Characterization of Phase Transitions and Dynamics in Reentrant Nematic Liquid Crystals by Xenon-129 Nuclear Magnetic Resonance

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In this paper, the ability to detect phase transitions and characterize the dynamics in binary and tertiary reentrant nematic liquid crystal mixtures via ^{129}Xe NMR chemical shifts and spin−spin (T_2) and spin−lattice (T_1) relaxation times is demonstrated. A comparison of the T_1 temperature dependence acquired at 9.40 T and 11.7 T supports the proposition that the relaxation of the dissolved xenon is dominated by dipolar fluctuations. The experimental results show that the spin relaxation times and the chemical shift are continuous functions at the nematic → smectic and smectic → reentrant nematic phase transitions. The spin relaxation times are found to be much more sensitive than the chemical shifts to these transitions in these particular liquid crystal systems. Upon entering the smectic phase, a reduction in the slopes of $\ln(T_{1,2})$ versus $1/T$ indicates a decrease in the activation energy for the motions responsible for spin relaxation. The activation energies of the dominating relaxation process within the nematic and reentrant nematic phases are determined from $|d(\ln T_{1,2})/d(1/T)|$. The results for the binary and tertiary reentrant nematic liquid crystal mixtures are compared in terms of the molecular packing and the dynamical modes responsible for nuclear spin relaxation.

1. Introduction

The discovery by Cladis[1] that certain liquid crystals (LCs) can undergo a transition from the relatively more ordered smectic-A phase to an apparently less ordered nematic phase upon *lowering* the temperature has stimulated extensive studies of this intriguing phenomenon. Various theoretical models have been proposed to account for the reentrance into the nematic phase.[1,2] Perhaps the most widely accepted of these is the dimer model,[1,3] wherein the expression for the free energy F contains, in addition to the rotational entropy (S_{rot}), a packing entropy (S_{pack}), and hence $F = U - TS_{rot} - TS_{pack}$. With decreasing temperature, strong antiparallel correlations of the rodlike LC molecules induce dimer formation. The excessive formation of dimers interferes with the molecular packing, thereby destabilizing the smectic phase and leading to a nonlayered nematic structure (i.e., the reentrant nematic phase) which minimizes the free energy.

A variety of experimental techniques have been employed to study the dynamics, ordering, and molecular interactions responsible for the reentrant nematic behavior, including X-ray diffraction,[4−6] optical birefringence,[7] dielectric measurements,[8] ESR,[9] and NMR.[10−22] X-ray diffraction has revealed structural details such as layer spacings in the smectic phase and the existence of pretransitiononal states. Previous NMR studies have focused primarily on molecular ordering and dynamical aspects of the reentrant nematic LC phases. One particular reentrant nematic LC which has been extensively studied by NMR is a mixture of 4-cyano-4′-*n*-hexyloxybiphenyl (6OCB) and 4-cyano-4′-*n*-octyloxybiphenyl (8OCB).[10−17,20,21] Carbon-13 chemical shifts[16] and deuteron quadrupole splittings[12−15] have been measured as the temperature was varied through known phase transitions of this system. However, these NMR observables
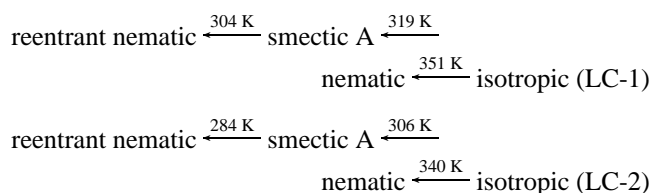
did not bear any unequivocal signature of the liquid crystalline phase transitions. For example, the ^{2}H spectrum of the extrinsic probe molecule *p*-xylene-d_{10} dissolved in the 6OCB/8OCB mixture was measured as a function of temperature,[14] but once again, the observed quadrupole splittings were only smoothly varying across the nematic → smectic phase transition and the data exhibited only a slight indication of the smectic → reentrant nematic transition. The temperature dependence of the ^{1}H spin lattice relaxation time, T_1, was also recorded in this same system,[10,11,17] but here too, the phase transitions were not obvious. Details about the underlying modes of spin relaxation were nonetheless obtained from the T_1 dependence on the Larmor frequency.[10,11,17] The rotational viscosity measurements by Sailaja et al.[20] and Dong[21] in the nematic phases and smectic phase of the 6OCB/80CB reentrant nematic mixture should also be mentioned. Collectively, these studies have provided a better understanding of how the packing and ordering effect the mechanical properties of this LC system. Finally, we note that a ^{1}H and ^{2}H NMR study of a doubly reentrant, single-component LC system has been reported.[22] It was determined that the rotational viscosity of this LC is sensitive to the phase transitions while the orientational order parameter is not, an observation that was analyzed in terms of molecular packing, dipolar order, and conformation order.

The present work involves the application of ^{129}Xe NMR to the problem of nematic reentrance in LCs, and to our knowledge, this is the first study of its kind. At low densities, it is well-known that xenon can serve as a noninvasive probe of its surroundings. Xenon-129 is an attractive isotope for NMR studies as a consequence of the high dynamic range of its relaxation time and chemical shift to the local environment and due to the ability to enhance the signal intensity by optical pumping.[23,24] Xenon NMR has found applicability in studies of a wide range of materials, including porous solids,[25−29] surfaces,[23,29,30] and proteins.[31] However, there have been only


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a few previous reports on the xenon dynamics and spin relaxation in anisotropic media such as liquid crystals. Jokisaari and Deihl[32−34] showed that the chemical shifts, quadrupole coupling constants, and spin relaxation times of ^{129}Xe and ^{131}Xe can provide information about the local chemical environment, the occurrence of phase transitions, and the spatial distribution of the dissolved xenon in several ordinary (non-reentrant) nematic LC systems.

Here, we investigate the nematic reentrance phenomenon in two different LC mixtures using ^{129}Xe NMR. The first sample, referred to as LC-1, consists of 27.16 wt % 6OCB in 8OCB.[3,10,15] The composition of this sample has been chosen to facilitate comparison with previous NMR data on similar samples. The second sample, LC-2, is a three-component mixture[35] consisting of 73% 4-n-heptyl-4′-cyanobipenyl (7CB), 18% 8OCB, and 9% 4-n-pentyl-4′-cyanoterphenyl (5CT). LC-2 has not been previously studied by NMR. Upon cooling, LC-1 and LC-2 are known to exhibit the following phase transitions:[10,15,35]

$$\text{reentrant nematic} \xleftarrow{\text{304 K}} \text{smectic A} \xleftarrow{\text{319 K}}$$
$$\text{nematic} \xleftarrow{\text{351 K}} \text{isotropic (LC-1)}$$

$$\text{reentrant nematic} \xleftarrow{\text{284 K}} \text{smectic A} \xleftarrow{\text{306 K}}$$
$$\text{nematic} \xleftarrow{\text{340 K}} \text{isotropic (LC-2)}$$

A third sample, designated LC-3, consists of a mixture of 6OCB (35%) and 8OCB and will serve as an experimental control. LC-3 possesses an ordinary nematic phase below the isotropic phase but does not exhibit the smectic-A or reentrant nematic phases:

$$\text{nematic} \xleftarrow{\text{350 K}} \text{isotropic (LC-3)}$$
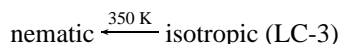
The results will show that phase transitions can indeed be detected in reentrant nematic liquid crystal mixtures via the ^{129}Xe NMR chemical shift, the spin−lattice relaxation time, and the spin−spin relaxation time (T_2). A comparison of the T_1 temperature dependence acquired at 9.40 T and 11.7 T in one of the liquid crystal systems supports the proposition that the relaxation of the dissolved xenon is dominated by $^{129}Xe-^1H$ dipolar fluctuations. The slopes of plots of $\ln T_{1,2}$ versus $1/T$, which yield the activation energies (E_a) for the motions responsible for spin relaxation, exhibit discontinuities at the phase transition temperatures in both LC-1 and LC-2, but are constant within each phase. We will interpret the observed reduction of $|d(\ln T_{1,2})/d(1/T)|$ upon entering the smectic phase in terms of a reduction in E_a. Since we do not observe a decrease in $\Delta\sigma$ upon entering the smectic phase in LC-1 and LC-2, there is no direct evidence for redistribution of xenon toward the *interspaces* between the layers of the smectic phase, as was described in a previous ^{129}Xe NMR study in the smectic phase of an ordinary (nonreentrant) nematic LC.[34] Finally, we will present the activation energies of the dominating relaxation process in the nematic and reentrant nematic phases, as derived from experimentally measured temperature dependence of T_1 or T_2. These activation energies are found to be similar in the nematic and reentrant nematic phases of LC-2, but different in the nematic and reentrant nematic phases of LC-1. This result is interpreted in terms of the molecular packing and the dynamical modes responsible for nuclear spin relaxation.

2. Experimental Section

Natural abundance xenon (99.99%) gas was obtained from Matheson gas products, Inc. The LC compounds 6OCB, 8OCB,
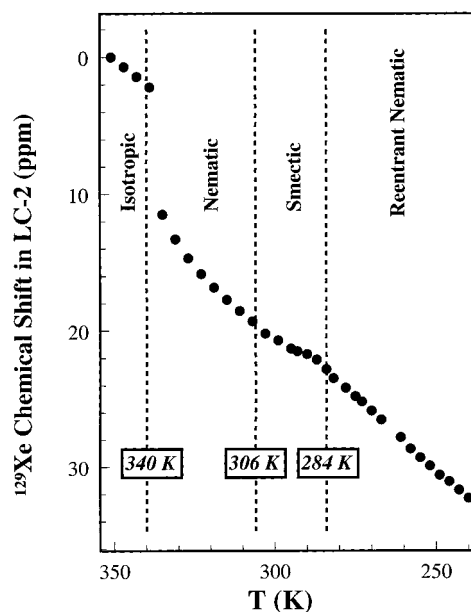

Figure 1. Temperature dependence of the change in ^{129}Xe chemical shift (relative to the value in the isotropic phase) in LC-2. The known phase transitions of this system are indicated by the vertical dashed lines. Similar data was obtained in LC-1, but the features were less pronounced.

and 7CB were purchased from Aldrich Chemicals, and 5CT was purchased from Merck. These materials are 98% pure and were used without further purification. The LC samples were mixed in 10 mm medium wall Pyrex tubes fitted with Teflon valves (Chemglass model CG-512). After removal of gaseous impurities by several freeze−pump−thaw cycles, the samples were allowed to mix in the isotropic phase for 12 h under a vacuum of $\sim 10^{-6}$ Torr. The tubes containing LC-1, LC-2, and LC-3 were pressurized with 2, 5, and 2 atm of xenon, respectively. A xenon pressure of 5 atm above LC-2 yielded a dissolved xenon concentration of 30 ± 5 mM at 301 K and 50 ± 5 mM at 274 K, as determined by comparing the signal integral in the LC with the signal integral from a xenon gas reference at the same temperature. The nuclear spin relaxation times T_1 and T_2 were measured with the standard inversion−recovery and CPMG sequences, respectively, using a Varian Unity-500 spectrometer operating at a ^{129}Xe Larmor frequency of 138.231 MHz. The temperature dependence of T_1 in LC-2 was also recorded at 9.40 T using a 400 MHz Bruker Avance Spectrometer. Temperatures reported below are accurate to within 2 K. To ensure uniform orientational order in the magnetic field, each sample was first heated to its isotropic phase and then cooled in 1 or 2K decrements. The temperature was allowed to equilibrate for 30 min prior to each measurement.

3. Results and Discussion

3.1. Chemical Shifts. The ^{129}Xe chemical shift can serve as a probe of the local chemical environment in liquid crystals because it is sensitive to the average perturbation of the xenon electron cloud due to dispersion interactions with the solvent. We have measured the change in the isotropic chemical shift $\Delta\sigma$ in LC-1 and LC-2 as a function of temperature. We present only the data for LC-2 in Figure 1 because the features of interest were somewhat more pronounced in this sample. A sharp downfield shift of about 9 ppm is observed at the isotropic → nematic transition temperature due to an increased density of the solvent in the nematic phase. Thereafter, the shift appears to vary continuously through the nematic → smectic transition.

Both LC-1 and LC-2 are expected on the basis of McMillan Theory[41] to exhibit first order nematic → smectic-A phase transitions (T_{SN}/T_{NI} = 0.91 for LC-1 and 0.90 for LC-2). Experimentally, however, X-ray data[5] has shown that the nematic → smectic transition is second order (or perhaps weakly first order) due to the pretransitional effects arising from the smectic order fluctuations in the nematic phase. A discontinuity in the slope of the chemical shift at the nematic → smectic-A phase transition in LC-1 and LC-2 is not clearly apparent in Figure 1, indicating that the number density varies continuously through this phase transition. Hence, a second order classification would be consistent with the chemical shift temperature dependence in this case.

In Figure 1, note that $\Delta\sigma$ monotonically increases upon passing through the smectic phase with decreasing temperature. This behavior is in contrast to the $\Delta\sigma$ temperature dependence in NCB-84, an ordinary nematic LC exhibiting a smectic phase over a comparatively large temperature range.[34] To explain the decrease in $\Delta\sigma$ in NCB-84 upon entering the smectic phase, it has been proposed that xenon preferentially occupies the *interspaces* between the smectic layers where the number density of LC molecules is lowest. It was estimated that the xenon obtains a 5% deviation from a uniform distribution. The observation of only a single ^{129}Xe resonance indicates that the xenon is in rapid exchange between the interspaces and the *interstices* (i.e., sites between the LC dimers). The packing configuration is illustrated in Figure 5. The temperature dependence of $\Delta\sigma$ in LC-1 and LC-2, however, does not indicate a higher propensity to occupy the interspaces between the layers in these LC systems. A slight decrease in d($\Delta\sigma$)/dT in LC-1 and LC-2 does occur, suggesting that the number density changes more slowly with temperature in the smectic phase. The inability to detect a nonuniform distribution by means of the chemical shift and spin relaxation data could be attributed to differences in packing and the smaller temperature range (~15 K) of the smectic phase in LC-1 and LC-2. Disorder within this phase would also mask the chemical shift response.

3.2. Nuclear Spin Relaxation. The ^{129}Xe spin−spin and spin−lattice relaxation times are clearly sensitive to the presence of phase transitions in the two reentrant nematic LCs studied here. The 1/T dependence of ln T_1 and ln T_2 for LC-1 and LC-2 are shown in Figures 2 and 3, respectively, while 1/T versus ln T_2 for LC-3 is shown in Figure 4. The magnetization recovery curves are found to be exponential in all samples. While T_1 and T_2 appear to be continuous at the phase transitions, discontinuities in d(ln $T_{1,2}$)/d(1/T) are apparent at 351, 319, and 304 K for LC-1 and at 340, 306, and 284 K for LC-2. This indicates that the spectral densities are the same but that different dynamic environments occur on either side of the discontinuity points. The temperatures at which these discontinuities occur correlate well with the reported isotropic → nematic, nematic → smectic, and smectic → reentrant nematic phase transitions,[10,15,35] as indicated by the dashed vertical lines in Figures 2 and 3. The derivatives d(ln T_1)/d(1/T) and d(ln T_2)/d(1/T) are constant within each phase, yielding well-defined activation energies for the motions. Let us compare the temperature dependence of T_1 and T_2 in LC-1 and LC-2 with T_2 in LC-3, an LC having no smectic phase. In the nematic and reentrant nematic phases of LC-1 and LC-2, {ln(T_1),ln(T_2)} ∝ 1/T. Similarly, ln(T_2) ∝ 1/T in the ordinary nematic phase of LC-3. However, T_1 and T_2 are nearly temperature independent in the smectic phase of both LC-1 and LC-2. Consequently, it is possible to detect the nematic → smectic and smectic → reentrant nematic phase transitions due to the change in slope.
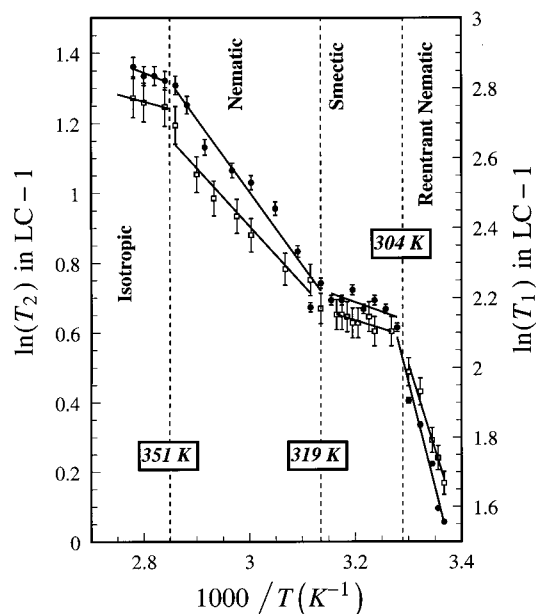

Figure 2. Reciprocal temperature dependence of ln(T_1) (square symbols, axis at right) and ln(T_2) (circles, axis at left) for ^{129}Xe dissolved in LC-1, recorded at a field of 11.7 T. The temperatures at which phase transitions are known to occur in this system are indicated by dashed vertical lines. The absence of error bars on some data points indicates that the error in the measurement is less than the size of the symbol. Solid lines represent linear regression fits to the data in each phase. The activation energies obtained from these fits are reported in Table 1.
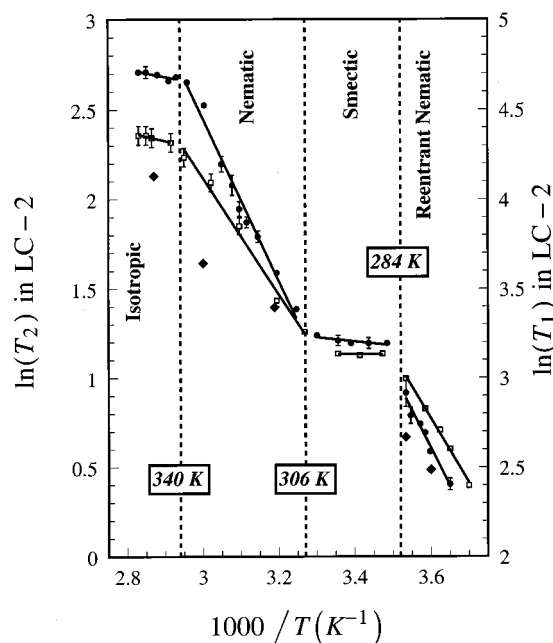

Figure 3. Reciprocal temperature dependence of ln(T_1) (square symbols, axis at right) and ln(T_2) (circles, axis at left) for ^{129}Xe dissolved in LC-2, recorded at a field of 11.7T. The diamonds indicate ln(T_1) values recorded at a field of 9.40 T. The temperatures at which phase transitions are known to occur in this system are indicated by dashed vertical lines. The absence of error bars on some data points indicates that the error in the measurement is less than the size of the symbol. Solid lines represent linear regression fits to the data in each phase. The activation energy is reported in Table 1.

The ^{129}Xe relaxation behavior in these LC systems can be explained in the context of known relaxation mechanisms for this atomic species, which we briefly review here. Due to the relatively low value of the ^{129}Xe gyromagnetic ratio, the Xe−
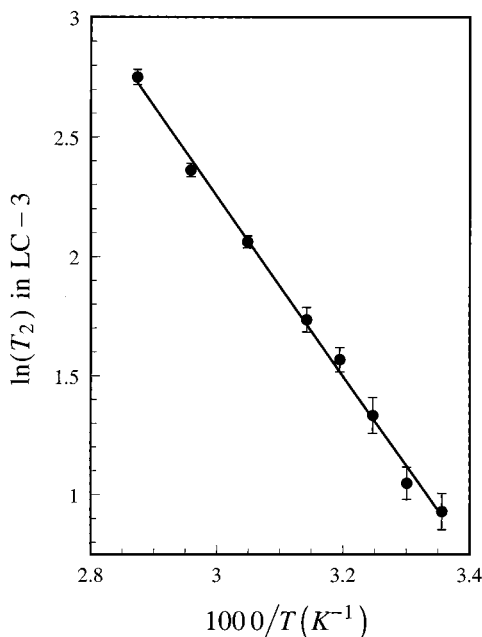
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Figure 4. Reciprocal temperature dependence of $\ln(T_2)$ for ^{129}Xe dissolved in LC-3, recorded at 11.7 T. This LC is known to exist only in the nematic phase over the entire temperature range presented. The solid line was determined from linear regression of the data.

Xe dipolar coupling is weak and the relaxation in pure xenon gas is dominated by the spin-rotation (SR) mechanism which is operative during the transient existence of diatomic Xe formed upon collision.[36,37] The T_1 value of pure, natural abundance xenon gas (1 atm) in 8 mm ID Pyrex glass samples tubes at 11.74 T was measured by us to be 87.7 min. This value was obtained by monitoring the decay of hyperpolarized xenon using small tip angle rf pulses. However, the observed T_1 values of dissolved ^{129}Xe in the present study are 2 orders of magnitude shorter than this, suggesting that a stronger relaxation mechanism dominates over the SR contribution. The substantial difference between T_1 and T_2 for ^{129}Xe dissolved in LC-1 and LC-2 at all temperatures suggests that slow motional modes dominate the spin relaxation in these samples. In the extreme narrowing limit, where $\omega_o \tau_c \ll 1$ (where ω_o = Larmor frequency and τ_c = correlation time), the spectral densities $J(0)$, $J(\omega_0)$, and $J(2\omega_0)$ are equal and thus $T_1 \approx T_2$ in the case of dipolar relaxation. Instead, $T_1 \gg T_2$ is observed for the dissolved ^{129}Xe, and the primary relaxation process in these systems is therefore sensitive to the spectral density at lower frequencies. In this case, the limit $J(0) \gg J(\omega_o) > J(2\omega_o)$ is applicable, leading to[38]

$$\frac{1}{T_1} \propto \{J(\omega_o), J(2\omega_o)\} \quad \text{and} \quad \frac{1}{T_2} \propto \{J(0), J(\omega_o), J(2\omega_o)\}$$

In a previous study comparing the spin−lattice relaxation times of ^{129}Xe dissolved in various hydrogenated and deuterated organic solvents, it was concluded that the ^{129}Xe−^{1}H intermolecular dipole coupling[32,39] provides a substantial contribution to the relaxation rate. For example, T_1 = 240 s in C_6H_6, yet T_1 = 570 s in C_6D_6 at 300 K.[32] That the relaxation mechanism is predominantly dipolar in C_6H_6 is further confirmed by the existence of an NOE effect[32] and the observed field independence (between 5.87 T and 9.40 T) of the ^{129}Xe T_1 in this solvent.[39] To verify that the dominant relaxation mechanism for ^{129}Xe dissolved in the LC systems studied here is also dipolar in character, we measured T_1 for several temperatures corre-

sponding to the nematic and reentrant nematic phases in LC-2 in a field of 9.40 T. These data are included in Figure 3. The only other mechanism which could be significant at high field is chemical shift anisotropy (CSA) relaxation. In the extreme narrowing limit, CSA relaxation[38,40] would lead to a relaxation rate $(1/T_1)$ which increases as the square of the field, but for a dipolar mechanism, the rate would be field independent. In the slow motional limit, which is presumed to be the case for xenon dissolved in the LCs, the dipolar relaxation rate should decrease with field while chemical shift anisotropy relaxation should be field independent. Within both nematic phases of LC-2, T_1 at 9.40 T is found to be less than T_1 at 11.7 T, a finding not predicted by CSA relaxation theory, regardless of the motional regime. Hence, as in previous ^{129}Xe NMR studies of (nondeuterated) anisotropic liquids, we will assume that the dominant contribution to the spin relaxation is the stochastic modulation of the heteronuclear dipolar interaction[34] between dissolved ^{129}Xe and ^{1}H nuclei residing on the LC molecules. The relaxation rate of ^{129}Xe spins due to modulation of the ^{129}Xe−^{1}H dipolar interactions by reorientation of the internuclear vector can be expressed as[38,40]

$$\frac{1}{T_1} = \frac{1}{10}\gamma_{Xe}^2\gamma_H^2\hbar^2\tau_c\sum_i\frac{1}{r_i^6}\left[\frac{1}{1+(\omega_H-\omega_{Xe})^2\tau_c^2}+\right.$$
$$\left.\frac{3}{1+\omega_{Xe}^2\tau_c^2}+\frac{6}{1+(\omega_H+\omega_{Xe})^2\tau_c^2}\right] \quad (1)$$

and

$$\frac{1}{T_2} = \frac{1}{20}\gamma_{Xe}^2\gamma_H^2\hbar^2\tau_c\sum_i\frac{1}{r_i^6}\left[4+\frac{1}{1+(\omega_H-\omega_{Xe})^2\tau_c^2}+\right.$$
$$\left.\frac{3}{1+\omega_{Xe}^2\tau_c^2}+\frac{6}{1+\omega_H^2\tau_c^2}+\frac{6}{1+(\omega_H+\omega_{Xe})^2\tau_c^2}\right] \quad (2)$$

where γ_{Xe}, γ_H, ω_{Xe}, and ω_H are the gyromagnetic ratios and Larmor frequencies for ^{129}Xe and ^{1}H, respectively. Note that, for the purposes of understanding the relaxation mechanism of xenon dissolved in liquid crystals, these equations are only qualitatively correct since they assume a constant internuclear distance r as in a rigid molecule. Nonetheless, the expressions 1 and 2 illustrate that $T_1 \gg T_2$ in the slow modulation regime where $|(\omega_{Xe} \pm \omega_H)\tau_c| \gg 1$. For xenon dissolved in an LC solvent, the intermolecular dipolar interaction will be modulated due to diffusion of the probe and motions of the LC molecules themselves.

On the basis of a dipolar relaxation mechanism, the temperature dependence of T_1 and T_2 can now be interpreted. In the isotropic phase, relatively fast motions of the LC molecules and xenon atoms yield long relaxation times which decrease with temperature. At the isotropic → nematic transition, the correlation time τ_c (eq 1 and 2) of the dipolar interaction begins to increase. Unlike the change in chemical shift upon entering the nematic phase, there is no sudden jump in the values of T_1 and T_2. This suggests that the spin-relaxation times are not effected by changes in the packing density but are predominantly determined by changes in the spectral density of the relative xenon−LC molecule motions. In the slow motional limit, as is applicable here, τ_c is thermally activated and therefore, the slope $d(\ln T_{1,2})/d(1/T)$ yields the activation energy for the motion.[33] The observed reduction of $|d(\ln T_{1,2})/d(1/T)|$ upon entering the smectic-A phase indicates that the activation energy for this type of motion decreases. In the case of reentrant LCs, the
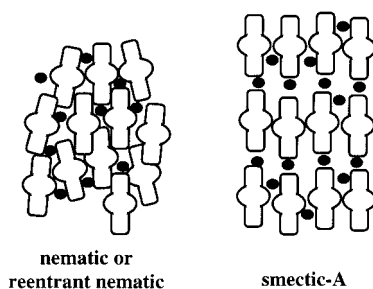
Figure 5. Smectic representation of the distribution of xenon (black circles) in the nematic, smectic, and reentrant nematic phases of a 6OCB/8OCB mixture. The LC dimers are represented as antiparallel rods with overlapping phenyl rings. The xenon is distributed between the interstices and interspaces formed by the packing of LC dimers. The xenon is in rapid exchange between sites, as evidenced by the occurrence of only a single narrow peak in the NMR spectrum.

smectic phase is packed with dimers. In comparison to the tightly packed nematic and even more tightly packed reentrant nematic phases, the arrangement of the dimers into layers in the smectic phase forms interstices and interspaces which can be occupied by xenon atoms as shown in Figure 5. The temperature independence of T_1 and T_2 suggests that the size of the interstices and interspaces occupied by xenon atoms and the correlation time of the dynamical modes associated with the ^{129}Xe spin relaxation in LC-1 and LC-2 do not change appreciably over this temperature range. This finding is supported by X-ray studies of LC-1[6] which show that the layer spacing of 33.5 Å changed by only 1% over a temperature range of 35 K.

Upon further cooling of LC-1 and LC-2 a sudden increase in $|d(\ln T_{1,2})/d(1/T)|$ correlates well with the established reentrant nematic phase transitions in these systems. According to Cladis,[3] an increased dimer concentration in the smectic phase leads to a packing configuration that is so unfavorable that reentrance into the nematic phase is induced. The ^{129}Xe spin relaxation behavior in the reentrant nematic phase should be comparable to the ordinary high-temperature nematic phase. For an LC such as LC-3, which exhibits only a high-temperature nematic phase with no nematic → smectic phase transition, a continuous decrease in the spin relaxation times with temperature should be expected. This is confirmed by the experimental data presented in Figure 4. The variation of $\ln T_2$ in LC-3 is linear, since this system has no smectic phase.

In summary, both the chemical shift and spin-relaxation data suggest that the mass density and spectral densities $J(0)$, $J(\omega_o)$, and $J(2\omega_o)$ are observed to vary continuously across the nematic → smectic and smectic → reentrant nematic phase transitions of LC-1 and LC-2. The activation energy of the motion appears to be discontinuous. For a second order phase transition or when pretransitional effects occur, continuity in the chemical shift and spin relaxation times can be expected, since abrupt changes in mass density or the spectral density of the internal motions would cause the chemical potential to be discontinuous, thereby violating the second order classification. At the isotropic → nematic phase transition, the chemical shift is clearly discontinuous (consistent with a first order classification which is also observed by differential scanning calorimetry) in both samples while the spin-relaxation times appear to be continuous. This interesting observation, which has been noted previously in another LC system,[32,33] demonstrates that the variation of spectral densities $J(0)$, $J(\omega_o)$, and $J(2\omega_o)$ and the mass density need not behave similarly across a phase transition in a LC system. Hence, continuity in the spin relaxation times is consistent with but cannot be used as a proof of a second order phase transition. This is because the relaxation times are sensitive to only a single frequency component of the motion, which may be a local motion not connected with collective motions. Discontinuity in the spin relaxation times, on the other hand, indicates a high likelihood that a phase transition is first order.

3.3. Activation Energies. Finally, it is informative to compare the spin relaxation temperature dependence for LC-1 (the two-component mixture) with LC-2 (the three-component mixture). The intermolecular dipolar interaction is modulated by molecular motions with an activation energy determined from the slopes of $\ln(T_1)$ or $\ln(T_2)$ versus $1/T$. Activation energies determined for the isotropic, nematic, and reentrant nematic phases are given in Table 1. The E_a in the nematic phase of LC-1 is comparable to that observed in other nematic LCs,[32] while E_a in the reentrant nematic phase is 3 times higher than that of the high-temperature nematic phase. X-ray studies by Guillon et al.[6] have revealed that the reentrant nematic phase of LC-1 coexists with a microcrystalline phase in a quasiequilibrium with a lifetime of several months. Upon an increase in the temperature, these individual phases melt at the same temperature to form the smectic phase. In the present study, the observed increase in E_a in the reentrant nematic phase of LC-1 is most likely due to the presence of this microcrystalline phase.[6] In contrast, E_a in the nematic and reentrant nematic phases of LC-2 are within experimental error the same, indicating that these phases have comparable physical properties. This is consistent with the observation that the temperature dependence of the rate constant for isomerization of *cis-N,N′*-diacetylindigo dissolved in LC-2, as determined from optical absorption,[35] has the same slope in the nematic and reentrant nematic phases. Finally, we report that, in the nematic phase of LC-3, $E_a = 31.0 \pm 0.8$ kJ/mol.

4. Conclusions

We have demonstrated that the phase transitions in LC-1 and LC-2 can be detected via the spin relaxation times and chemical shifts. In LC-1 and LC-2, discontinuities in $d(\ln T_{1,2})/d(1/T)$ at are observed at temperatures coinciding with the known isotropic → nematic, nematic → smectic, and smectic → reentrant nematic phase transitions. The observed increase in T_1 upon increasing the magnetic field from 9.40 T to 11.7 T is consistent with a heteronuclear dipolar relaxation. This finding is consistent with the previously noted dramatic increase in the ^{129}Xe T_1 upon deuteration of the solvent[39] and the field independence of the ^{129}Xe T_1 in benzene.[32] The reentrant nematic behavior is clearly detected in LC-1 and LC-2 but not in LC-3, which only exhibits an ordinary nematic phase. It is evident from the activation energies that nematic and reentrant nematic phases of LC-2 are similar, while they differ in LC-1 due to a change in the packing

TABLE 1: Activation Energies (E_a) Calculated from the Slopes of $\ln(T_1)$ or $\ln(T_1)$ versus $1/T$ in Each of the Phases of LC-1 and LC-2

| sample | isotropic E_a (kJ/mol) | | nematic E_a (kJ/mol) | | reentrant nematic E_a (kJ/mol) | |
	T_1	T_2	T_1	T_2	T_1	T_2
LC-1		4.8 ± 0.2	14.6 ± 0.2	15.5 ± 0.2	40.8 ± 0.4	48.2 ± 0.8
LC-2	3.6 ± 0.2	3.5 ± 0.2	32.4 ± 0.2	35.7 ± 0.3	32.0 ± 0.2	36.3 ± 0.3

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environment in the reentrant nematic phase. The chemical shift and spin relaxation times are observed to vary monotonically with temperature through the smectic phase. Hence, there is no evidence for a preferential occupation of the interspaces between the layers of the smectic phases as was observed in a previous ^{129}X NMR study in NCB-84. In summary, our results show that ^{129}Xe NMR is a viable technique to investigate the dynamics, packing and evolution of reentrance phenomena liquid crystals. However, this is a complex subject and much more still remains to be understood about the details of the xenon relaxation dynamics in these systems.

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