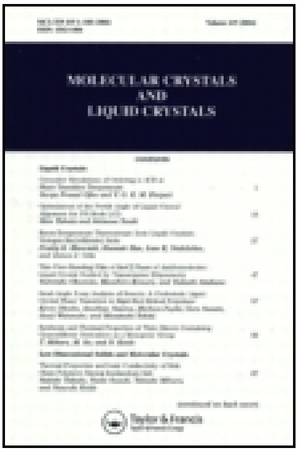

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NMR Determination of the ^{129}Xe Shielding Anisotropy for Xenon Gas Dissolved in Liquid Crystals

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The anisotropy of the ^{129}Xe shielding tensor for natural xenon gas dissolved in the nematic and smectic phases of some pure and mixed thermotropic liquid crystals was studied with the aid of NMR spectroscopy. Apart from the ^{129}Xe NMR spectra, the ^{1}H NMR spectra of ^{13}C-enriched methane in the same solutions were recorded. It was found, that the magnitude of the ^{129}Xe shielding anisotropy, $\Delta\sigma$, correlates with the magnitude of the anisotropic C-H coupling of methane, $D_{CH}(CH_4)$. The reason is the deformation of the originally spherical symmetry of the electron cloud and geometry, respectively, in the anisotropic potential of the liquid crystalline environment.

Keywords: ^{129}Xe NMR, xenon shielding tensor, anisotropy of LC-potential

1. INTRODUCTION

NMR spectroscopy of noble gases possesses a wide range of applications in various fields of physical and chemical research. Until now, the sensitivity of the shielding of the spin-$\frac{1}{2}$ isotope ^{129}Xe to its physical environment has been utilized in particular to derive information about the structures of zeolites[1,2] and clathrates,[3] but also to investigate interactions between xenon and bioorganic ligands and specific interactions between mixed aprotic solvents.[4,5,6] Recently Bayle *et al.*[7] and the present authors[8,9] used ^{129}Xe NMR to gain insight into the properties, such as phase transition temperatures and formation of induced smectic phases, of liquid crystals. The magnetic resonances of the quadrupolar noble gas isotopes, ^{131}Xe and ^{83}Kr, in turn, were used to probe static electric field gradients in various liquid crystals[10,11];

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the isotopes are able to detect very weak external electric field gradients, since they are enhanced by the corresponding Sternheimer antishielding factors being of the order of ca. −168 and −80 for ^{131}Xe and ^{83}Kr, respectively.

Although the nuclear shielding of the ^{129}Xe isotope of xenon dissolved, adsorbed or trapped in surroundings of interest has been relatively widely used, the primary reasons for the shielding variation (correlation between the xenon shielding and, for example, the structure of a zeolite) are still not fully understood. In order to increase knowledge, we studied in the present work the shielding anisotropy, $\Delta\sigma$, of the ^{129}Xe isotope in pure nematics, in a liquid crystal possessing a nematic and a smectic A phase, and in mixtures of thermotropic nematogens that form smectic A and B phases.

The smectic phases have the property, that they keep their orientation for a long time, when being cooled down from the isotropic or nematic phase in the magnetic field of a spectrometer. In a field produced by a conventional electromagnet, this conservation of the preferred orientation provides a simple means to vary the angle between the liquid crystal director and the field. This is consequently a very straightforward method to determine the isotropic average, σ_{iso}, and the anisotropy, $\Delta\sigma$, of a shielding tensor.

In order to derive additional information, the ^{1}H NMR spectra of ^{13}C-enriched methane ($^{13}CH_4$) were recorded and the anisotropic C-H couplings were determined. Moreover, dibromomethane (Br_2CH_2) was dissolved in one of the liquid crystal mixtures, and its ^{1}H NMR spectrum was used to confirm the nature of phases, i.e. whether one of these induced smectic phases is tilted.

2. EXPERIMENTAL

The liquid crystals used in this study are listed in Table I. They were placed in heavy wall tubes (outer diameter 10 mm, inner diameter 7 mm) and carefully degassed before transferring natural xenon gas (partial pressure ca. 4 atm.) and ^{13}C-enriched methane gas (partial pressure ca. 1 atm.) into a sample in a vacuum line. The tubes were finally sealed under a flame.

The ^{1}H and ^{129}Xe NMR spectra were recorded on a JNM-GX400 (^{129}Xe frequency 110.6 MHz, proton frequency 399.6 MHz) and on a JNM-FX100 (27.6 and 99.6

TABLE I

Liquid crystals used

Code name	Composition[a]
EBBA	4-ethoxy-benzylidene-4′-*n*-butylaniline
mixture I[b]	EBBA(64.9)/ZLI1132(35.1)
mixture II	EBBA(73.5)/ZLI1132(26.5)
7AB[c]	4,4′-di-*n*-heptylazoxybenzene

[a] The figures in the parentheses represent the concentration in weight per cent of the compound.

[b] ZLI1132 (product of Merck AG Darmstadt, Germany) is an eutectic mixture of trans-4-*n*-alkyl-4-cyanophenyl-cyclohexanes (alkyl = 24% propyl, 36% pentyl and 25% heptyl) and 15% of trans-4-*n*-pentyl-4′-cyanobiphenyl-cyclohexane.

[c] In many earlier papers denoted as HAB.

MHz) from non-spinning samples without lock. The latter spectrometer is equipped with a conventional electromagnet and thus can be used (in the case of smectic phases) to record NMR spectra at various angles, α, between the liquid crystal director and the external magnetic field. Then the anisotropic interactions are scaled by the second-order Legendre polynominal with the cosine of the angle as an argument. The various orientations of the director were produced by using a simple goniometer.

The mixed liquid crystals (mixture I and mixture II in Table I) form induced smectic phases.[9,12,13] The ^{1}H NMR spectrum of Br_2CH_2 dissolved in the mixture II was recorded at various α angles to confirm, that the smectic phases are non-tilted ones as preliminarily proposed in[12,13] on the basis of optical microscopy. It appeared, that the proton line shape of Br_2CH_2 remained Lorentzian independently of the angle α as it should for a non-tilted phase.[14]

3. RESULTS AND DISCUSSION

The NMR studies on the ^{129}Xe shielding of xenon gas dissolved in various liquid crystals indicate abrupt changes in shielding at phase transitions.[7–9] At the isotropic (I)—nematic (N) transition, the change is considered to arise almost totally from the anisotropy of the ^{129}Xe shielding tensor, which is a consequence of the deformation (from the originally spherical shape) of the electron cloud in the anisotropic environment. In order to see what happens at the nematic-smectic A phase transition, we carried out ^{129}Xe NMR experiments in the S_A phase, which make the determination of the anisotropy as well as of the isotropic average of the shielding tensor possible.

The experimental shielding, $\langle\sigma_{zz}\rangle$, of ^{129}Xe in a uniaxial anisotropic environment can be represented in the form

$$\langle\sigma_{zz}\rangle = \sigma_{iso} + \frac{2}{3}\Delta\sigma P_2(\cos\alpha) \tag{1}$$

where the isotropic shielding constant $\sigma_{iso} = \frac{1}{3} Tr\,\bar{\bar{\sigma}}$, the shielding anisotropy $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$ and $P_2(\cos\alpha) = \frac{1}{2}(3\cos^2\alpha - 1)$ is the second-order Legendre polynomial with α being the angle between the liquid crystal director and the external magnetic field. Equation (1) is based upon the assumption, that the solvent shielding contributions, such as the bulk and local effects can be neglected. This assumption is, however, well justified and was discussed in details in.[8] Equation (1) can be rewritten as

$$\Delta\sigma = \frac{3}{2}\frac{\langle\sigma_{zz}\rangle - \sigma_{iso}}{P_2(\cos\alpha)} \tag{2}$$

which further leads to

$$\Delta\sigma = \frac{3}{2}(\langle\sigma_{zz}\rangle - \sigma_{iso}) \tag{3}$$

when $\alpha = 0°$, i.e. the liquid crystal director lies along the external magnetic field.

For a smectic liquid crystal, NMR spectra can be recorded with various values of the angle α. According to Equation (1), the slope of the straight line obtained by plotting $\langle\sigma_{zz}\rangle$ as a function of P_2 gives $\frac{2}{3}\Delta\sigma$, whereas the intercept gives σ_{iso}. On the other hand, when the spectra are taken at $\alpha = 0°$ and at $\alpha = 90°$, one gets

$$\Delta\sigma = \langle\sigma_{zz}\rangle_{\parallel} - \langle\sigma_{zz}\rangle_{\perp} \tag{4}$$

and

$$\sigma_{iso} = \frac{1}{3}\left(\langle\sigma_{zz}\rangle_{\parallel} + 2\,\langle\sigma_{zz}\rangle_{\perp}\right) \tag{5}$$

where $\langle\sigma_{zz}\rangle_{\parallel}$ and $\langle\sigma_{zz}\rangle_{\perp}$ are the experimental shielding values measured, when the liquid crystal director is parallel with ($\alpha = 0°$) and perpendicular to ($\alpha = 90°$) the external field, respectively.

Figure 1 shows the behaviour of the $\Delta\sigma$ as a function of temperature for the liquid crystal mixture II. The data in the nematic phase were calculated from Equation (3) assuming, that the σ_{iso} follows the linear behaviour observed in the isotropic phase (see Figure 4), while the data in the smectic A phase were resolved from Equation (4). In the same figure is also plotted the anisotropic C-H coupling, $D_{CH}(CH_4)$, of methane. The two quantities behave in a very similar manner. In 7AB (see Figure 2) the situation is not as clear as in the mixture II: the shape of

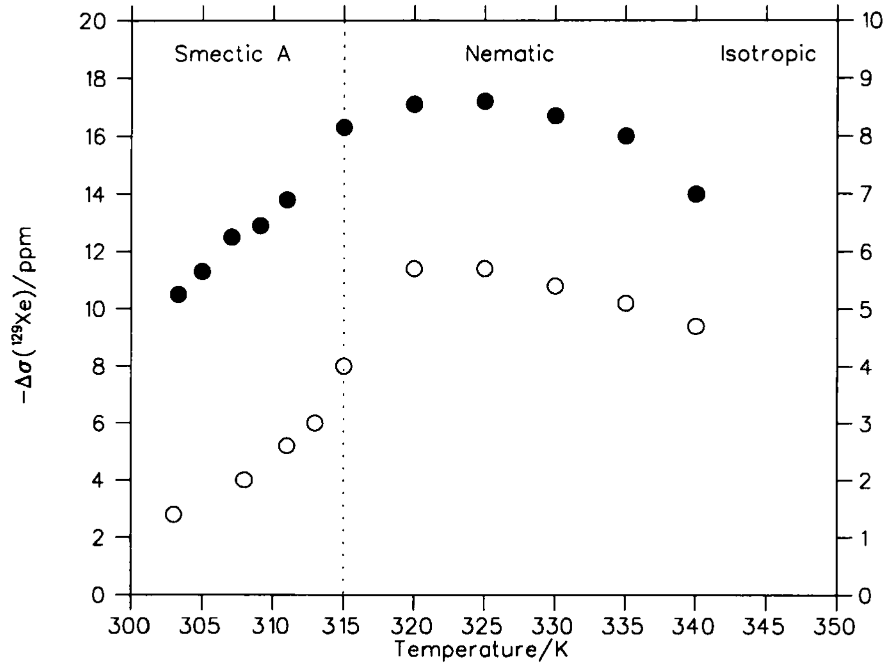

FIGURE 1 The shielding anisotropy, $\Delta\sigma$, of ^{129}Xe (●) and the anisotropic C-H coupling, $D_{CH}(CH_4)$, (○) of methane dissolved in the liquid crystal mixture II.

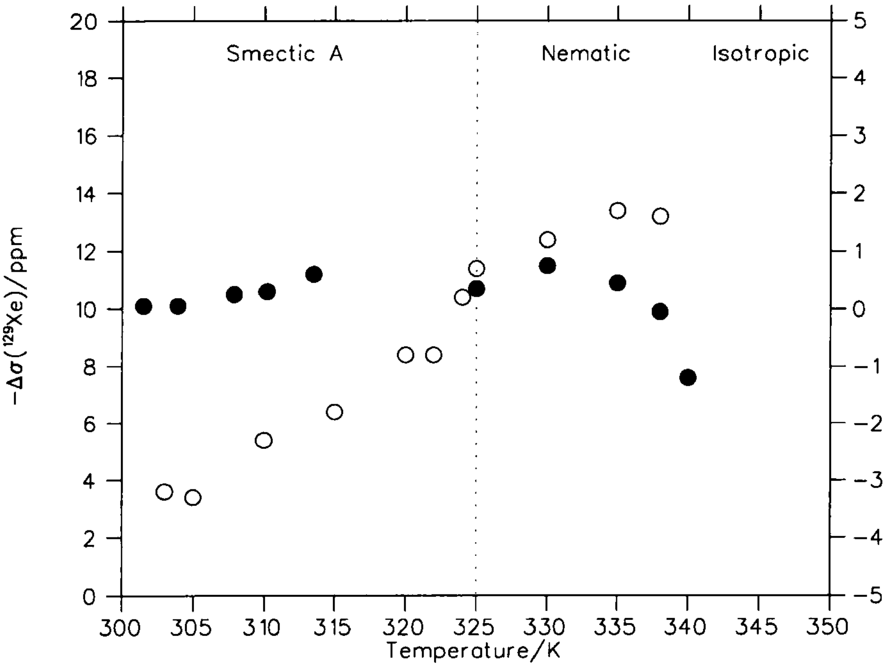

FIGURE 2 The shielding anisotropy, $\Delta\sigma$, of ^{129}Xe (●) and the anisotropic C-H coupling, $D_{CH}(CH_4)$, (○) of methane dissolved in the liquid crystal 7AB.

the $\Delta\sigma$ and $D_{CH}(CH_4)$ versus the temperature curves is rather similar, but the former is more "horizontal." On the other hand, 7AB has been found exceptional also in other cases, as for example in the study of the deformation of the geometry of the benzene molecule.[15]

Figures 1 and 2 show, that in the nematic phase the absolute value of the $\Delta\sigma$ increases as also does the degree of order of the solute Br_2CH_2 (or the degree of order of the liquid crystal) with decreasing temperature in the mixture II (see Figure 3). At the N-S_A phase transition, the $\Delta\sigma$ starts to diminish. On the other hand, also the degree of order of Br_2CH_2 drops roughly by a factor of two within the S_A phase. Contradictory to this observation, the degree of order of the liquid crystal (determined from the ^{2}H quadrupole splitting of d_2-EBBA)[9] increases monotonically (with jumps at the phase transitions) to low temperature. These two findings together indicate that in the smectic states, in which the density waves (or layers) appear, the solutes, xenon, methane and Br_2CH_2, are expelled from the more dense regions to the less dense ones. At the same time, the orienting and deforming forces become weaker and the σ_{iso} and $\Delta\sigma$ change.

The correlation between the $\Delta\sigma(^{129}Xe)$ and the $D_{CH}(CH_4)$ is further confirmed by the measurements in the nematic states of four liquid crystals listed in Table I. In the studies dealing with the geometry of solutes in liquid crystals, it has been found, that the most distorted geometries (and the largest $D_{CH}(CH_4)$) are detected in EBBA.[15-17] Now this study shows, that the ^{129}Xe shielding anisotropy gets the highest absolute value in this particular liquid crystal; in EBBA the $\Delta\sigma(^{129}Xe)$

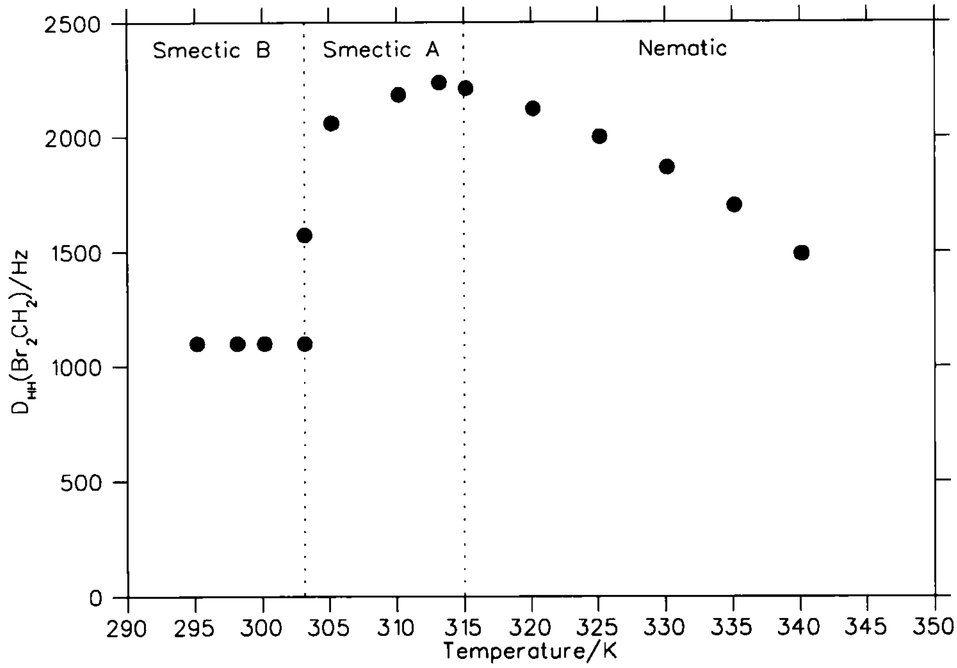

FIGURE 3 The dipolar H-H coupling of Br_2CH_2 vs. temperature.

varies from −17 to −24 in the other liquid crystals from −10 to −17 ppm. The mixing of ZLI1132 with EBBA decreases the absolute value of the $\Delta\sigma(^{129}Xe)$, as it also does decrease the $D_{CH}(CH_4)$, but the $\Delta\sigma(^{129}Xe)$ does not reach the value of zero. In all the liquid crystals studied till now, the shielding anisotropy of ^{129}Xe was found negative. On the contrary, the $D_{CH}(CH_4)$ is negative, for instance, in ZLI1132 and positive in EBBA, and consequently vanishes in a proper mixture of them.[16,17]

Figures 4 and 5 show the temperature dependences of the $\langle\sigma_{zz}\rangle$ and σ_{iso} for ^{129}Xe in the liquid crystals mixture II and 7AB, respectively. These figures show, that in the approximation that neglects the shielding contributions from the local and bulk effects, the isotropic shielding constant, σ_{iso}, seems to increase abruptly by 2 to 3 ppm at the N-S_A phase transition. In the smectic A phase, the temperature gradient of the σ_{iso}, $\Delta(\sigma_{iso})/\Delta T$, equals −0.129 ppm/K for the mixture II, while for 7AB it is +0.112 ppm/K. In the isotropic phase, the corresponding value is +0.190 ppm/K for both liquid crystals.

There are not many studies dealing with $\Delta\sigma$ of xenon. Ripmeester *et al.*,[3,18] however, have measured $\Delta\sigma$ values for ^{129}Xe trapped in various clathrates: they range from −170 to +45 ppm. In our earlier study on xenon, in a so-called critical mixture of two thermotropic nematogens (EBBA and Merck ZLI1167) with opposite anisotropy of the diamagnetic susceptibility, we measured $\Delta\sigma(^{129}Xe)$ of −16.4 (5) ppm.[8] The experiments by Ripmeester indicated a ^{129}Xe NMR line shape typical for an axially symmetric shielding tensor. Furthermore, the sign of the $\Delta\sigma$ was found dependent upon the shape of the cavity: for xenon in oblate cavities $\Delta\sigma >$

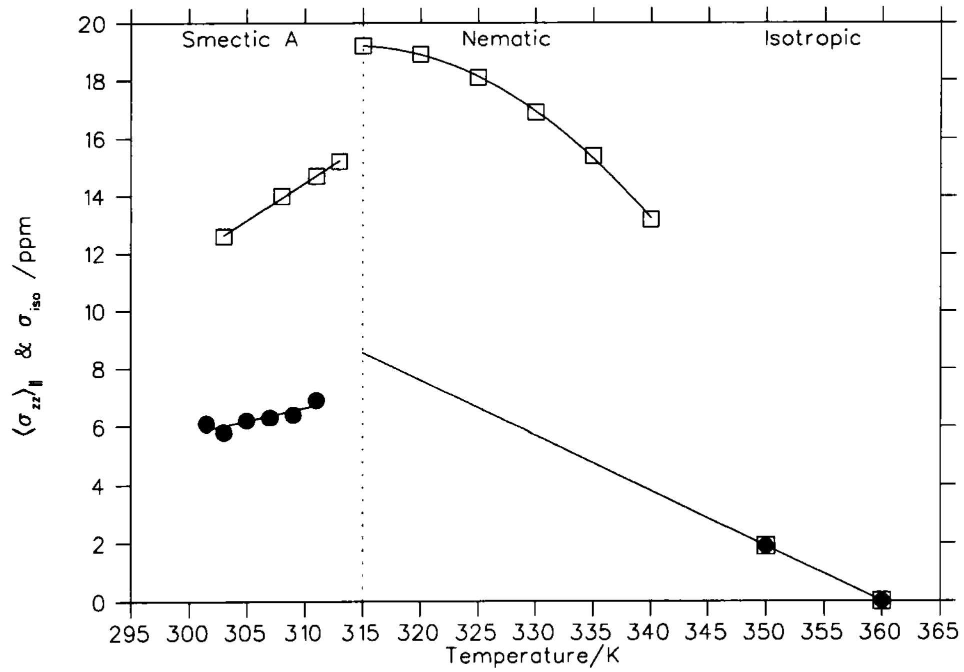

FIGURE 4 The ^{129}Xe shielding $\langle\sigma_{zz}\rangle_{\parallel}$, (□) and σ_{iso} (●; ▣), for the liquid crystal mixture II.

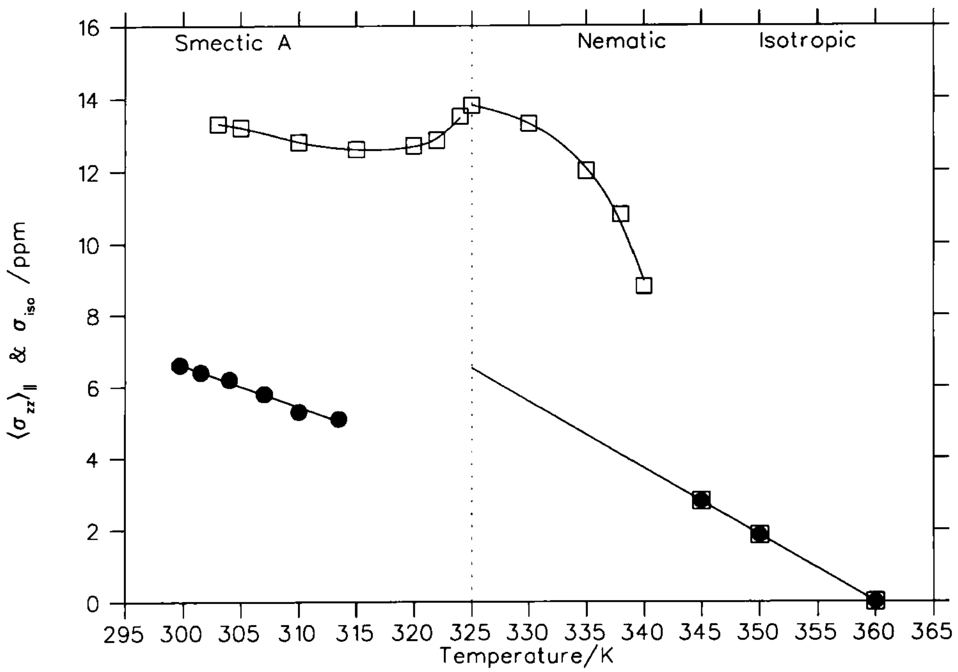

FIGURE 5 The ^{129}Xe shielding $\langle\sigma_{zz}\rangle_{\parallel}$, (□) and σ_{iso} (●; ▣) for the liquid crystal 7AB.

0, whereas the prolate cavities $\Delta\sigma < 0$. According to Springuel-Huet and Fraissard,[19] the anisotropic shielding tensor of ^{129}Xe adsorbed on molecular sieves is a consequence of the shape of the channels (rectilinear channels with elliptical cross-section) and the sign of $\Delta\sigma$ may change because of xenon-xenon collisions in the direction of the channel axis. In the liquid crystal solutions, the collisions between xenon atoms are rare, and thus the deformation of the electron cloud arises from the collisions of xenon with liquid crystal molecules.

4. CONCLUSIONS

This study on xenon and methane gases in the nematic and smectic phases of liquid crystal shows, that the ^{129}Xe shielding anisotropy, $\Delta\sigma$, behaves in a similar fashion as the anisotropic coupling, D_{CH}, of methane. The results in addition indicate, that solute molecules are expelled from the more dense regions to the less dense ones in smectic phases. This leads to a less anisotropic ^{129}Xe shielding tensor in the smectic A phase than in the nematic phase.

Acknowledgments

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