)
(b) Order parameters			
	$\overline{\kappa_{xx}}$	0.061	0.036
	$\overline{\kappa_{yy}}$	−0.039	0.011
	$\overline{\kappa_{zz}}$	−0.022	−0.047
	$\overline{\tau}$	−0.31	−0.13

τ'_1 was forced to be identical for both solutes.

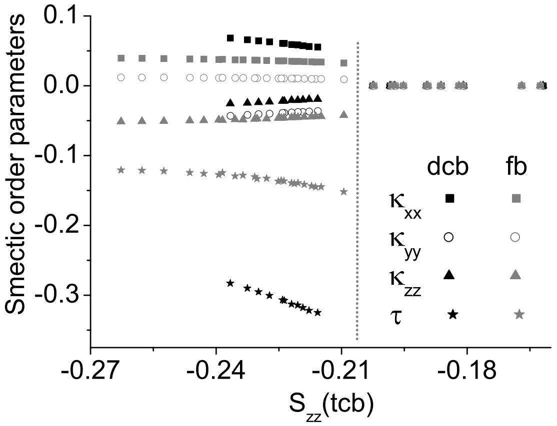

Fig. 3. Calculated smectic order parameters (Eq. (11)) κ_{xx}, κ_{yy}, κ_{zz} and τ (all identically zero by construction in the nematic phase, to the right of the gray vertical line) for solutes dcb and fb as a function of S_{zz}(tcb).

4. Conclusions

We thus obtain a self-consistent, good fit between experimental molecular measurements and Kobayashi–McMillan-like mean-field theoretical model parameters for solutes in a uniaxial liquid crystal. The smectic-A term in the Hamiltonian contains solute-dependent scale factors ($\tau'_{\mathrm{dcb}} \neq \tau'_{\mathrm{fb}}$) that increase with decreasing temperature. This is expected since $\tau' \propto \tau_{\mathrm{lc}}$. The nematic–smectic-A coupling appears to be a solute-independent liquid-crystal quantity: $\kappa'_{\mathrm{dcb}} \approx \kappa'_{\mathrm{fb}} \equiv \kappa'_{\mathrm{lc}}$.

The solute smectic order parameter and three nematic–smectic-A coupling order parameters have been self-consistently determined for both solutes. Finally, we have demonstrated in this Letter that a simple smectic ordering mechanism allows us to explain the observed change in orientational ordering of simple solute molecules in the smectic-A phase and to obtain quantitative values for the coupling and smecticity parameters in a mean-field smectic-A Hamiltonian.

Acknowledgements

We acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada. We thank Dr. D. Zimmerman, Dr. L. ter Beek and Dr. T. Chandrakumar for valuable assistance, and Professor G.S. Bates for the sample of 5CB-d$_4$.

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