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An NMR study on the shielding of the ^{129}Xe isotope of xenon dissolved in thermotropic liquid crystals

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The variation of the nuclear shielding of the ^{129}Xe isotope in natural xenon dissolved in various liquid crystals and liquid crystal mixtures has been studied over the temperature range from 300 to 360 K. The temperature dependence is linear in the isotropic phase of the liquid crystals. An abrupt change in the shielding is observed when passing through the nematic–isotropic and smectic A–nematic phase transitions as well as when the liquid crystal director rotates by 90° in the so-called critical mixture of ZLI 1167 and EBBA. This is interpreted as being mainly the consequence of the shielding anisotropy of xenon arising from the deformation of its electronic distribution. The shift changes observed for 4,4′-di-*n*-heptylazoxybenzene at the nematic–isotropic phase transition on the one hand and at the smectic A–nematic phase transition on the other are found to be opposite in sign, reflecting the change in the liquid crystal structure.

1. Introduction

^{129}Xe NMR spectroscopy is surprisingly widely used to characterize properties of liquids and various solids. In particular, it has been applied to investigate structures of zeolites [1, 2] and clathrates [3]. This is based on the high sensitivity of the ^{129}Xe shielding, $\langle\sigma_{zz}\rangle$, to its physical environment. For example, it has been found that there is a correlation between the shielding (or shielding anisotropy) and the dimensions (or shape) of channels and cages in zeolites and clathrates. The data represented in literature are, however, qualitative, i.e. the effects contributing to the total shielding of ^{129}Xe in different environments are not well understood. The reaction field model, which correlates the ^{129}Xe shielding with the function

$$f(n) = (n^2 - 1)/(2n^2 + 1),$$

where n is the refractive index of the solvent, explains the shielding behaviour within groups of isotropic solvents with similar properties but is not valid generally [4]. The modified reaction field model introduced by Muller [5], which takes into account the solvent cohesive energy density, seems to work relatively well in saturated hydrocarbons. Recently, Luhmer *et al.* [6] applied their pair interaction structureless approximation model to calculate the xenon–solvent dispersion energies, E_{dis}, for various solvents. They found that E_{dis} correlates better with the ^{129}Xe shielding than does the function $f(n)$.

We have recently started a series of studies in which NMR spectroscopy of the magnetic isotopes of noble gases is used to probe the physical properties of liquid crystals. In the first paper [7], we utilized ^{131}Xe NMR to obtain information on

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the static electric field gradients in the nematic phases of some thermotropic liquid crystals. In this paper, we report ^{129}Xe shielding data over the temperature range from 300 to 360 K for xenon dissolved in various liquid crystals and liquid crystal mixtures. Earlier, Bayle *et al.* [8] studied ^{129}Xe shielding in the so-called critical mixture (a mixture of two liquid crystals with a vanishingly small diamagnetic anisotropy) of MBBA (positive diamagnetic anisotropy) and ZLI 1167 (negative diamagnetic anisotropy).

2. Experimental

Xenon has nine stable isotopes of which only two have a non-zero spin quantum number, ^{129}Xe and ^{131}Xe. ^{129}Xe has a spin of 1/2 and natural abundance of 26·4 per cent. The corresponding figures for the ^{131}Xe isotope are 3/2 and 21·2 per cent.

Xenon was dissolved in pure and mixed liquid crystals which were carefully degassed so that the best linewidth reached was *c.* 0·5 Hz in a liquid-crystalline phase. The compositions of the pure, commercially available liquid crystals used in this study are given in table 1. The samples were prepared in either 10 mm heavy wall tubes (xenon pressure *c.* 5 atm) or normal 8 mm tubes (*c.* 1 atm). In the former case, the ^{129}Xe NMR spectra were taken without lock whereas in the latter case external D_2O lock was used, D_2O being in the annulus of the coaxial 8/10 mm double tube system. The spectra were recorded on a Bruker AC250 spectrometer operating at 69·2 MHz for ^{129}Xe. The error in the shielding values shown in the figures is estimated to be less than 0·02 ppm.

3. Results

The temperature dependence of the ^{129}Xe shielding constant, $\langle\sigma_{zz}\rangle$, for xenon dissolved in various thermotropic liquid crystals is illustrated in figures 1–5. These figures show the shielding values referenced to the value at 360 K. The shielding differences for ^{129}Xe in the liquid crystal and gas phase (both at 360 K and a pressure in the gaseous sample of *c.* 2 atm), $\langle\sigma_{zz}(\mathrm{LC})\rangle - \langle\sigma_{zz}(\mathrm{gas})\rangle$, are collected in table 2. As the table shows, the resonance signal of the ^{129}Xe isotope shifts by -190 to

Table 1. Liquid crystals used in the study of ^{129}Xe shielding.

Code name†	Composition
ZLI 1167	Mixture of 4-*n*-alkyl-trans,trans-bicyclohexyl-4′-carbonitriles [alkyl = propyl (36 per cent), pentyl (34 per cent) and heptyl (30 per cent)]
ZLI 1132	Mixture of trans-4-*n*-alkyl-(4-cyanophenyl)-cyclohexanes [alkyl = propyl (24 per cent), pentyl (36 per cent) and heptyl (25 per cent)] and of trans-4-*n*-pentyl-(4′-cyanobiphenyl-4)-cyclohexane (15 per cent)
ZLI 3308	Mixture of alkylphenylcyclohexane, alkylcyclo-hexylbiphenyl and dicyclohexylbiphenyl
EBBA	4-ethoxybenzylidene-4′-*n*-butylaniline
HAB	4,4′-di-*n*-heptylazoxybenzene

† The ZLI liquid crystals are products of Merck. ZLI 1167 possesses a negative anisotropic diamagnetic susceptibility and its director orients perpendicular to the external magnetic field. In all the other cases, the director lies along the field direction.

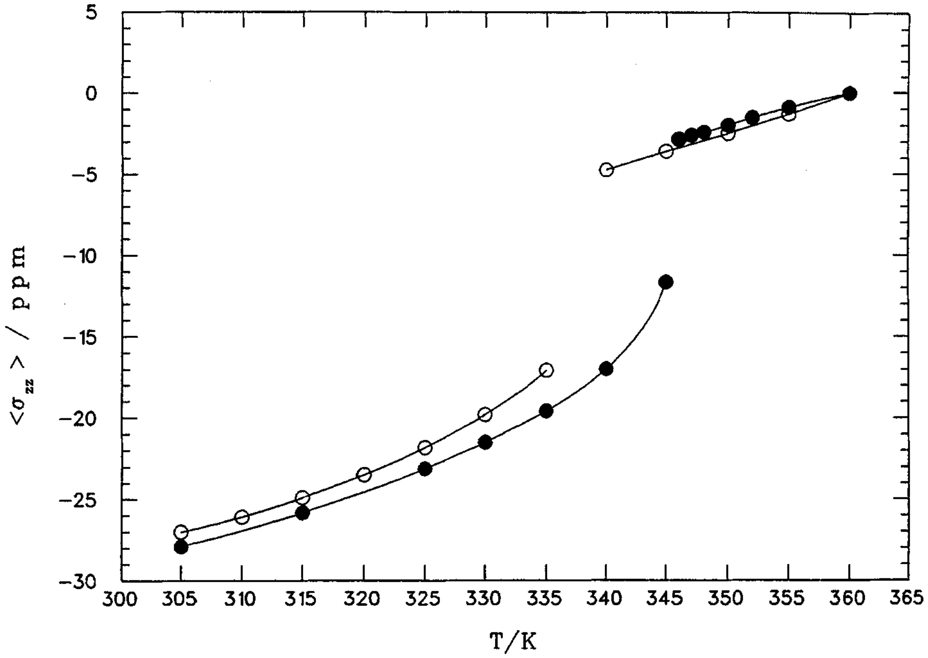

Figure 1. The ^{129}Xe shielding as a function of temperature for xenon dissolved in EBBA: (●) xenon pressure c. 1 atm, (○) xenon pressure c. 5 atm.

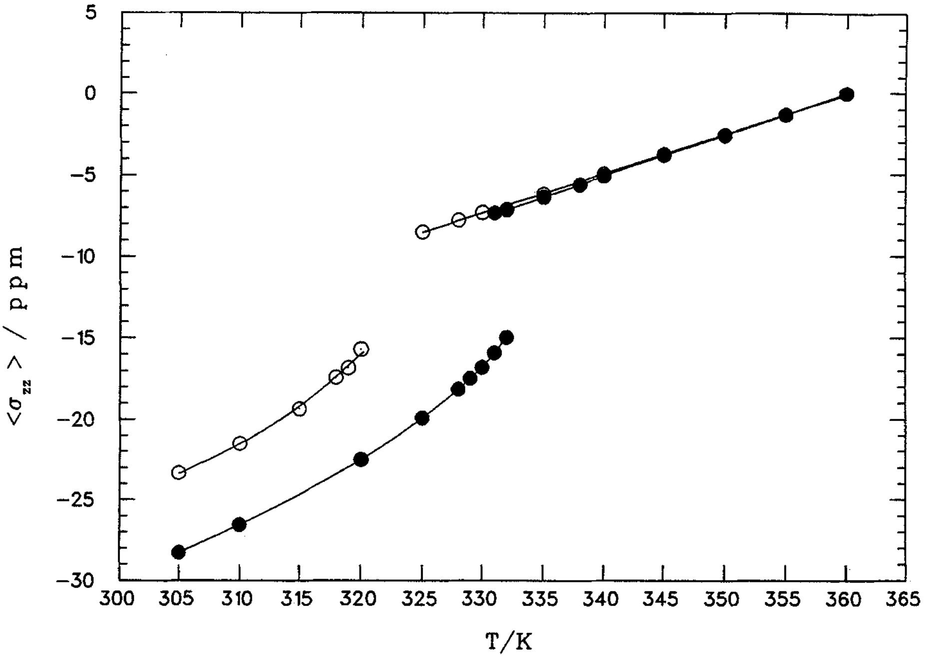

Figure 2. The ^{129}Xe shielding as a function of temperature for xenon dissolved in ZLI 1132 (●) and in the mixture of ZLI 1132 (55 wt %) and EBBA (45 wt %) (○).

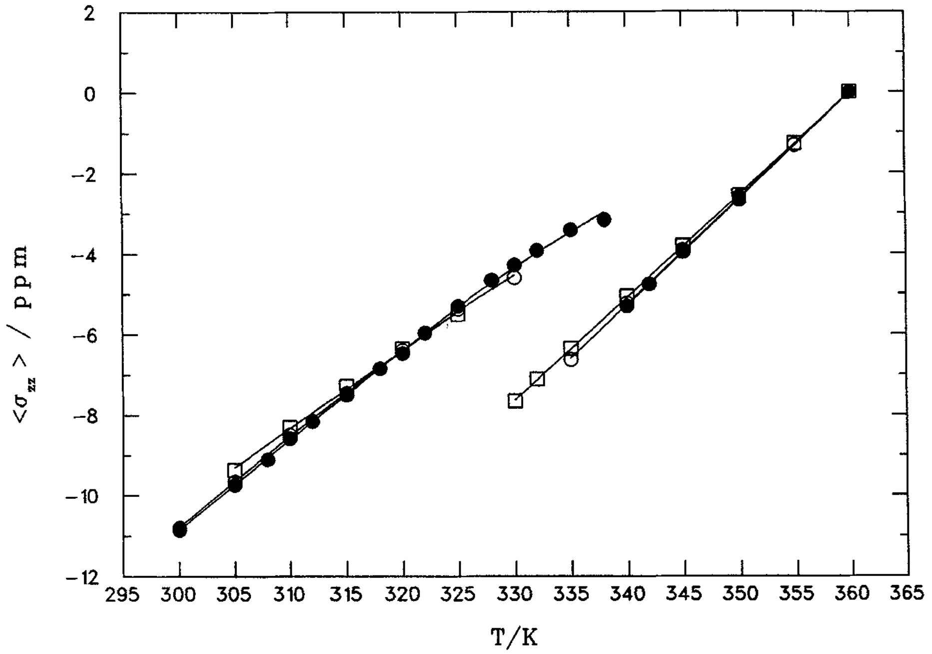

Figure 3. The ^{129}Xe shielding as a function of temperature for xenon dissolved in ZLI 1167 (●), in the 87·5 wt%: 12·5 wt% (○), and in the 78·0 wt%: 22·0 wt% (□) mixture of ZLI 1167 and EBBA.

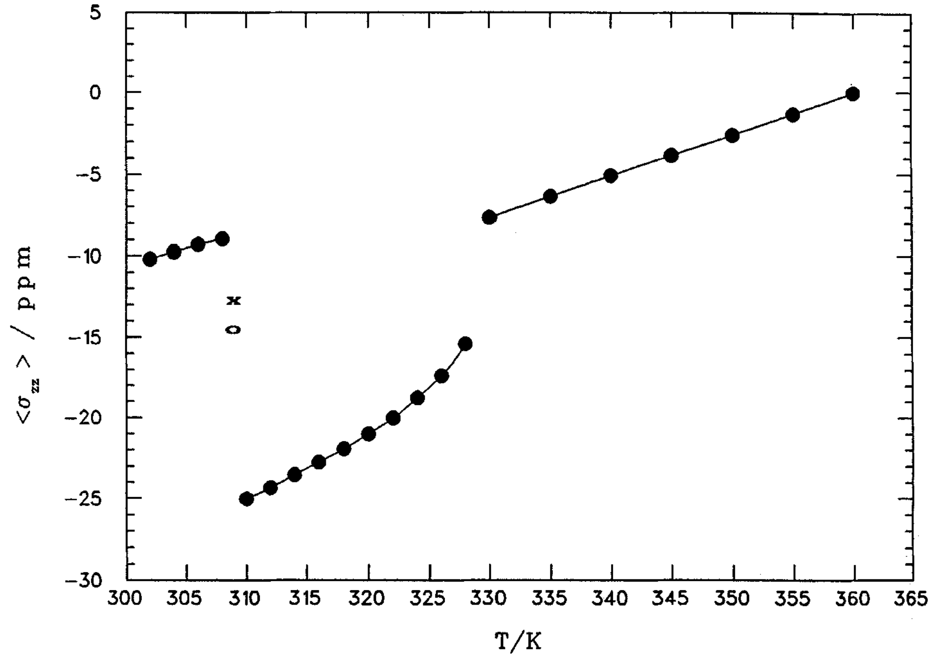

Figure 4. The ^{129}Xe shielding as a function of temperature for xenon dissolved in the critical mixture of ZLI 1167 (77 wt %) and EBBA (23 wt %). The points given at 309 K, where the director rotates by 90°, possess the following meanings: (x) extrapolated from the isotropic phase, (○) calculated from the shielding data corresponding to the two orientations of the director (see text).

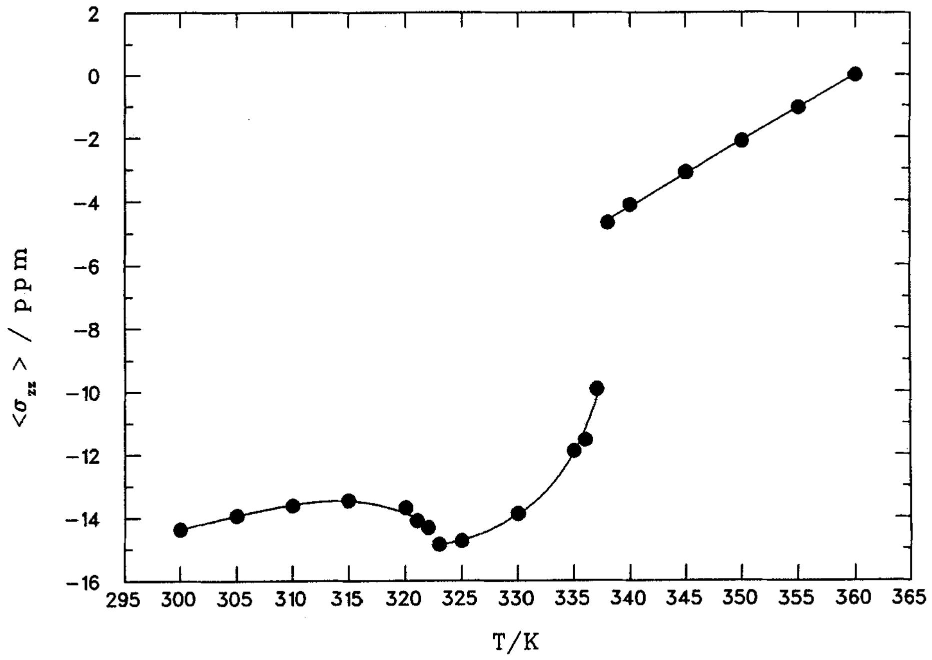

Figure 5. The ^{129}Xe shielding as a function of temperature for xenon dissolved in HAB.

Table 2. Temperature dependence of the ^{129}Xe shielding, $\Delta\langle\sigma_{zz}\rangle/\Delta T$, in the isotropic phase of some liquid crystals and the ^{129}Xe shielding difference between xenon dissolved in liquid crystals and pure xenon gas (both at 360 K), $\langle\sigma_{zz}(\mathrm{LC})\rangle - \langle\sigma_{zz}(\mathrm{gas})\rangle$. No susceptibility corrections were applied.

Liquid crystal†	$\Delta\langle\sigma_{zz}\rangle/\Delta T$/ppm K^{-1}	$\langle\sigma_{zz}(\mathrm{LC})\rangle - \langle\sigma_{zz}(\mathrm{gas})\rangle$/ppm
ZLI 1167	0·264	−189·34
ZLI 1167 (87·5) EBBA (12·5)	0·264	−189·15
ZLI 3308	0·258	‡
ZLI 1167 (77·0) EBBA (23·0)	0·254	−187·02
ZLI 1167 (78·0) EBBA (22·0)	0·254	−187·08
ZLI 1132	0·253	−189·80
ZLI 1132 (55·0) EBBA (45·0)	0·242	−186·82
EBBA§	0·235 0·203	−187·84 −190·18
HAB	0·209	−184·04

Note: The gas reference used is about 1·1 ppm downfield from the gas reference at zero pressure.

† The figures in parentheses indicate the concentration (in wt %) of the compound in the mixture.

‡ Not given because ZLI 3308 is nematic while all other liquid crystals are isotropic at 360 K.

§ In the upper case, the pressure of xenon gas was c. 5 atm while in the lower case it was c. 1 atm.

-184 ppm to higher frequency (lower external field), i.e. the nucleus becomes less shielded, on passing from the gas phase to the isotropic phase of a liquid crystal. The tabulated shielding differences are not corrected for susceptibility, but the contribution from this effect is estimated to be insignificant. We shall discuss this contribution in the next section.

In the isotropic phase of all the pure or mixed liquid crystal solvents used in this study, the ^{129}Xe shielding varies linearly with temperature so that the nucleus becomes more shielded at higher temperatures. The temperature coefficients (see table 2) range from 0·264 ppm/K to 0·203 ppm/K (18·3 Hz/K to 14·0 Hz/K at a magnetic field of 5·87 T) depending upon the solvent and amount of xenon dissolved. The corresponding value for gaseous xenon was found to be 0·009 ppm/K (0·6 Hz/K).

When passing through the nematic–isotropic transition from the isotropic side the ^{129}Xe shielding changes abruptly by about -8 to $+3$ ppm: when the director is parallel to external magnetic field the ^{129}Xe shielding decreases (see figures 1, 2, 4 and 5), whereas when the director is perpendicular to the magnetic field the xenon shielding increases (figures 3 and 4). The abrupt jump in the xenon shielding can be measured quite accurately by creating a slight temperature gradient over the sample volume.

An interesting behaviour of the xenon shielding is observed in HAB (see figure 5): the shielding changes in opposite ways at the nematic–isotropic and smectic A–nematic transitions. This obviously demonstrates the structural change taking place at the smectic A–nematic transition.

Figure 1 shows the effect of the xenon concentration in EBBA on the shielding of the ^{129}Xe isotope. When the concentration is increased (xenon gas pressure increases from *c.* 1 to *c.* 5 atm) the transition temperature decreases, the gradient $\Delta\langle\sigma_{zz}\rangle/\Delta T$ increases by almost 16 per cent, and in the nematic phase $\langle\sigma_{zz}(^{129}\mathrm{Xe})\rangle$ slightly increases. However, it seems that at lower temperatures, i.e. in more ordered phases, ^{129}Xe shielding becomes independent of the concentration (the two curves in figure 1 converge to a common value).

Figures 2 and 3 show the effect of mixing liquid crystals on the xenon shielding. In figure 2, the $\langle\sigma_{zz}(^{129}\mathrm{Xe})\rangle$ versus temperature curves for xenon dissolved in ZLI 1132 and in the 55:45 wt % mixture of ZLI 1132 and EBBA are given. The temperature coefficients of $\langle\sigma_{zz}\rangle$ in the isotropic phase differ by only *c.* 4 per cent, being smaller in the mixture. A more drastic change is measured in the shielding jump at the nematic–isotropic transition; it is 30 per cent smaller in the mixture than in pure ZLI 1132. In general, the ^{129}Xe shielding in the nematic phase of these two materials differs by 5 to 6 ppm. This presumably reflects again structural changes in the liquid crystal environment. When EBBA is mixed with ZLI 1167, only slight changes in the xenon shielding can be detected up to an EBBA concentration of 22 wt % (see figure 3) independently of whether the sample is isotropic or nematic. Obviously the average environment seen by a xenon atom has not changed.

There is a group of liquid crystal mixtures which is particularly useful to obtain information on the physical properties of solute molecules through their NMR spectra. Such a liquid crystal is produced by mixing two thermotropic nematogens with the opposite anisotropic diamagnetic susceptibility, $\Delta\chi$, so that $\Delta\chi$ of the mixture is small [9, 10]. (The mixture is commonly called a critical mixture.) In fact, by a slight change in temperature the sign of $\Delta\chi$ can be changed leading to the 90° rotation of the director. This in turn means the rescaling of the anisotropic molecular properties, such as the dipole–dipole coupling and nuclear shielding, by the proper value of the

Legendre polynomial,

$$P_2(\cos\theta) = 1/2(3\cos^2\theta - 1),$$

where θ is the angle between the external magnetic field and the director. In the present study, the critical mixture of ZLI 1167 (77 wt %) and EBBA (23 wt %) was used. The ^{129}Xe shielding is shown as a function of temperature for xenon dissolved in this mixture in figure 4. The first jump (when approaching from the isotropic side) in the xenon shielding is observed at the nematic–isotropic transition (the director orients along the external field) and the second at the temperature (*c.* 309 K) where the director rotates from parallel to perpendicular with respect to the magnetic field. At this point the shielding tensor, which generally speaking may include contributions from the bulk and local effects that are also anisotropic, must be multiplied by $-1/2$ ($= P_2(\cos 90°)/P_2(\cos 0°)$). If the same linear dependence of the ^{129}Xe shielding on temperature as observed in the isotropic state is assumed to be valid also in the nematic state, this ratio is not fulfilled. This result differs from that of Bayle *et al.* [8]. A possible reason for this is discussed in the next section.

4. Discussion

In general, the shielding of a molecule in a medium can be written as

$$\langle\sigma_{zz}\rangle = \sigma_0 + \sigma_b + \sigma_a + \sigma_w + \sigma_{\mathrm{aniso}} + \sigma_{\mathrm{E1}} + \sigma_{\mathrm{E2}} + \dots, \qquad (1)$$

where $\langle\sigma_{zz}\rangle$ is the average of the zz-component of the shielding tensor in the laboratory frame and the terms from the second one on the right hand side are due to medium effects: σ_b results from the bulk susceptibility, σ_a from the magnetic anisotropy of the neighbouring solvent molecules (the so-called local effect), σ_w from the dispersive van der Waals interactions, σ_{aniso} is the contribution from the anisotropy of the shielding tensor and is non-zero for solutes in anisotropic environments (such as liquid crystals), σ_{E1} originates from the reaction field induced in the solvent by the permanent electric dipole of the solute, and σ_{E2} is the shielding caused by the permanent electric dipole moment of the solvent. For xenon, σ_{E1} can be dismissed immediately because xenon has no electric dipole. Furthermore, σ_{E2} has been estimated to be negligible for non-polar solutes [11]. The remaining contributions will be discussed in the following sections.

4.1. *Bulk and local effect on the ^{129}Xe shielding*

The reported shielding values are not corrected for the bulk susceptibility. The effective magnetic flux density, B_{eff}, experienced by the nuclei in a liquid-crystalline sample placed in a cylindrical NMR tube in a superconducting magnet (the tube axis and the magnetic field, B_0, being parallel) can be presented, in the SI system, as [12]

$$B_{\mathrm{eff}} = B_0\{1 + 1/2\chi_a + 1/3[\chi_{\mathrm{LC}} + 2/3\Delta\chi_{\mathrm{LC}}\langle P_2(\cos\theta)\rangle]\}, \qquad (2)$$

where χ_a is the diamagnetic susceptibility of air, χ_{LC} and $\Delta\chi_{\mathrm{LC}}$ are the average value and the anisotropy of the volume diamagnetic susceptibility tensor of the liquid crystal solvent, respectively. This equation can be used to estimate the bulk effect, σ_b, on the nuclear shielding arising from the temperature variation of the sample and from the nematic–isotropic transition (the effect of the diamagnetic anisotropy), since

$$\sigma_b = -1/3[\chi_{\mathrm{LC}} + 2/3\Delta\chi_{\mathrm{LC}}\langle P_2(\cos\theta)\rangle]. \qquad (3)$$

The volume susceptibility depends upon the solvent density, ρ, according to

$$\chi_{LC} = (\chi_{MLC}/M)\rho, \tag{4}$$

where χ_{MLC} is the molar susceptibility and M is the molecular mass. Thus σ_b becomes temperature dependent through the temperature dependence of the density. Unfortunately, neither the temperature dependence of density nor that of the volume susceptibility of the ZLI liquid crystals are known to us. The relevant data is, however, available for EBBA (see the next section). σ_b depends on the degree of order of the liquid crystal solvent because of the second term in equation (3).

At the nematic–isotropic transition, equation (3) gives

$$(\sigma_b)_{NI} = 1/3(\delta\chi_{LC}) + 2/9\Delta\chi_{LC}\langle P_2(\cos\theta)\rangle \tag{5}$$

for the change of the bulk effect where the change, $\delta\chi_{LC}$, of the isotropic part as well as the anisotropic susceptibility tensor of thermotropic nematic liquid crystals are typically of the order of $\pm 10^{-7}$ [13, 14]. Consequently, the bulk effect contribution to the ^{129}Xe shielding jump at the phase transition is minute compared to the experimental values of several ppm. Furthermore, the shape of the $\langle\sigma_{zz}(^{129}\text{Xe})\rangle$ versus temperature curve cannot be explained by the bulk effect.

For a critical mixture of liquid crystals the difference of the bulk effects corresponding to the parallel (the diamagnetic anisotropy $\Delta\chi_{LC}(0°) \gtrapprox 0$), $\sigma_b(0°)$, and perpendicular ($\Delta\chi_{LC}(90°) \lessapprox 0$), $\sigma_b(90°)$, orientation of the director is

$$\sigma_b(0°) - \sigma_b(90°) = -1/9[2\Delta\chi_{LC}(0°) + \Delta\chi_{LC}(90°)] \approx 0. \tag{6}$$

Therefore, we can conclude that the bulk susceptibility has a negligible effect on the ^{129}Xe shielding jump arising from the 90° rotation of the director in the critical liquid crystal mixture.

4.2. *The density dependence of the ^{129}Xe shielding*

The ^{129}Xe nuclear shielding in xenon gas and in mixtures of xenon with other gases has been fitted to [15]

$$\sigma = \sigma_0 + \sigma_1\rho + \sigma_2\rho^2 + \sigma_3\rho^3, \tag{7}$$

where ρ is the gas density, σ_0 is the ^{129}Xe shielding *in vacuo*, and σ_1, σ_2 and σ_3 are the virial coefficients which correspond to the shielding effects arising from the two body (σ_1) and many body (σ_2 and σ_3) collisions. In the gaseous phase of xenon, the many body interactions were found to be important [15].

The temperature dependence of the density of EBBA can be derived from the study of Bahadur and Chandra [16] which deals with the specific volume of EBBA. Since both the ^{129}Xe shielding and the density of EBBA change linearly with temperature in the isotropic phase of the liquid crystal, a linear relation between the $\langle\sigma_{zz}(^{129}\text{Xe})\rangle$ and ρ can be expected. The slope of the resulting straight line is approximately -257 ppm/cm^3 g^{-1}. This figure, however, includes the bulk susceptibility effect from the isotropic part of the susceptibility tensor besides, for example, the van der Waals effect [17]. The density of EBBA changes abruptly at the nematic–isotropic transition but varies also linearly with temperature on the nematic side. If we assume that the isotropic average of the ^{129}Xe shielding tensor is also linearly dependent upon the density in the oriented phase, we can estimate the ^{129}Xe shielding jump, due to the sudden change in the EBBA density, to be *c.* -1 ppm. This phenomenon also provides an explanation for an observation in the critical mixture of ZLI 1167 and EBBA mentioned at the end of §3. Because nuclear shielding is a second rank tensorial property, the equation

$$[\sigma(0^\circ) - \sigma_{\mathrm{iso}}]/[\sigma(90^\circ) - \sigma_{\mathrm{iso}}] = -2 \tag{8}$$

should be fulfilled in cases where the director is rotated by 90°, where

$$\sigma_{\mathrm{iso}} = 1/3\,\mathrm{Tr}\,\boldsymbol{\sigma} = 1/3[\sigma(0^\circ) + 2\sigma(90^\circ)] \tag{9}$$

is the isotropic shielding constant. When using the σ_{iso} value of $-12{\cdot}8$ ppm determined by extrapolation from the isotropic phase, the ratio on the left hand side of equation (8) equals $-3{\cdot}1$. The use of equation (9) leads to an σ_{iso} of $-14{\cdot}3$ ppm. The difference of the two σ_{iso} values is probably due to the density effect as we have discussed.

4.3. *Shielding anisotropy*

In the critical mixture of ZLI 1167 and EBBA, the bulk and local anisotropy effects on the ^{129}Xe shielding are believed to be of minor importance. Therefore, the sudden change in the observed ^{129}Xe chemical shift arises from the σ_{aniso} term in equation (1). The nuclear shielding for a solute in a liquid-crystalline environment can be written as (with the z axis parallel to the external magnetic field)

$$\langle\sigma_{zz}\rangle = \sigma_{\mathrm{iso}} + \left[2/3 \sum_{\alpha,\beta} S_{\alpha\beta}\sigma_{\alpha\beta}\right] \langle P_2(\cos\theta)\rangle, \tag{10}$$

where $S_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are the elements of the order tensor (with respect to the liquid crystal director) and of the shielding tensor, respectively. For a xenon atom, this equation reduces to

$$\langle\sigma_{zz}\rangle = \sigma_{\mathrm{iso}} + 2/3\Delta\sigma\,\langle P_2(\cos\theta)\rangle, \tag{11}$$

where $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$ is the anisotropy of the shielding tensor and $\sigma_{\parallel}$ and $\sigma_{\perp}$ are the shielding tensor elements in the directions parallel and perpendicular to the director, respectively. Equation (11) disagrees with that suggested by Bayle *et al.* [8] in that we have left out the degree of order, S, of the dissolved Xe. $\Delta\sigma$ is an actual average shielding anisotropy due to the deformation of the solute. This approach furthermore avoids the postulation of an impossible degree of order $S = 1$ for xenon in clathrates as has been introduced [8].

For xenon shielding in a critical mixture,

$$\langle\sigma_{zz}(0^\circ)\rangle - \langle\sigma_{zz}(90^\circ)\rangle = \Delta\sigma, \tag{12}$$

where $\langle\sigma_{zz}(0^\circ)\rangle$ and $\langle\sigma_{zz}(90^\circ)\rangle$ correspond to the ^{129}Xe shielding when the director is parallel and perpendicular to the external magnetic field, respectively. By applying this result, we can conclude that $\Delta\sigma(^{129}\mathrm{Xe}) = -16{\cdot}4(5)$ ppm in the critical mixture of ZLI 1167 and EBBA at 309 K. Ripmeester *et al.* [3, 18] have reported $\Delta\sigma(^{129}\mathrm{Xe})$ data for xenon trapped in the cages of various clathrates. They range from $+30$ to -171 ppm depending upon the symmetry and size of the cage. Recently, Springuel-Huet and Fraissard [19] studied the ^{129}Xe shielding of xenon adsorbed on molecular sieves. They determined, on the basis of lineshapes, that $\Delta\sigma(^{129}\mathrm{Xe})$ can be either negative or positive depending not only upon the shape of the cavity but also upon the xenon concentration. However, no anisotropy values are given.

In the other liquid crystals of this study, $\Delta\sigma(^{129}\mathrm{Xe})$ cannot be determined as accurately as in a critical mixture. This arises from the fact that the isotropic shielding, σ_{iso}, in equation (11) is temperature (or phase) dependent. However, no major error is introduced when σ_{iso} is derived by extrapolation from the isotropic phase. Then

$$\Delta\sigma = 3/2(\langle\sigma_{zz}\rangle - \sigma_{\mathrm{iso}})/\langle P_2(\cos\theta)\rangle. \tag{13}$$

The resulting $\Delta\sigma$ values will vary with temperature, i.e. with liquid crystal order, and, of course, with the liquid crystal solvent. The detailed nature of the interaction which causes the average deviation of the xenon electron distribution from spherical is not known. We could, however, imagine that the interactions (or deforming forces) become stronger when the liquid crystal environment becomes more highly ordered. On the other hand, similar arguments (cavities and their shapes) as applied for xenon in zeolites and clathrates could also be utilized. Probably, a corresponding investigation with other noble gases will cast further light on this problem.

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References

[1] Fraissard, J., and Ito, T., 1988, *Zeolites*, **8**, 350.
[2] Fraissard, J., 1988, *Z. phys. Chem.*, **269**, 657.
[3] Ripmeester, J. A., Ratcliffe, C. I., and Tse, J. S., 1988, *J. chem. Soc. Faraday Trans. I*, **84**, 3731.
[4] Stengle, T. R., Reo, N. V., and Williamson, K. L., 1981, *J. phys. Chem.*, **85**, 3772.
[5] Muller, N., 1982, *J. phys. Chem.*, **86**, 2109.
[6] Luhmer, M., Dejaegere, A., and Reisse, J., 1989, *Magn. Reson. Chem.*, **27**, 950.
[7] Diehl, P., and Jokisaari, J., 1990, *Chem. Phys. Lett.*, **165**, 389.
[8] Bayle, J. P., Courtieu, J., and Jullien, J., 1988, *J. Chim. phys.*, **85**, 147.
[9] Khetrapal, C. L., and Kunwar, A. C., 1981, *Molec. Crystals liq. Crystals*, **72**, 13.
[10] Khetrapal, C. L., and Kunwar, A. C., 1981, *Chem. Phys. Lett.*, **82**, 170.
[11] Rummens, F. H. A., 1976, *Can. J. Chem.*, **54**, 254.
[12] Diehl, P., Jokisaari, J., Moia, F., and Lounila, J., 1982, *Molec. Crystals liq. Crystals*, **87**, 319.
[13] Kelker, H., and Hatz, R., 1980, *Handbook of Liquid Crystals* (Verlag Chemie).
[14] Diehl, P., and Jokisaari, J., 1982, *Chem. Phys. Lett.*, **87**, 494.
[15] Jameson, A. K., Jameson, C. J., and Gutowsky, H. S., 1970, *J. chem. Phys.*, **53**, 2310.
[16] Bahadur, B., and Chandra, S., 1976, *J. Phys.* C, **9**, 5.
[17] Rummens, F. H. A., 1975, *Van der Waals Forces and Shielding Effects* (NMR Basic Principles and Progress, Vol. 10), edited by P. Diehl, E. Fluck and R. Kosfeld (Springer-Verlag).
[18] Ripmeester, J. A., 1982, *J. Am. chem. Soc.*, **104**, 289.
[19] Springuel-Huet, M. A., and Fraissard, J., 1989, *Chem. Phys. Lett.*, **154**, 299.