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Proton magnetic relaxation study of pretransitional phenomena in the isotropic phase of a nematic liquid crystal

II. Presence of inner magnetic field gradients as revealed by self-diffusion study

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Above the clearing point of a nematic LC self-diffusion was studied by the Hahn pulse sequence (90°-*t*-180°) in the presence of a weak (up to 4 Gs cm^{-1}) permanent external magnetic field gradient $G = \partial\mathbf{H}/\partial z$. The non-linearity of spin-echo decays was interpreted as a result of the inner magnetic field gradient Γ, indicating the magnetically non-homogeneous nature of the pretransitional zone of the LC. The pretransitional zone was considered to be biphasic (locally ordered clusters ⇔ isotropic surrounding). Due to the orientation of clusters in the magnetic field and the anisotropy of the diamagnetic susceptibility of their molecules, the diamagnetic susceptibility of clusters in the *z* direction should be different from that of their disordered surroundings. Therefore, clusters behave as specific filled particles, their diamagnetic response in the presence of *G* being different from that of their isotropic surroundings, i.e. clusters can experience a translational motion in the external field gradient. This leads to the peculiar diamagnetic separation in space, accompanied by an increase of the field gradient. The inner field gradient was shown to be proportional to G^2t^3 and to decrease with temperature.

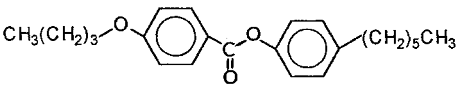
1. Introduction

In Part I of this work [1], pretransitional phenomena in the isotropic phase of a low molecular mass nematic LC were studied by means of transverse magnetic relaxation. These data were interpreted in terms of the magnetically inhomogeneous nature of the pretransitional zone, considered to a first approximation to be biphasic, consisting of clusters and their isotropic surroundings. Magnetic dipole–dipole interactions in clusters are unaveraged due to the local ordering, whereas the isotropic character of the motion of the rest of the molecules effectively averages their local fields. Therefore, exchange of molecules between clusters and their isotropic surroundings during the local order fluctuations is accompanied by a change of the local magnetic field. On the basis of this model, the results of the Carr–Purcell–Meiboom–Gill (CPMG) experiment above the clearing point (T_c) have been interpreted [1, 2]. The same experimental manifestations of the local order fluctuations that we observed previously in isotropic solutions of liquid crystalline main chain polyesters in deuteriated chloroform [2–6] were found.

In this article the transverse magnetization decay in a permanent external magnetic field gradient, applied in the *z* direction ($G = \partial\mathbf{H}/\partial z$), is studied for the macroscopically isotropic phase of the same low molecular mass nematic as in Part I. A self-diffusion study is a necessary supplement to the investigation of the exchange presented in [1], since the CPMG experiment is sensitive to both motions. We shall show that a real field gradient acting in the isotropic phase of the nematic differs from *G* due to the presence of the inner magnetic field gradient Γ. These observations support the idea of the magnetically heterogeneous nature of the pretransitional zone of the LC. After corrections for the inner field gradients the self-diffusion coefficients above T_c will be obtained.

2. Experimental

The structural formula of the 4*n*-hexylphenyl ester of 4-*n*-butyloxybenzoic acid (HEOB) studied in this work and exhibiting nematic properties at 29° < *T* < 49° is:



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The chemical structure of HEOB was confirmed by PMR spectroscopy; the spectra from the chloroform-d solution were recorded with a Bruker AC-200 spectrometer at a resonance frequency of 200 MHz.

Measurements of proton magnetic relaxation were carried out at 16 MHz using a pulsed relaxometer (made in the Institute Neftechimavtomatica, St.-Petersburg) equipped with a variable temperature unit and with field gradient coils. Spin–spin relaxation was measured with the help of a 90°-t-180° pulse sequence. In the homogeneous system, a spin-echo decay (SED) in the presence of G depends on the self-diffusion coefficient (D) [7–9]:

$$\begin{aligned} A(2t)/A_0 &= \exp(-2t/T_2)\exp(-2G^2\gamma^2Dt^3/3) \\ &= R\exp(-2G^2\gamma^2Dt^3/3) \qquad (1) \end{aligned}$$

where $A(2t)$ is the amplitude of the spin-echo observed at $2t$, A_0 is the initial magnetization, T_2 is the spin–spin relaxation time, γ is the gyromagnetic ratio, and R is the relaxation term, independent of G. Magnetic field gradients were calibrated relative to water, i.e. by inserting the known value of D of water in equation (1). By least square fitting, the dependence of the field gradient vs. the current in the gradient coils (I) was obtained: $G = 0.22 + 0.05I$, where G is in G cm^{-1} and I is in mA. Permanent field gradients were changed up to 4 G cm^{-1}. According to equation (1), the limitations of the value of the self-diffusion coefficients that could be determined arise from the inequality $D > 12/(\gamma G)^2 T_2^3$ [8]. In the isotropic phase of the LC studied, the values of $T_2 \approx 0.2$–1 s were determined in Part I (see the table, column headed T_0^2). Therefore, only translational motions with $D > 10^{-6}$ cm^2 s^{-1} can produce a noticeable effect on the spin-echo decay (SED) at $G < 4$ G cm^{-1}.

3. Results

In figure 1 the semi-log dependences of spin-echo attenuation at different magnetic field gradients are presented. It is seen that at small external field gradients, the SED are modulated, i.e. the relaxation term R in equation (1) is non-exponential. The origin of this modulation can be manifold: indirect spin–spin couplings, as well as exchange between sites with different local fields. Since the corresponding equations describing SED contain too many parameters [10, 11], it is impossible to fit them reasonably to experimental data. Assuming the independence of the relaxation term in equation (1) on G, the self-diffusion can be examined. To exclude the relaxation term, we studied the gradient dependences of A/R_0, where R_0 is the amplitude of spin-echo at the zero external gradient (figure 2).

Figure 1 shows that the magnetic field gradient does not influence the beginning of SED: different SED almost coincide at $2t < 40$ ms, i.e. in the range of pulse spacing t_{cp} used in the CPMG sequence [1]. Therefore, qualitatively it is obvious that in the CPMG experiment the influence of self-diffusion on the SED is negligible. Since equation (1), used in NMR for obtaining self-diffusion coefficients, holds only for simple liquids, estimation of D above the T_c of a LC can be complicated by a non-homogeneous nature of the 'isotropic' phase of the LC. In general, dependences of ln A/R_0 vs. G_2 used for the determination of D should not be exponential [9, 12, 13] in multicomponent systems. Moreover, in the presence of an exchange system, the self-diffusion attenuation of SED depends on the exchange rate. In the case of a slow exchange, the dependence of ln A/R_0 on G_2 is the sum of exponents with the self-diffusion coefficients and populations corresponding to each phase.

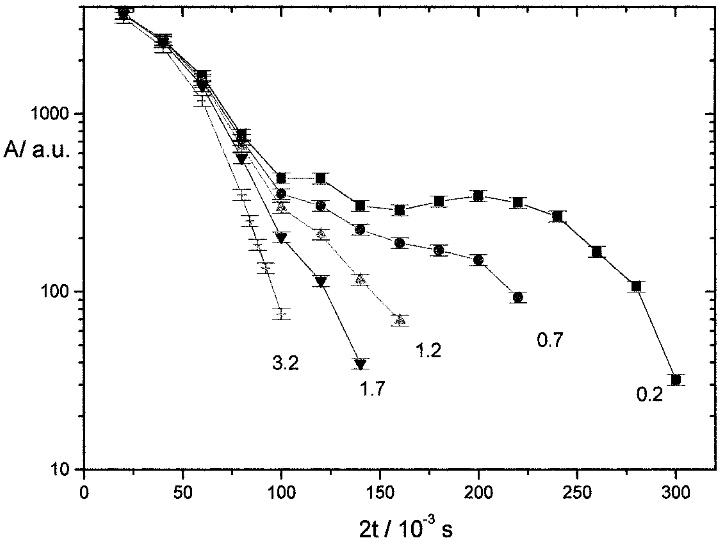

Figure 1. Dependence of SED measured at 90°C in a 90°-t-180° experiment at different values of the external magnetic field gradient G_j (in G cm^{-1}) the values of which are indicated in the figure.

Fast and intermediate exchange ‘spoils’ the populations of states and leads to the dependence of self-diffusion attenuation of A on t. Therefore, contrary to non-exchanging systems, in the presence of exchange the slopes of ln A vs. G^2 can be unequal at different t. Figure 2 shows the self-diffusion attenuation of SED measured at different t. It is seen that for each temperature, all dependences fall onto one curve. However, the form of the SED is unusual. These dome-shaped curves were fitted by a second-order polynomial:

$$\begin{aligned}\ln A/R_0 &= -a - b_1 t^3 G^2 - b_2 (t^3 G^2)^2 \\ &= -a - b_1 t^3 G^2 [1 + (b_2/b_1) G^2 t^3] \qquad (2)\end{aligned}$$

where $b_1 = 2D\gamma^2/3$. Supposing that this non-linearity can be explained by the intrinsic magnetic inhomogeneity of the pretransitional zone due to which corrections for inner field gradients should be made, we can write: $G^2[1 + (b_2/b_1)G^2 t^3] = (G + \Gamma)^2$, where Γ is the internal field gradient, i.e.

$$\Gamma \approx \beta G^2 t^3, \qquad (3)$$

where $\beta = b_2/2b_1$. According to equation (3), Γ increases with G and t. Figure 3 shows temperature dependences of D and of Γ (the last is calculated for $t = 50$ ms, $G = 1$ G cm^{-1}). It is seen that both quantities decrease with temperature.

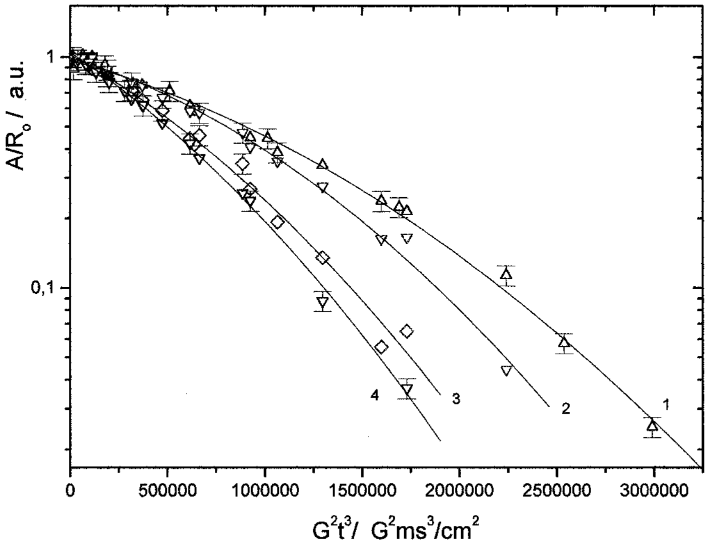

Figure 2. Dependences of spin-echo amplitudes (A) normalized to the amplitudes without a field gradient (R_0) on $G^2 t^3$ (different points correspond to different pulse spacings). The curves 1–4 correspond to temperatures of 65, 70, 80, and 90°C, respectively.

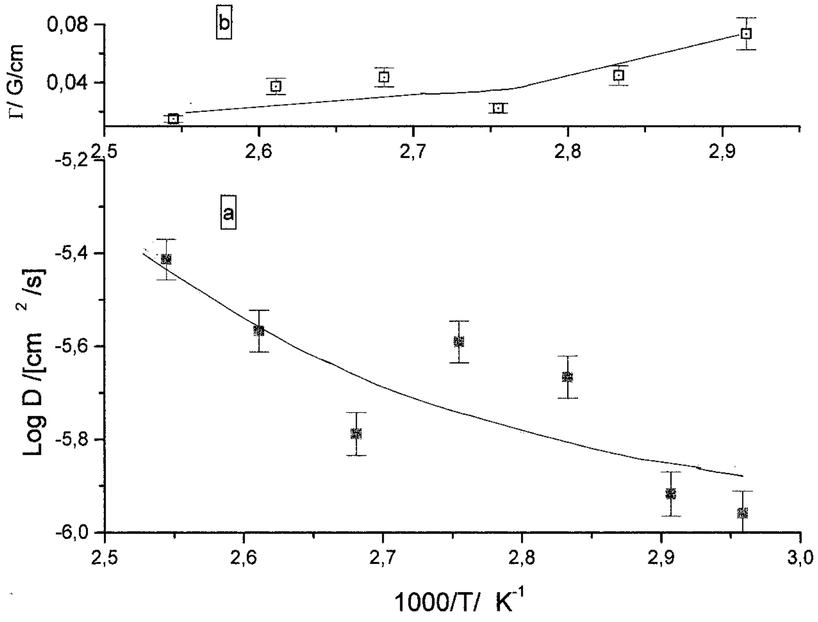

Figure 3. Dependences of ln D (a) and Γ (b) vs. the reciprocal temperature.

4. Discussion

If the liquid above T_c consists of locally ordered clusters in the isotropic surroundings, figure 4(*a*), then the differences in the diamagnetic responses of these subphases can arise due to the different orientational influence of the magnetic field on the locally ordered and disordered subphases, figure 4(*b*). In fact, in the disordered surroundings, the magnetic field is acting on individual molecules, whereas in clusters the molecules are moving collectively. Therefore, the diamagnetic response of a cluster to the external magnetic field is N times higher than that of an individual molecule, N being the number of molecules in a cluster [14]. Considering the low viscosity of their isotropic surroundings, clusters can be oriented even in the rather low external magnetic field of our NMR experiment, figure 4(*b*).

Due to the anisotropy of the magnetic susceptibility χ of the molecules in a cluster, its magnetization depends on its orientation. In the case of an arbitrary angle between the liquid crystalline director **n** and the magnetic field **H**, the anisotropy of the magnetic susceptibility of a LC (and a liquid crystalline cluster as well) is [15]:

$$\chi_{\parallel} - \chi_{\perp} = (A_{\parallel} - A_{\perp})S \tag{4}$$

where $A_{\parallel}$ and $A_{\perp}$ are the susceptibilities of perfectly oriented molecules and S is the order parameter (when this equation is applied to a cluster in an isotropic phase of a LC, S is the local order parameter). Therefore, due to the orientation of clusters in the external magnetic field, the difference in magnetic susceptibilities between clusters and their isotropic surroundings in the direction of the applied field is $(A_{\parallel} - A_{\perp})S$. The order parameter in clusters was determined as in Part I: $S \approx 0.001$. The susceptibility of a molecule is a sum of the susceptibilities of its groups and bonds, but we shall take as a first approximation the value of $(A_{\parallel} - A_{\perp})$ for benzene. In benzene $A_{\perp} = -34.9 \times 10^{-6}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$, $A_{\parallel} = -94.6 \times 10^{-6}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ and the anisotropy of the magnetic susceptibility is $A_{\parallel} - A_{\perp} = -59.7 \times 10^{-6}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$.

Since in the z direction the diamagnetic susceptibility of clusters differs from that of the isotropic surroundings, clusters can be treated as specific filled particles. Therefore, they can produce inner field gradients. To find out what values of the inner field gradients should be expected in the isotropic phase of the LC, we calculated our data according to the results of analyses of the spin-echo decay in a magnetically heterogeneous system [16]: here Glasel studied the self-diffusion of water filled with glass beads. Glasel has accounted for the inner field gradients in the z direction as arising from the differences in diamagnetic susceptibilities of water and glass. According to [16], Γ at a distance r from a glass bead of radius r_0 depends upon the difference in local magnetic field between beads and water $\delta\mathbf{H}$:

$$\delta\mathbf{H} \approx \Gamma r (r \geqslant r_0). \tag{5}$$

The inner field gradient at $r \geqslant r_0$ is determined by:

$$\Gamma = \frac{9\mathbf{H}_0 A}{4 r r_0}\,\frac{1}{r^2 + r r_0 + r_0^2} \tag{6}$$

where $A = 4\pi r_0^3(\chi_1 - \chi_2)/3$, $\chi_1 - \chi_2$ is the difference in magnetic susceptibilities between the glass beads and water.

We have estimated the inner field gradients in the isotropic phase of the LC according to [16], inserting $\chi_1 - \chi_2 = S(A_{\parallel} - A_{\perp})$ in equation (6). The value of the order parameter in the clusters $S \approx 0.001$ and, as discussed above, the anisotropy of the magnetic susceptibility of a molecule was taken to be $A_{\parallel} - A_{\perp} = 59.7 \times 10^{-6}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$. The dependences of the internal field gradients in the z direction on the distance from the surface of the clusters for arbitrary cluster radii ($r_0 = 10$, 50, and 100 nm), were calculated. They are demonstrated in figure 5. The area around the clusters, where the internal field gradient still exists, is approximately equal to r_0. Therefore, an appreciable number of molecules in the isotropic surroundings can experience the influence of internal field gradients even at $G = 0$. This effect will contribute to the coefficient b_1 in equation (2), thus making it impossible to obtain the real values of the self-diffusion coefficients. The self-diffusion in local field gradients can influence also the form of SED at $G \to 0$ (figure 1).

At $G \neq 0$ the differences in translational motion of clusters and individual molecules in the external

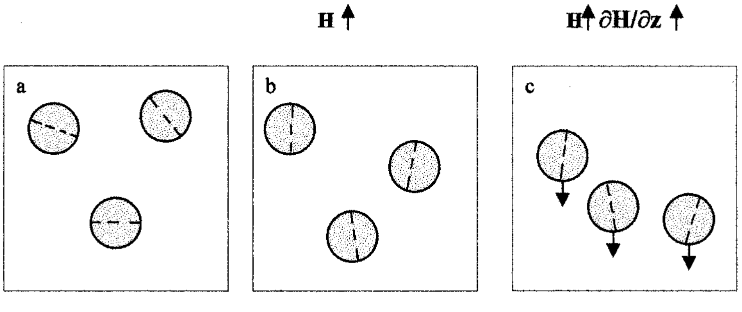

Figure 4. Biphasic models of the isotropic phase of a LC at $\mathbf{H} = 0$, $\partial\mathbf{H}/\partial z = 0$ (*a*), at $\mathbf{H} \neq 0$, $\partial\mathbf{H}/\partial z = 0$ (*b*), $\mathbf{H} \neq 0$, $\partial\mathbf{H}/\partial z \neq 0$ (*c*).

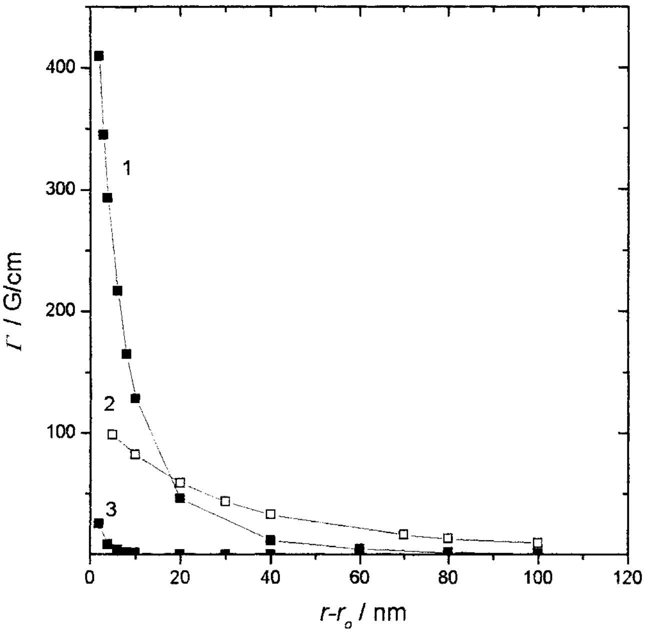

Figure 5. Dependence of the inner magnetic field gradient of a cluster on the radius from the cluster centre for three arbitrary cluster radi: 10, 50, and 100 nm (respectively, curves 1–3). These dependences are calculated according to Glasel's model [16].

magnetic field gradient should be considered, figure 4 (*c*). The driving force for the translational motion in the external field gradient is:

$$F = \chi V \mathbf{H} \partial \mathbf{H} / \partial z \qquad (7)$$

where V is the volume. Since the volume and $|\chi|$ of the clusters are greater than those of the individual molecule, diamagnetic separation of clusters and individual molecules can take place at $G \neq 0$. Clusters will be pushed out in the region of lower magnetic field with a higher force than the individual molecules of the isotropic surroundings. This can produce a concentration gradient of clusters opposite to the direction of the field gradient, figure 4 (*c*). Since the overall diamagnetic susceptibility χ in the z direction depends on the fractions (p_a, p_b) and susceptibilities (χ_a, χ_b) of clusters and isotropic subphases $\chi = p_a\chi_a + p_b\chi_b$, it depends on z in the case of the concentration gradient of χ. Therefore, the overall magnetization $\mathbf{M} = \chi\mathbf{H}$ should also depend on z. Considering the diamagnetic nature of the clusters (i.e. the nagative value of χ), the magnetization $\mathbf{M}$ opposes the external magnetic field $\mathbf{H}$. Therefore, the real magnetic field will be lowered towards the low-gradient edge of the sample, leading to the increase in the real field gradient: instead of G it becomes $G + \Gamma$ in our notation. Since clusters are not permanent particles, these effects are taking place within their lifetime. Therefore, the observed decrease of Γ with temperature, figure 3 (*b*), could be explained by the decrease of the pathway of cluster motion in the external field gradient due to the decrease of their lifetime. The corresponding decrease of local order parameter S with temperature, leading to the decrease of the differences in susceptibilities of the cluster and isotropic phases would also be explained.

It should be mentioned that the dependence of additional attenuation of SED due to the internal field gradient has a 'diffusion' character (G^2t^3) typical for NMR, thus indicating that some additional diffusion contribution is in fact producing the above effect. Therefore, in spite of the fact that the cluster self-diffusion is not observed separately in our experiment, the possibility of an indirect influence of cluster motion on the overall inner field gradient is shown. These non-linear effects could have led to the greater deviation of the self-diffusion results in the isotropic phase of a LC than that in the ordinary liquids mentioned in [17].

5. Conclusions

The spin–spin nuclear magnetic relaxation of the isotropic phase of a LC in the presence of an external magnetic field gradient G was studied. To a first approximation, the isotropic phase of the LC was considered to be biphasic, consisting of clusters and their isotropic surroundings. Since the diamagnetic susceptibility of clusters is N times greater than of the individual molecule (N being the number of molecules in clusters), their motion is more sensitive to external magnetic fields and external magnetic field gradients than are the corresponding motions of individual molecules. As a result of cluster orientation in the external magnetic field, the diamagnetic susceptibility of clusters in the direction of the applied magnetic field differs from that of their isotropic surroundings. In this respect, clusters behave as specific filled particles, producing inner magnetic field gradients in the z direction even at zero G. At $G \neq 0$ the translational motion of clusters can produce specific diamagnetic separation in space of clusters and isotropic surroundings, leading to the observed dependences of the internal field gradient on G. After corrections for the internal field gradient, the self-diffusion coefficients were obtained.

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