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Structure Effect of Solute on Orientational Order in Binary Mixture by ^{2}H-NMR and Molecular Simulations

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The orientational order parameters of six solutes with different shapes and sizes dissolved in two nematic solvents have been measured as a function of temperature. The parameter, S_{xx}-S_{yy} is correlated with the molecular geometrical structure, while S_{zz} is affected by not only the geometry but also the anisotropy in the polarizability. The molecular dynamics simulations are carried out using a realistic atom-atom potential for evaluating the ordering properties in the nematic phase. The results provide reasonable values of S_{zz} corresponding to experimental ones for solutes and solvents, and also a prediction of uniaxiality for the nematic phase.

Keywords: binary mixture; nematic phase; order parameter; ^{2}H-NMR; molecular dynamics simulation

INTRODUCTION

When a solute of non-liquid crystalline molecule is dissolved in nematic solvent, the interaction between solute and solvent molecules results in an orientational ordering of the solute. The solute-solvent interactions responsible for solute orientation in nematic solvents have been the subject of much interest. In our previous work, ordering properties in binary mixture of solutes and liquid crystalline molecule have been

evaluated by Monte Carlo simulations with mean field approximation to discuss ordering relations between molecular shapes or interaction strength of solutes and liquid crystalline molecules as a solvent.[1] We have shown that the degree of induction order for isotropic solutes is dependent not only on the shape anisotropy but also on the characteristic parameter related to the ability to follow the surrounding orientation.

Deuterium NMR spectroscopy has proved to be a unique and powerful technique for determination of the orientational order parameters of solutes dissolved in the nematic solvent. There have been many studies of the orientational order of non-liquid crystalline solute dissolved in liquid crystalline phase by deuterium NMR [2,3]. On the other hand, the substantial increase in available computer speed has led to the use of computer simulations as a tool for understanding liquid crystal phases. Several studies have been reported for the simulations of liquid crystalline systems using realistic models. In order to make progress in understanding the forces responsible for solute alignment, the possibility exists of extending these realistic atom-atom models for a mesogen to mixture systems.[4]

This study is concerned with a systematic study of such binary systems and a microscopic interpretation of the experimental results based on the molecular dynamic simulations to a better understanding of the solute-solvent interactions.

METHOD

Experimental

The liquid crystal solvents of 4-(4-hexyloxyphenyl)benzenecarbonitrile (6OCB) and 4-cyano-1-(4-heptylcyclohexyl)benzene (PCH-7) were obtained from BDH Chemicals Ltd. The solutes of phenylcyclohexane-d_5 and *p*-terphenyl-d_{14} were synthesized and purified according to the reported procedure [5]. Remaining chemicals were purchased

from commercial sources and used without further purification. For all solutes 5 mol per cent solutions were prepared in the liquid crystal solvent.

The deuterium NMR spectra were recorded using JNM-LA500 spectrometer with an 11.7 T magnetic field. The temperature of the sample was controlled with a gas-flow temperature controller to within a fluctuation of ±0.1K. Each spectrum was obtained by averaging 800 transients with a spectral width of 100 kHz, using 45° pulse. The spectra were recorded at every 1K on cooling, starting from *ca.* 5K above the nematic-isotropic transition until the sample was crystallized.

Simulations

Molecular dynamics simulations were performed using DL_POLY 2.0 (CCP5) for binary mixtures of 6OCB containing four solutes: biphenyl, naphthalene, phenylcyclohexane and pyrene. The simulations in the nematic phase were carried out on a system of 182 solvent and 10 solute molecules in an *NPT* ensemble. We used the OPLS united atom-atom potentials except for phenyl rings and the SHAKE algorism for stretching to constrain all bond lengths to their equilibrium values. The partial charges were estimated from an *ab initio* method with Gaussian 98, B3LYP/6-311+G(2d,p) basis set. The number of steps was 5×10^5 in a time step of 1 fs. The system was equilibrated under 0.1 MPa, and the density was close to 1 g/ml in that state.

RESULTS AND DISCUSSION

It is noting that even in the case of the uniaxial nematic phase, two order parameters are necessary to describe the orientational order of biaxial particles. To obtain the order parameters S_{zz} and $S_{xx}-S_{yy}$ from the quadrupolar splittings, the following equation is used for a deuteron at the *i*-th site where the C-D bond has direction cosine $l'_{\alpha i}$ with axis

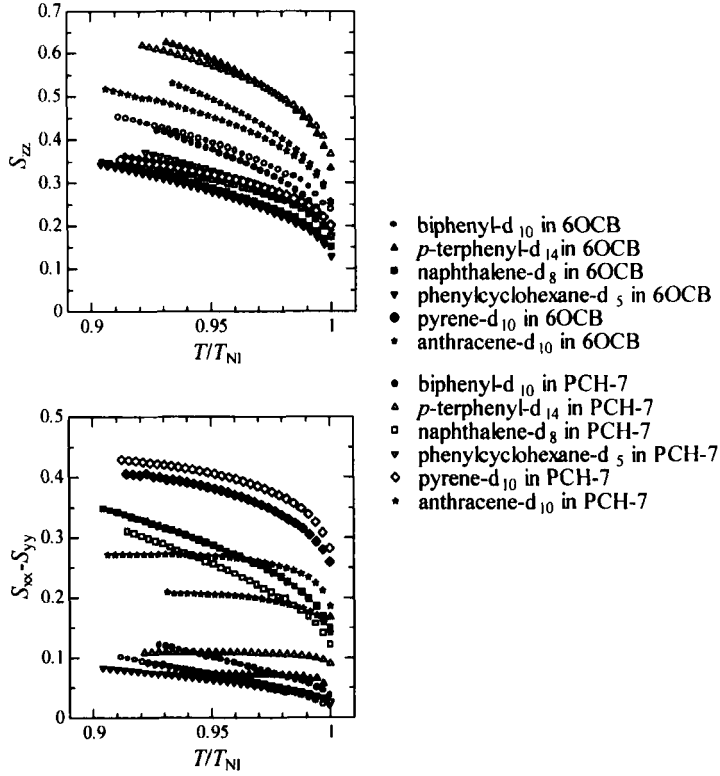

FIGURE 1. The variation of the order parameters S_{zz} (top) and S_{xx}–S_{yy} (bottom) with the reduced temperature T/T_{NI}.

α(x,y,z).

$$\Delta\upsilon' = \frac{3}{2} q'_{\alpha\alpha} \left\{ S_{zz} (3l'^{2}_{z\alpha} - 1)/2 + (S_{xx} - S_{yy}) l'^{2}_{x\alpha} \right\}$$

where $q_{\alpha\alpha}$ is qudrupolar coupling constant taken to be 182kHz.

The experimental values of order parameters, S_{zz} and S_{xx}–S_{yy} for solutes in 6OCB and PCH-7 are plotted against reduced temperature in FIGURE 1. Both of order parameters are notably depended upon the solutes, but the values for each solute show a little difference in two

solvents. However, the values of S_{zz} for phenylcyclohexane in PCH-7 are somewhat greater than those in 6OCB as shown in FIGURE 1(top). The PCH-7 with saturated ring differs from the 6OCB, and so may interacts with solutes in different way to 6OCB containing purely aromatic rings.

In FIGURE 1(bottom) we show the temperature dependence of $S_{xx}-S_{yy}$ for the six solutes in both solvents. Even though the maximum is expected to occur because the value must vanish both in the isotropic and under perfect order, the curves show no maxima. This is attributed to the measurements of small temperature range near the transition point. The variation of $S_{xx}-S_{yy}$ with temperature is much larger for naphthalene and biphenyl, which give the greater values in 6OCB than those in PCH-7. A difference in $S_{xx}-S_{yy}$ is found for anthracene in two solvents.

It is of interest to compare those values with predictions using a molecular model. It is reasonable to expect that the average orientation of solutes is governed by their shape and size based on the moment of inertia tensor. The principal values S_{xx}, S_{yy} and S_{zz} are given by the equivalent ellipsoid semiaxes such that for example, S_{zz} has the

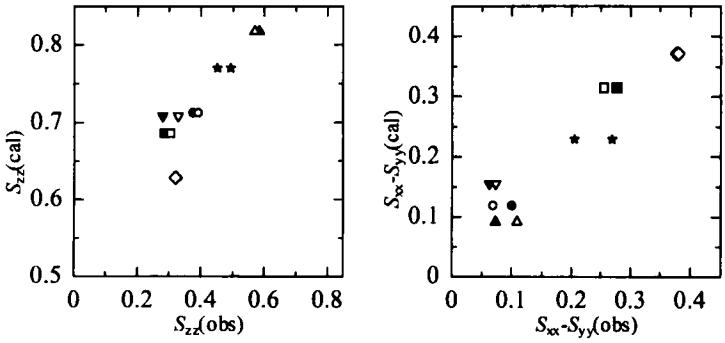

FIGURE 2. Calculated and experimental order parameters. Symbols are the same as cited in FIGURE 1.

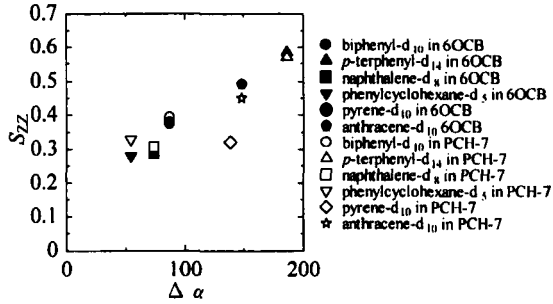

FIGURE 3. S_{zz} against anisotropy in polarizability.

limits of 1 and 0 for infinite rod and ideal sphere, respectively.[6]

The order parameters calculated from the moment of inertia tensor are plotted against observed one at a reduced temperature of 0.95 as shown in FIGURE 2. The calculation values of S_{zz} are estimated to be about 0.3 higher than the observed values. For the order parameters, S_{xx}–S_{yy}, the calculated values are in good agreement with experimental ones. This result suggests that the geometry of molecules is a dominant factor governing the values of S_{xx}–S_{yy}.

To examine a long-range contribution based on the interaction between polarizability of the solutes, their physical properties were evaluated from the *ab initio* method, Gaussian 98 based on HF/6-31G(d,p). It should be noted that different solutes experience the same anisotropy of polarizability in a given solvent. It is seen in FIGURE 3 that the order parameter S_{zz} is correlated with the anisotropy, $\Delta\alpha = \frac{1}{2}(2\alpha_{zz} - \alpha_{xx} - \alpha_{yy})$ in polarizability.

TABLE 1. Order parameters calculated by MD simulations.

System	T / K	6OCB			solute
		S_{zz}	P	S_{xx}–S_{yy}	S_{zz}
6OCB	335	0.66	0.03	0.18	
biphenyl/6OCB	331	0.60	0.04	0.17	0.38
naphthalene/6OCB	331	0.61	0.06	0.16	0.39
Phenylcyclohexane/6OCB	331	0.60	0.04	0.17	0.38
pyrene/6OCB	335	0.65	0.03	0.20	0.38

TABLE 1 shows the mean values of the order parameters averaged over the final 200 ps of each run in the MD simulation. The S_{zz} value of 0.66 was obtained for the pure system of 6OCB and was slightly higher than the experimental value of 0.53[7]. Note that the biaxiality of the nematic phase can be defined as $P = -\frac{3}{2}\sin^2\theta\cos 2\phi$ [8]. The uniaxial nematic phase was obtained because the value of P was actually calculated to be zero at 335K. A snapshot of sample configurations for a mixture of naphthalene and 6OCB is shown in FIGURE 4, and a nematic phase is clearly visible. On the other hand, the nonzero value of $S_{xx}-S_{yy}$ is attributed to the non-cylindrical structure of 6OCB. This value is also higher than the reported value of 0.04 [7]. In the binary mixtures, the uniaxial nematic phase was also obtained, but the values of S_{zz} for 6OCB were slightly smaller than the value of the pure solvent. The ordering of the solutes is induced in the nematic phase, and almost the same values of $S_{zz} \approx 0.4$ are obtained for all solutes calculated. Their values are close to the experimental ones rather than the calculated

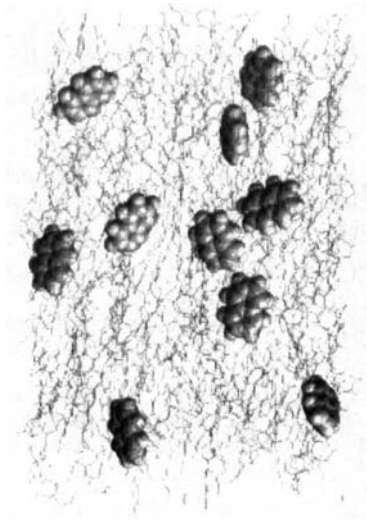

FIGURE 4. A snapshot for a mixture of naphthalene and 6OCB.

values based on the moment of inertia. For S_{xx}–S_{yy} of the solutes, the pertinent estimation could not be made taking account of large standard deviation. It is clear that problems are being caused by too small number of solutes in the system.

CONCLUSIONS

It is apparent from this study that solvents of 6OCB and PCH-7 gives almost same orientations for solutes. The short range interaction based on the molecular shape can account for the observed order parameter, S_{xx}–S_{yy} of solutes. Both of the short range and long range interactions affect the parameter, S_{zz}.

The simulations suggest that solvent molecules forms an uniaxial nematic phase, and orientations of solutes are induced from the surrounding solvent molecules. The induced order parameter is in agreement with the experimental values.

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