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The effect of solutes on the orientational ordering of liquid-crystalline solvents

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The effect of solutes on the orientational ordering of the liquid-crystalline solvents 4-*n*-heptyl-4′-cyanobiphenyl (7CB) and 4-*n*-octyl-4′-cyanobiphenyl (8CB) has been studied by ^{13}C NMR. The technique used was a combination of variable-angle spinning (VAS) and a two dimensional method called separated local field (SLF) spectroscopy. 7CB exhibits only a nematic phase. The effects of four different solutes (carbon tetrachloride, cyclohexane, benzene, hexane) with mole fractions of *c.* 0·08 as well as different mole fractions of hexane were studied. 8CB has a nematic phase and a smectic A phase, and the effect of hexane with mole fraction of *c.* 0·07 was investigated. It was found that the effect of solutes in reducing the nematic to isotropic temperature (T_{NI}) has the order $CCl_4 \approx$ cyclohexane > benzene > hexane. The incorporation of hexane in 8CB reduce T_{NI} more significantly than T_{SN}, the smectic to nematic transition temperature. On the other hand, at the same reduced temperature (T/T_{NI} for 7CB an T/T_{SN} for 8CB), there is no significant change in the order parameters of either the core or the chain of the host liquid crystals, except for a fairly high concentration of hexane (mole fraction of 0·16) in 7CB. This indicates that the solute molecules do not have appreciable preferential association with any special part of the solvent molecules.

1. Introduction

The interaction between solutes and liquid crystal hosts has been of interest to people involved in both basic research and practical applications. Some of the applications of liquid crystal solutions are (1) the fabrication of coloured liquid crystal displays by doping dyes in liquid crystal media [1–3], (2) the creation of new chiral smectic C (S_C^*) materials by dissolving chiral dopants in S_C hosts [4], (3) the use of liquid crystals as an anisotropic solvent for the studies of molecular geometry and chemical shift anisotropy of solute molecules [5–14], and (4) measurement of order parameters of the host by using the solute as a 'probe' [15–18].

The early work by Dave and Dewar showed that the addition of non-mesomorphic compounds to a nematic liquid crystal results in a depression of both the melting point and the nematic–isotropic transition point T_{NI}, and the disturbing effect of the solute to its host increases with the molecular size of the solute [19]. Because of difficulties in studying the nematic solvent phase itself, the perturbation of various solutes on the orientational ordering of the host has often been estimated by observing properties of the solute, including the use of special 'probe' molecules. For example, Khetrapal and Martire used proton NMR to measure the alignment of the H–H axis of a number of polar and non-polar solutes in various liquid crystal solvents [20, 21]. Their results showed that the orientational parameters of the solute as a function of relative temperature ($T - T_{NI}$) depend only upon the liquid crystal solvent as long as there is no change in the internal structure of the solutes, such as aggregation, decomposition or ionization. Luckhurst and Chen used ESR to study the alignment of a paramagnetic probe as a function of temperature in mixtures of *p*-azoxyanisole with various non-mesomorphic solutes [22]. Although the addition of solutes results in a large depression of T_{NI}, the alignment of the probe is essentially unaffected, suggesting that the presence of the solute does not seriously disturb the highly ordered structure of the mesophase. A more systematic investigation on the effect of solute size and shape on the ordering of liquid crystal solvent was performed by Kronberg *et al.* [23] by applying wide-line proton NMR to observe the doublet splitting arising from the dipole–dipole interaction between the *ortho*-protons of the benzene rings in MBBA. Their results indicated that the order parameter of MBBA as a function of reduced temperature gives a universal curve even for solutes having widely different molecular shape. Their results suggested that the shape of the solute only affects the transition temperature of the solvent, but not its order parameter at a constant value of $T - T_{NI}$. In addition to the study of order parameters, Moseley and Loewenstein used proton and deuterium NMR to measure the translational diffusion of methane and chloroform in nematic, smectic A and smectic B liquid crystal solvents [24]. They found that the diffusion coefficient parallel to the director ($D_{\parallel}$) is greater than that perpendicular to the director ($D_{\perp}$) for liquid crystals forming only nematic phases, while $D_{\parallel}/D_{\perp} < 1$ for nematic phases of smectic-forming materials, and $D_{\parallel}/D_{\perp} \ll 1$ for smectic materials. The latter was interpreted by the expulsion of solute from the aromatic cores into the aliphatic end chains as a result of the smectic layering behaviour [24].

Recently, we have developed a powerful technique to study the orientational ordering of bulk liquid crystals [25]. The essence of this technique is a combination of variable-angle spinning (VAS) and a two-dimensional method called separated local field (SLF) spectroscopy. The results give C–H dipolar coupling constants for each carbon atom in the molecule, from which the order parameters can be calculated. A remarkable advantage of this technique is that the order parameters of each segment in the liquid crystal molecule can be determined at the same time without isotope substitution. Therefore, the investigation of liquid crystal solvent in a solution by this VAS/SLF technique will not only provide the overall orientational information of the host, but also the effect of solutes on each part of the host molecules.

In this work, we have studied the orientational ordering of nematic 4-*n*-heptyl-4′-cyanobiphenyl (7CB) in the presence of four different solutes (hexane, benzene, cyclohexane and carbon tetrachloride) by the application of this VAS/SLF technique. For comparison, the effect of hexane on the orientational parameters of 4-*n*-octyl-4′-cyanobiphenyl (8CB), which has a bilayer smectic A structure in addition to the nematic phase [26], has also been studied. The results indicate that in the presence of solutes, the nematic–isotropic transition temperature is depressed significantly for both 7CB and 8CB, but the smectic–nematic transition temperature for the 8CB has a smaller depression. On the other hand, the order parameters of both the rigid core and the flexible chain stay essentially unchanged at the same reduced temperature for both compounds.

2. Experimental

The liquid crystal solvent 4-*n*-heptyl-4′-cyanobiphenyl (7CB) and 4-*n*-octyl-4′-cyanobiphenyl (8CB) were purchased from EM Chemicals, Hawthorne, New York.

The nematic ranges as specified by the manufacturer are 30–42·8°C and 33·5–40·5°C, respectively, and the smectic range for 8CB is 21·5–33·5°C. The nematic–isotropic and the smectic–nematic transition temperature are designated by T_{NI} and T_{SN}, respectively. GR grade Benzene, cyclohexane, and hexane were purchased from EM Chemicals, and carbon tetrachloride was purchased from J. T. Baker Chemical Co. They were all used without further purification.

The ^{13}C NMR spectra were measured with a Varian XL-300 NMR spectrometer equipped with a variable-angle spinning probe manufactured by Doty Scientific, Columbia, South Carolina. The SLF pulse sequence was used with a ^{13}C spin echo and the BLEW-48 decoupling sequence [27]. A VXR-4000 data station was used to process the data.

Details of experimental conditions and data processing have been described previously [25], except for the calibration of the angle of the spinning axis with respect to the magnetic field (θ). The angle was determined by measuring the ratio of the F–F dipolar coupling of 2,2-difluoro-1,1,1,2-tetrachloroethane in the nematic mixture ZLI-1291 with and without spinning (spinning rate c. 1 kHz)

$$\Delta\nu_{(\text{spinning})}/\Delta\nu_{(\text{non-spinning})} = (3\cos^2\theta - 1)/2. \tag{1}$$

The radiofrequency (r.f.) power used in this work was 25 W, with $\gamma B_2/2\pi$ varying from 20 to 24 kHz depending on the experimental temperature. To avoid r.f. overheating, a 0·7 per cent decoupler duty cycle was used with a total cycling time of 6 s. Temperature calibration was made by observing the nematic–isotropic transition of pure 7CB. For measurements below room temperature, filtered pressurized air was passed through a cooling coil in an ice–water bath to provide sufficient cooling for operation down to about 10°C.

3. Clearing point depression of the host by the dissolving solutes

The transition temperatures were determined by observing the discontinuities in the chemical shift dependence on temperature. The T_{NI} values of 7CB with four different solutes having about the same mole fraction of c. 0·08 are listed in table 1 (*a*), and the T_{NI} values having different mole fraction of hexane are listed in table 1 (*b*). Higher concentrations of hexane reduce T_{NI} too much and destroy the liquid-crystalline phase. The effect of the solutes in reducing T_{NI} of the host 7CB has the order: carbon tetrachloride ≈ cyclohexane > benzene > hexane, while the change T_{NI} with the mole fraction of hexane is essentially linear, obeying Henry's law for dilute solutions. (As a comparison, the dissolution of methane

Table 1. The T_{NI} values for 7CB (experimental errors ±0·5°C).

(*a*) Different solutes with mole fraction ≈ 0·08.

Solute	None	Hexane	Benzene	Cyclohexane	CCl_4
T_{NI}	42·5	39·0	35·5	32·7	32·2

(*b*) Hexane of varying mole fractions.

X_{hexane}	0·00	0·04	0·05	0·08	0·16
T_{NI}	42·5	41·3	40·5	39·0	32·7

in 7CB with a mole fraction of 0·04 reduces the $N \rightarrow$ I temperature to 40·5°C [24].)

From the results in table 1, we can see that the perturbation to the host by a solute is significantly related to the shape of solute. The order of T_{NI} depression indicates a more or less globular solute (CCl_4) disturbs the host the most. The disc-shaped benzene has a smaller effect than the bulkier cyclohexane. Hexane with a flexible chain has the smallest disturbance. This is in accordance with other results in the literature [19–24].

The values of T_{NI} and T_{SN} for 8CB and for hexane dissolved in 8CB (mole fraction of 0·073) are listed in table 2. It is noted that the incorporated of hexane depresses T_{NI} significantly more than T_{SN}, so that the nematic temperature range of the 8CB with hexane is smaller than that without solute.

Table 2. The T_{NI} and T_{SN} values for 8CB (experimental errors $\pm 0{\cdot}5$°C).

	Pure 8CB	$X_{hexane} \approx 0{\cdot}07$
T_{NI}	40·5	33·0
T_{SN}	36·5	31·0

4. Spectral analyses

The principles of the SLF/VAS method have been thoroughly discussed previously [24, 28–33]. Basically, rapid sample spinning about an axis forming an angle θ with the magnetic field B_0 causes the nematic director to align along the spinning axis and reduces C–H dipolar couplings by a factor of $(3\cos^2\theta - 1)/2$. The BLEW-48 decoupling sequence for proton–proton dipolar decoupling [24] is applied during the evolution period and broadband proton decoupling is applied during the acquisition period. With this method, spectra in two dimensions are obtained: the ω_2 dimension shows proton-decoupled ^{13}C spectra and the ω_1 dimension shows proton splittings for individual carbon atoms. As an example, the spectra of bulk 7CB at $T_{NI} - T = 5$°C is illustrated in figure 1. Spectra of all the other samples in this work

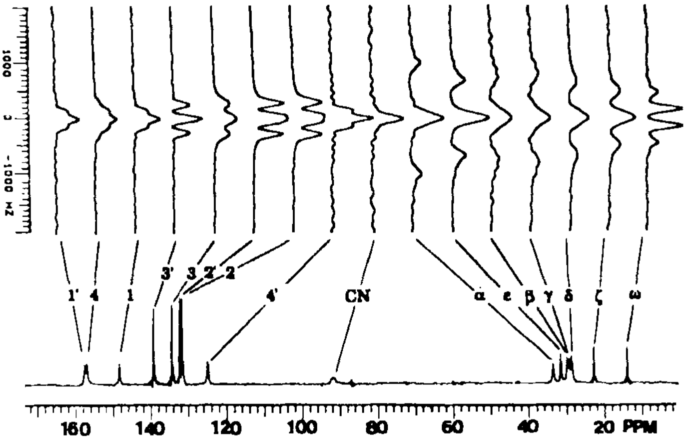

Figure 1. Carbon-13 VAS/SLF spectra of 7CB at 75·4 MHz: temperature = 35·5°C, $\theta = 47{\cdot}5$°, spinning rate = 1·0 kHz, spectra in the ω_1 dimension are shown on top and the first spectrum in the ω_2 dimension is shown at the bottom.

are of the same pattern. The peaks were assigned according to the results of a 2D carbon connectivity experiment [34]. The splitting of a multiplet in the ω_2 dimension is given by [35–37]

$$\Delta\nu = 0{\cdot}42[(3\cos^2\theta - 1)D + J], \tag{2}$$

where 0·42 is a scaling factor the BLEW-48 dipolar decoupling sequence [12], D is the C–H dipolar coupling constant, and J is the C–H scalar coupling. The scalar coupling constants used in this work were obtained from measurements in an isotropic solution of 7CB in $CDCl_3$ [34]. Considering that their values are small compared to the dipolar couplings, it can be safely assumed that the differences in scalar couplings between liquid-crystalline phase and isotropic solution is negligible without appreciable error.

For the aliphatic chains, the $\Delta\nu$ values of each C–H bonding are readily obtained from the VAS/SLF experiment because the observed splittings for the CH_2 triplets and those for CH_3 quartets are large. The observed coupling of each C–H bond is determined by the weighed average orientation of that bond. Therefore, the expression for the order parameters is

$$S_{\mathrm{C\text{-}H}} = (-4\pi^2 r^3 D_{\mathrm{C\text{-}H}})/(\gamma_{\mathrm{C}}\gamma_{\mathrm{H}} h) = -4{\cdot}407 \times 10^{-5} D_{\mathrm{C\text{-}H}} \tag{3}$$

where an interatomic distance of 0·110 nm was used.

For the aromatic rings, the splitting pattern for the protonated carbons is a doublet of doublets resulting from the interaction of the directly bonded proton and the *ortho*-proton, respectively. A genuine triplet is observed for the quaternary-carbons, because the rapid jumps of the benzene rings between four equilibrium positions make the *ortho*-protons identical [38]. Since all the peaks in each group overlap to a certain extent, the multiplets were fitted to the sum of the corresponding number of gaussian peaks using the non-linear least-squares program SPIRAL [39]. The standard errors of the splittings obtained in the calculations are usually 0·5 per cent or less. For the doublet of doublets, the large C–H splitting is assigned to that of the *ipso*-proton, and the small splitting is assigned to that of the *ortho*-proton. For the spectra obtained at temperatures close to the clearing point, the triplets for the quaternary carbons are sometimes too broad to be deconvoluted. In these cases, only the splittings from the doublet of doublets were used for further calculation of the core order parameters. Once the $\Delta\nu$ values for each C–H pair was obtained, the C–H dipolar coupling constants D were readily calculated by using equation (2).

Because of the effective D_2 symmetry of each phenyl ring in 7CB and 8CB, only S_{zz} and $S_{xx} - S_{yy}$ are required to describe the orientational ordering of each ring. The observed dipolar coupling can be expressed by

$$D_{ij} = -\gamma_i\gamma_j h/(8\pi^2 r_{ij}^3)\,[S_{zz}(3\cos^2\Phi_{ijz} - 1) + (S_{xx} - S_{yy})(\cos^2\Phi_{ijx} - \cos^2\Phi_{ijy})]. \tag{4}$$

The z axis denotes the C_2 axis, whereas x is the in-plane axis perpendicular to z. The bond-lengths used in this calculation were 0·140 nm for $r_{\mathrm{C\text{-}C}}$ [40, 41] and 0·108 nm for $r_{\mathrm{C\text{-}H}}$ [42, 43]. For each phenyl ring in the molecule, the order parameters and the bond-angles were obtained by using a non-linear least-squares program to fit the relevant order parameters. In the following notations, the x, y and z axes refer to the ring with the alkyl chain, and the x', y' and z' axes refer to the ring with the cyano group. Since the calculated values of $S_{xx} - S_{yy}$ and $S_{x'x'} - S_{y'y'}$ are very small compared to that of S_{zz} and $S_{z'z'}$ and they do not show systematic dependence on temperature, only S_{zz} and $S_{z'z'}$ will be considered in our discussion of the effect of solutes on solvent ordering. The calculated bond angles are essentially unchanged for all the samples under investigation at different temperatures. For the rings with the aliphatic chain, ∠H2–C2–C3 = 119·5° ± 0·2°, ∠C2–C3–H3 = 120·7° ± 0·2°; for the rings with the cyano group, ∠H2′–C2′–C3′ = 120·1 ± 0·2°, ∠C2′–C3′–H3′ = 121·1° ± 0·2°. The ∠H3′–C3′–C2′ and ∠C2–C3–H3 angles are slightly larger than 120° because there is less steric hindrance along the direction of the cyano group and the alkyl chain respectively.

5. Effect of solutes on the orientational ordering of 7CB

The order parameters for all the chain-segments of the 7CB with different solutes are plotted as a function of reduced temperature (T/T_{NI}) in figure 2. The values of this and other systems (7 pages) are available, as a Supplementary Publication, from the British Library Lending Division and may be obtained by using the procedure described at the end of this issue and by quoting the number SUP 16517. The order parameters S_{zz} and $S_{z'z'}$ calculated for the two phenyl rings of 7CB with different solutes are plotted as a function of temperature in figures 3 (*a*) and (*b*), respectively.

The data of T_{NI} themselves do not give specific information on the distribution of the solutes in the host. On the other hand, our study of the order parameters of the solvent does provide such information. If there is a tendency for a solute to associate with specific parts of the solvent, the order parameters of different parts in the

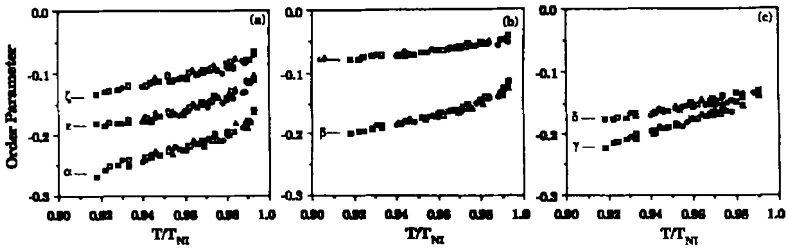

Figure 2. The C–H bond order parameters for the alkyl chain of 7CB at different reduced temperatures (T/T_{NI}). (*a*) α-CH_2, ε-CH_2, and ζ-CH_2, (*b*) β-CH_2 and ω-CH_3, (*c*) δ-CH_2 and γ-CH_2. ▣, pure 7CB; ◆, with benzene; ◇, with carbon tetrachloride; ⊟, with cyclohexane, all having a mole fraction of *c*. 0·08; ■, □, ▲, ▲, with hexane (mole fractions being 0·04, 0·05, 0·08, 0·16, respectively).

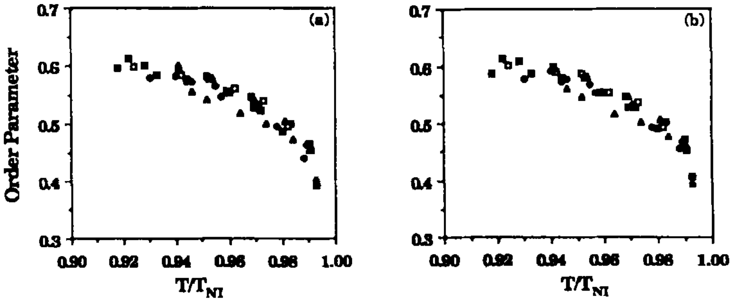

Figure 3. The core order parameters of 7CB at different reduced temperatures (T/T_{NI}). (*a*) S_{zz} of phenyl ring with the alkyl chain and (*b*) S_{zz} of the phenyl ring with the cyano group; symbols used are defined in the caption to figure 2.

molecules of the host liquid crystal would be affected differently. This could be the case if benzene is specially associated with the phenyl rings of the solvent [24], or the solvent excludes the solute from the rigid core segments to the mroe flexible part [3]. However, as it is shown in figures 2 and 3, when the reduced temperature (T/T_{NI}) is considered, the order parameters for each segment of the host are essentially the same with and without solute except for $X_{(hexane)} = 0{\cdot}16$. The divergence of the rest of the data falls within the experimental uncertainties (about 5 per cent or less). This can be explained by a lack of significant preferential association of the solute molecules with any particular part of the solvent molecules. To put it in another way, if there is a preferential distribution of solute molecules in the liquid crystal host, the effect on the orientational ordering of the host molecules is too small to be detected within our experimental error (5 per cent). This is quite reasonable because the molecules in the nematic phase are very mobile. There is no reason to believe that the solute molecules would have preferential association with certain parts of the liquid crystal host molecules, unless there are some specific interactions such as hydrogen bonding. Nevertheless, we believe that it is the first time that this aspect has been demonstrated unequivocally. In the case of a large mole fraction of hexane (0·16), we note that there is a slight reduction in the core ordering (figure 3), whereas the effect on the chain ordering is not noticeable (figure 2).

In the molecular field theory of nematic liquid crystals, the order parameter of a molecule is determined by the mean field created by all other molecules [44]. For rigid rods, the order parameter is a universal function of the reduced temperature T/T_{NI} [45]. This turns out to be a reasonable approximation for many systems [45]. From our results, this assumption is applicable to 7CB with various solutes having a mole fraction of *c*. 0·08. The presence of a large mole fraction of hexane (0·16) obviously changes the mean field to an appreciable extent, so that the core order parameters become lower (figure 3). In a theory extended to consider the ordering of the flexible chain in a liquid crystal molecule, a potential of mean torque [45, 46] is used. The order parameters of the chain segments are determined by the interaction between the core and the chain as well as the segmental motions of the chain itself. Our data in figure 2 indicate that these factors do not seem to change appreciably with different solutes and throughout the concentration range studied. Even the presence of a mole fraction of 0·16 hexane reduces the order parameters of the core, the core–chain interaction seems not to be affected within our experimental error.

6. Effect of hexane on the orientatinal ordering of 8CB

Unlike its homologue 7CB which displays only loosely packed nematic phase, 8CB has a smectic A phase with a bilayer packing arrangement [26, 47]. As mentioned in the introduction, Moseley and Loewenstein observed the anisotropic diffusion of solute molecules in 8CB and proposed a possible preferential residence of solute molecules in the aliphatic chain domain of the host [24]. If this is true, the incorporation of the solute into the liquid crystal solvent may cause differential disturbance to the ordering of the aliphatic chain of the host molecules. To investigate this, the effect of hexane on the orientational ordering of 8CB was studied at various temperatures.

The VAS/SLF data for 8CB with and without solute were processed in the same way as described above. The peak assignment was also made according to the former results in [30]. The S_{zz} values for each phenyl ring thus obtained are plotted as a function of T/T_{NI} in figure 4 (*a*). For the aliphatic chain, only the α, δ, ζ, η and ω peaks

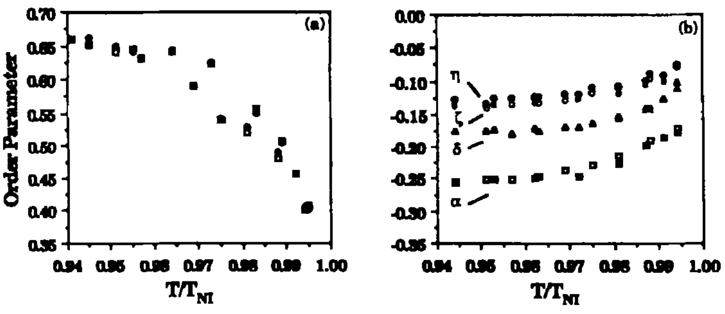

Figure 4. The order parameters of 8CB at different reduced temperatures (T/T_{NI}). The open symbols are for pure 8CB, and the closed symbols are for 8CB with hexane (mole fraction 0·07). (*a*) phenyl core; diamonds, S_{zz} of the phenyl ring with the octyl chain; squares, S_{zz} of the phenyl ring with the cyano group. (*b*) C–H bonds in the alkyl chain; squares, α-CH_2; triangles, δ-CH_2, diamonds, η-CH_2; circles, ζ-CH_2.

are well resolved because of partial overlapping of the carbon signals. The ω-CH_3 gives nearly zero splitting because of the odd–even effect [48–50]. The S_{C-H} values for the other carbons are plotted as a function of T/T_{NI} in figure 4(*b*).

From the data in figure 4, one might get an impression that the presence of hexane raises the ordering parameters of the host in the intermediate temperature range of $T/T_{NI} \sim$ 0·96 to 0·98. However, when the data are replotted to compare only the smectic A phase (figure 5), the order parameters for 8CB with and without solute are essentially the same at the same reduced temperature T/T_{SN}. The slight difference between the two types of data points near T_{SN} is likely due to experimental uncertainty, because there is a temperature gradient of about 1° in the sample, and the temperature dependence of the core order parameter near T_{SN} is quite steep. The overall result again indicates that the effect of a small amount of solute molecules on the ordering of a liquid crystal host is not significant when the reduced temperature is considered. In other words, the incorporation of hexane into the smectic A phase of 8CB only affects the phase transition temperature of the host, but does not cause significant changes in the order parameters of either the aromatic core or the aliphatic chain. This is different from the model proposed by Moseley and Loewenstein based on the diffusion measurement. It is possible that the anisotropic diffusion phenomena of solute in smectic A phase of 8CB observed by Moseley and

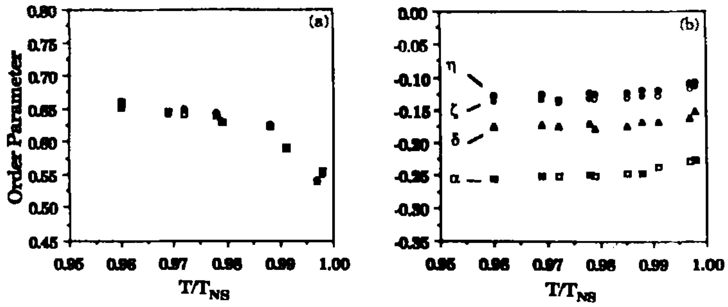

Figure 5. (*a*) The core order parameters of 8CB at different reduced temperatures (T/T_{SN}); symbols used are defined in the caption to figure 4(*a*). (*b*) The C–H bond order parameters for the alkyl chain of 8CB at different reduced temperatures (T/T_{SN}); symbols used are defined in the caption to figure 4(*b*).

Loewenstein may have been due to the inter-layer diffusion as mentioned by Priestley [51].

7. Conclusion

The incorporation of solutes (mole fraction *c.* 0·08) causes a significant clearing point depression of 7CB. The effect of the solutes in reducing T_{NI} has the order CCl_4 ≈ cyclohexane > benzene > hexane. The incorporation of hexane in 8CB causes depression of both T_{NI} and T_{SN}, but the change in T_{NI} is larger than that in T_{SN}. Therefore, the existence of solute decreases the nematic range of 8CB. On the other hand, at the same reduced temperature (T/T_{NI} for 7CB and T/T_{SN} for 8CB), there is no significant change in the order parameters of either the core or the chain in the host liquid crystals. This indicates that the solute molecules do not have significant preferential association with any special part of the solvent molecules.

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