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The smectic potential in a liquid crystal with a reentrant nematic phase: NMR of solutes

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Abstract

We test the application of Kobayashi–McMillan theory for the solutes *ortho*-, *meta*- and *para*-dichlorobenzene in a binary mixture of 6OCB/8OCB in which both high temperature nematic and low temperature reentrant nematic phases exist. Proton NMR spectra of these solutes are analyzed to give two independent order parameters from which the solute smectic potential can be parametrized. The derived smectic order parameters for the solutes in this binary mixture are discussed and compared with those previously found in pure 8OCB solvent.

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The degrees of orientational and positional order are central in the characterization of liquid crystals (LC) [1,2]. They are usually quantified by the order parameters derived from some anisotropic molecular property such as nuclear spin interaction, optical birefringence or magnetic susceptibility. The phase transition between a liquid crystal nematic phase (which has orientational order) and its smectic phase (which has both orientational and positional order) has long been studied for subtle effects that arise from the intrinsic coupling of their order parameters [3].

The mean-field behaviour of nematics is well described by Maier–Saupe theory [4,5]. The molecules that make up most nematic phases are rod-like and normally have a rigid core with flexible hydrocarbon ends. Although they have little symmetry, they are often approximated as axially symmetric rods and their NMR spectra are then determined by a single nematic order parameter, S_{lc}. Maier–Saupe theory [4,5] has been extended to describe smectic A phases (Kobayashi–McMillan theory) [6,7]. Kobayashi–McMillan theory invokes two additional order parameters to describe the smectic phase. The extent of layering is described by the smectic order parameter, τ, and the coupling of the nematic with the smectic order by the coupling order parameter, κ. However, crucial to mean-field theories is experimental determination of interaction parameters. The complexity of the nematic/smectic A (N–SmA) phase transition arises from the nematic/smectic coupling. Indeed several studies of the subtle effects of thermal fluctuations very close to the phase transition have been undertaken [3]. It is thus surprising in this context, that only recently has a systematic determination of the Hamiltonian prefactors in the Kobayashi–McMillan theory been undertaken [8]. One of the major obstacles is to estimate and account for the nematic potential in the smectic phase. There are non-trivial issues with the fitting procedure that involves extrapolation of the nematic behaviour. These issues are seen in recent work [9] of the selected solutes 1,2-dichlorobenzene (odcb), 1,3-dichlorobenzene (mdcb) and 1,4-dichlorobenzene (pdcb) in 4-*n*-octyl-4′-cyanobiphenyl (8CB) and in 4-*n*-octyloxy-4′-cyanobiphenyl

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(8OCB); a new temperature dependence of the smectic layering is proposed and found to produce physically reasonable smectic order parameters for these solutes. While this extrapolation gave reasonable results, the validity of such an extrapolation is untested. We consider in this work a liquid crystal with a reentrant nematic phase. In this case, one would expect that the contiguity of behaviour between the two nematic phases would inform us about the validity of the extrapolation. Alternatively, selective breakdown of such an extrapolation can yield information about the detailed behaviour of solutes in the three phases.

It is also expected that the strengths of both smectic and coupling terms depend on temperature. In the smectic A phase, the solutes 'see' a mean-field that is similar to that experienced by the liquid crystal molecules, and for the solutes used here (having either C_{2v} or D_{2h} symmetry) the interaction is

$$\begin{aligned} H_{\mathrm{A}}^{\mathrm{sol}} &= -\tau' \cos(2\pi Z/d) - \frac{3}{4} F_{ZZ} \beta_{zz} \\ &\times \left(\left(\frac{3}{2}\cos^2(\theta) - \frac{1}{2} \right) + \frac{b}{2} \sin^2(\theta) \cos(2\phi) \right) \\ &\times (1 + \kappa' \cos(2\pi Z/d)) \end{aligned} \tag{1}$$

where the asymmetry b in the energy is given by

$$b = \frac{\beta_{xx} - \beta_{yy}}{\beta_{zz}} \tag{2}$$

and Z is the space-fixed axis lying along the magnetic field; θ and ϕ are the polar and azimuthal angles that relate the molecule-fixed xyz axes to Z; d is the smectic layer spacing; and τ' and κ' are the solute smecticity and coupling terms. F and β denote a liquid crystal dependent tensor and a molecular tensor that depends on the solute, respectively. The nematic Hamiltonian $H_{\mathrm{N}}^{\mathrm{sol}}$ of solutes is given by Eq. (1) by setting τ' and κ' to zero. F_{ZZ} is in fact proportional to the liquid crystal mean-field.

The main problem (approximation) is that the nematic contribution in the smectic phase must be obtained by an extrapolation of the energy parameter, b, at high temperatures into the smectic region to allow the quantification of the 'smectic' contributions based on Kobayashi–McMillan theory. In the earlier studies [8,9], we have assumed a linear extrapolation. Two out of three solutes studied do give linear relations in the nematic phase, while the third solute (odcb) shows some curvature in the nematic phase and the linear extrapolation is not perfect. This work has, however, supported the application of Kobayashi–McMillan mean-field theory of smectic A phases to solutes dissolved in smectogens.

It would be interesting to examine additional systems to discover the reason(s) for the curvature in the nematic solute b parameter and to find a means of getting the nematic contribution in the smectics by using nematic results both above and below the SmA phase. The latter may be achieved in compounds that show a reentrant nematic (RN) phase. Indeed 8OCB can form a binary mixture with 6OCB to produce a phase diagram in which the SmA phase is sandwiched between the high temperature nematic and a low temperature RN phase [10]. The mixture also provides a new example in which insight into the solute partitioning may be achieved. NMR studies have been carried out in RN phases of pure liquid crystal (LC) compounds [11,12] and mixtures of LCs [13–15] with strong polar cyano end groups. In this work, the same set of solutes as used in Ref. [9] (odcb, mdcb, pdcb) is dissolved in a binary mixture of 6OCB/8OCB and some new and interesting results are generated to test further the application of Kobayashi–McMillan mean-field theory of smectic A phases.

A mixture of 72% 8OCB and 28% 6OCB by weight was prepared for dissolving the solutes odcb, mdcb, pdcb and 1,3,5-trichlorobenzene (tcb) with a total mole concentration of *ca.* 4%. The tcb was added as an internal orientational order reference and is not used in the present study. The final sample has a clearing temperature of 69 °C and a nematic/smectic A phase transition of 54 °C. Fig. 1(left) shows the variation of $-S_{zz}$ with temperature, which shows that the solute order parameters hardly change at the nematic/smectic A phase transition. However, as found in the earlier study [8], the transition for each solute is marked by a change in the slope of the solute order matrix asymmetry $R = (S_{xx} - S_{yy})/S_{zz}$ plotted *versus* parameters such as temperature, solute S_{xx}, *etc.*, as shown in Fig. 1(right). It is this change that is key to extracting information about the smectic potential.

The solute spectral parameters only depend on the solute orientational order parameters which can be calculated for the nematic phase using the solute nematic potential:

$$S_{ii} = \frac{\int \mathrm{d}\Omega \left(\frac{3}{2}\cos^2(\theta_i) - \frac{1}{2}\right) \mathrm{e}^{-\frac{H_{\mathrm{N}}^{\mathrm{sol}}}{k_{\mathrm{B}}T}}}{\int \mathrm{d}\Omega\, \mathrm{e}^{-\frac{H_{\mathrm{N}}^{\mathrm{sol}}}{k_{\mathrm{B}}T}}} \tag{3}$$

where θ_i is the angle between the i molecular direction and Z. Information on the smectic terms in $H_{\mathrm{A}}^{\mathrm{sol}}$, however, can only be obtained indirectly from the NMR observables. Once the smectic Hamiltonian is known, the order parameters of the solute in the smectic phase are then obtained from:

$$S_{ii} = \int \mathrm{d}\Omega \int_0^d \left(\frac{3}{2}\cos^2(\theta_i) - \frac{1}{2} \right) f_{\mathrm{A}}(\Omega, Z)\, \mathrm{d}Z \tag{4}$$

$$\tau = \int \mathrm{d}\Omega \int_0^d \cos\left(\frac{2\pi Z}{d} \right) f_{\mathrm{A}}(\Omega, Z)\, \mathrm{d}Z \tag{5}$$

$$\kappa_{ii} = \int \mathrm{d}\Omega \int_0^d \cos\left(\frac{2\pi Z}{d} \right) \left(\frac{3}{2}\cos^2(\theta_i) - \frac{1}{2} \right) f_{\mathrm{A}}(\Omega, Z)\, \mathrm{d}Z \tag{6}$$

where

$$f_{\mathrm{A}} = \frac{\mathrm{e}^{-\frac{H_{\mathrm{A}}^{\mathrm{sol}}}{k_{\mathrm{B}}T}}}{\int \mathrm{d}\Omega \int_0^d \mathrm{e}^{-\frac{H_{\mathrm{A}}^{\mathrm{sol}}}{k_{\mathrm{B}}T}}\, \mathrm{d}Z} \tag{7}$$

Thus, the orientational (S_{ii}) and positional (τ and κ_{ii}) order parameters of each of the C_{2v} and D_{2h} solutes in the smec-

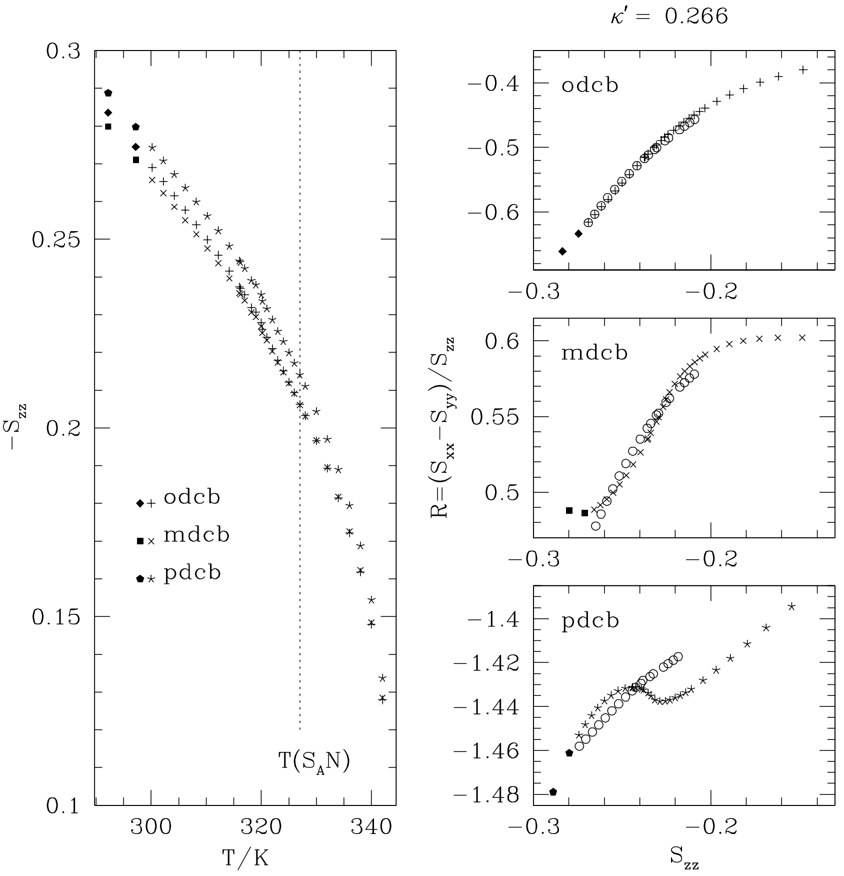

Fig. 1. Nematic phase points are to the right and smectic A phase points to the left in each plot with the two filled points to the far left being from the reentrant nematic (RN) phase. (Left) Variation of minus the experimental order parameter S_{zz} with temperature. The nematic/smectic A phase transition is marked with a vertical line. (Right) Order parameter ratio $R = \frac{S_{xx}-S_{yy}}{S_{zz}}$ *versus* S_{zz}. The same symbols as on the left are used for the experimental values and open circles are the values calculated from a fit to the three solutes odcb, mdcb and pdcb in the same liquid crystal mixture; $\kappa' = 0.266$ was varied but kept equal for all solutes. The value of τ'' is fitted for each solute and is scaled by $F_{ZZ}\beta_{zz}$ to give $\tau' = \tau'' F_{ZZ}\beta_{zz}$ for each experiment.

tic A phase are described by the four parameters $F_{ZZ}\beta_{zz}$, b, τ' and κ'. Note that in the limit $\kappa' \to 0$ and $\tau' \to 0$, Eq. (4) reverts to the nematic phase Eq. (3).

For all mesophases, we first fit the two independent order parameters measured in each spectrum for each of the three solutes odcb, mdcb and pdcb to the two energy parameters $F_{ZZ}\beta_{xx}$ and b of the nematic potential $H_{\mathrm{N}}^{\mathrm{sol}}$ (for this fitting we rewrite the Hamiltonian of Eq. (1) in terms of β_{xx} instead of β_{zz} and we set the smectic A coupling terms τ' and κ' to 0). The results of this fitting are presented in a plot of b *versus* $F'_{ZZ}\beta_{xx}$ (where $F'_{ZZ} = F_{ZZ}/k_{\mathrm{B}}$) in Fig. 2(left). The points to the left are energies for the nematic phase and those to the right are for the smectic A phase with the last two filled points to the far right being for the RN phase. As was the case for the order parameter asymmetry R, there is a change in slope of this plot at the nematic/smectic A phase transition for all three solutes in the binary mixture.

It is interesting to note that odcb in pure 8OCB [9] presents curvature in the nematic region of the b plot, and this behaviour is further exacerbated here, partly due to a larger nematic range in the mixture, as shown in Fig. 2(left). The use of a linear extrapolation of b for odcb into the SmA phase is therefore not a viable option. For the other solutes mdcb and pdcb, one can use linear extrapolation of the nematic results to get the contribution of the nematic potential in the SmA phase, giving a linear equation with intercept (0.541 for mdcb; −1.326 for pdcb) and slope (-9.97×10^{-4} for mdcb; 7.23×10^{-4} for pdcb). The smectic (and RN for pdcb) points of these two solutes show deviations from the linear behavior of the nematic points, while the RN points for mdcb do fall on the extrapolation line.

If we assume that b and $F_{ZZ}\beta_{xx}$ are correlated in the same way in all phases, this frees up one of the two experimentally determined S parameters. As a consequence, at each temperature one can determine one extra unknown in $H_{\mathrm{A}}^{\mathrm{sol}}$ (i.e. τ' or κ'). As demonstrated recently [9], a global fit of order parameters measured in the SmA phase to both τ' and κ' is possible if τ' is taken as a solute-dependent parameter with temperature dependence scaled according to $\tau' = \tau'' F_{ZZ}\beta_{zz}$ (with τ'' a constant for each solute), while κ' is assumed to be a constant specific to the solvent (LC) used.

Initially, we treated only the mdcb and pdcb with the above procedure. The RN phase in the binary mixture has a narrow temperature range, and unfortunately is

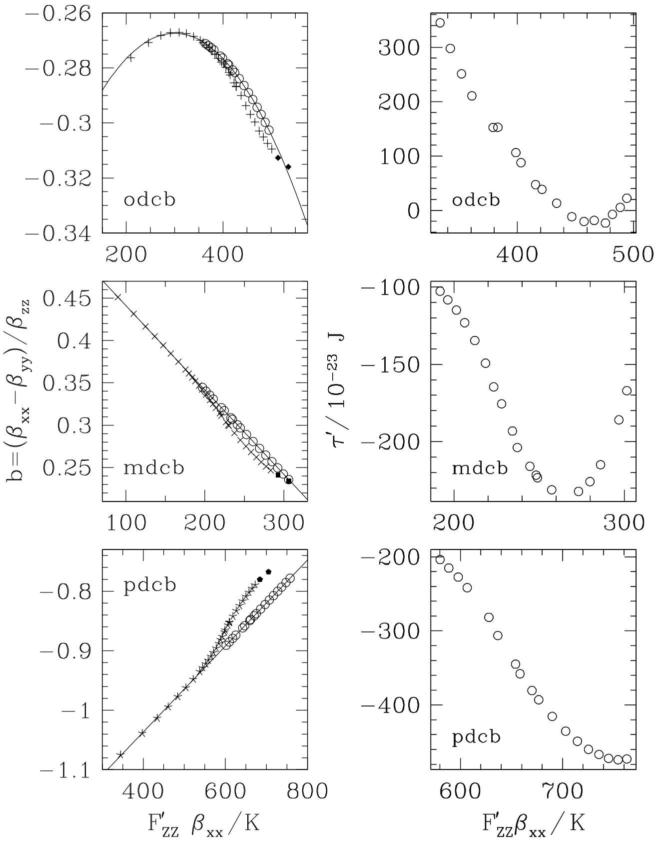

Fig. 2. (Left) Asymmetry in the energy b plotted *versus* $F'_{ZZ}\beta_{xx}$ where $F'_{ZZ} = F_{ZZ}/k_B$. The experimental symbols of Fig. 1(left) are now used for the exact fitting of the solute orientational order parameters to the two independent β_{ii} energy parameters b and β_{xx}. The intercepts and slopes of the straight lines drawn through the nematic points for mdcb and pdcb are reported in the text, while odcb has a curved fit to the nematic points as detailed in the text. The open circles are the b and $F'_{ZZ}\beta_{xx}$ values from the fit to the smectic potential, Eq. (1). The points for the nematic phase are to the left and those for the smectic A phase to the right in each plot. (Right) The fitting parameter τ' *versus* $F'_{ZZ}\beta_{xx} = F_{ZZ}\beta_{xx}/k_B$ for exact fits to each experiment; κ' was fixed to 0.266. Note that similar exact fits are possible with other values of κ'.

metastable close to the crystallization temperature. Hence we are cautious in using the order parameter results at low temperature as there is some uncertainty in locating the SmA/RN transition. If we include more points near the low temperature ends, the fits deteriorate with larger mean square errors. In fact, in fitting the SmA results the two lowest temperature (RN) points were excluded and a reasonable κ' of *ca.* 0.3 was obtained.

As seen in Fig. 2(left), in the case of pdcb we find that the two lowest temperature filled points do not fall on the line extrapolated from the high temperature nematic points. However, the lowest temperature filled points in mdcb do lie on the extrapolated nematic line and thus have no contribution from the smectic terms. Thus in order to deal with the nematic curvature for odcb in the b plot of Fig. 2(left), we assume a behavior similar to that for mdcb and have included the two lowest temperatures with the nematic results to interpolate the corresponding nematic contribution in the SmA phase based on the quadratic equation $b = -0.351 + 5.54\times10^{-4}y - 9.23\times10^{-7}y^2$ where $y = F'_{ZZ}\beta_{xx}$. This appears to be a reasonable way to overcome the difficulty in estimating the nematic potential for odcb in the SmA phase and we proceed to do the global analysis of all three solutes with one κ' for the liquid crystal mixture, one τ'' for each solute and a β_{xx} for each solute at each temperature.

The results are summarized in Fig. 2(left) as open circles giving the b and $F'_{ZZ}\beta_{xx}$ values from the fit to the smectic potential, Eq. (1). As required by the extrapolation (interpolation) procedure used to obtain the nematic part of the potential in the smectic A phase, these points all fall on the nematic line (curve). The optimized τ'' values are −0.015, 0.193 and 0.379 for odcb, mdcb and pdcb, respectively, and the optimized κ' value is 0.266 for the mixture.

The fitted order parameters (open circles) for the three solutes in the SmA phase are plotted in Fig. 1(right). As seen in this figure, the experimental R behavior of pdcb in the SmA phase cannot be reproduced; at this time, the reason for such a discrepancy is unclear. The fits of the R curves for the other solutes are rather good.

An alternative approach to fitting the results is to use a fixed κ' (we choose the value 0.266 from the global fit above) and do an exact fit to the two nematic order parameters with unknowns $F'_{ZZ}\beta_{xx}$ and τ' at each temperature. The τ' values obtained for each solute are shown in Fig. 2(right). Although the R behavior of all solutes can be faithfully reproduced in the SmA phase, the τ' values obtained depend on the choice of κ', and unfortunately the procedure here does not provide any new physical insight.

We assume that κ' is positive which is consistent with the nematic ordering being maximum near the core (centre of a smectic layer) [9,16]. The relative signs of τ' and κ' are determined by the fitting. The smectic order parameters are then calculated from Eq. (5) for the three solutes and are summarized for the global and exact fits in Fig. 3. The different approaches to the fitting show qualitatively the same trend, with $\tau_{odcb} > \tau_{mdcb} > \tau_{pdcb}$. In the pure 8OCB case, τ' is negative, and the three solutes all have negative smectic order parameter τ with $\tau_{mdcb} > \tau_{odcb} > \tau_{pdcb}$; Eq. (1) then predicts that the smectic potential in 8OCB is maximum at the origin and minimum at the interlayer interface, indicating that the solutes prefer to partition near the interface (hydrocarbon tail region of the liquid crystal molecules) [9]. Such is not the case in the mixture where τ for odcb is positive. In this case the values and signs of τ indicate that pdcb (and to a lesser extent mdcb) appears to favor the interlayer region, while odcb favors slightly the intralayer region. The coupling order parameters, κ_{ii}, are all small and values are not reported.

The observations in the mixture of the positive sign for τ_{odcb} and the curvature for odcb in the nematic phase (Fig. 2(left)) are interesting and must reflect on changes in the intermolecular interactions in the mixture compared to those in the pure 8OCB solvent. As noted in [9], the fact

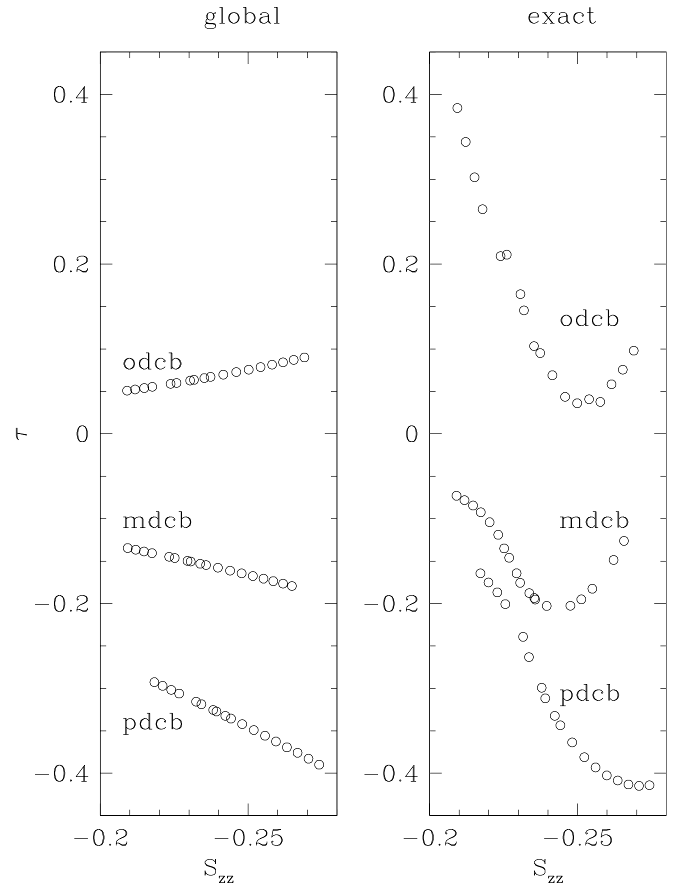

Fig. 3. Smectic order parameter τ *versus* S_{zz} (note increasing magnitude to the right) from the global fit (left) and the exact fits (right).

that b is not constant indicates that more than one mechanism is involved in the ordering of the solutes. Changes with solvent in the relative importance of mechanisms could result in the tendency of some solutes to partition more than others into selected regions of the layers. These changes might also lead to changes in the out-of-plane diffusion constants which can be measured by pulsed-field-gradient NMR experiments.

In conclusion, we have demonstrated that we can deal with the non-linearity of the nematic b points for odcb (Fig. 2(left)) in a manner that is consistent with our treatment of mdcb where a linear fitting of the nematic points is possible and the extrapolated line goes through one of the points in the RN phase. While the pdcb linear fit does not exhibit similar behaviour, the RN points appear to show a tendency to head towards the linear fit to the nematic points for this solute. A RN phase with a wider temperature range could be advantageous in this case.

The value of κ' obtained here from the global fit for the 6OCB/8OCB mixture (0.27) is smaller than the values obtained for pure 8CB and 8OCB (0.4) in earlier work [9]. This indicates that there is less variation in the nematic potential as one crosses a smectic layer. We conclude that the difference in phase structure induced by the mixing of different length liquid crystal solvents is affecting the variation of the nematic potential within the smectic layers. This difference also affects the partitioning of the solutes as demonstrated by the opposite signs of the τ smectic order parameters obtained for odcb in the mixture compared to the values found in pure 8CB and 8OCB. Experiments utilizing a pure liquid crystal that has a larger and more stable RN phase than that for the mixture used here would be helpful to clarify further and to check critically these results.

Acknowledgements

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