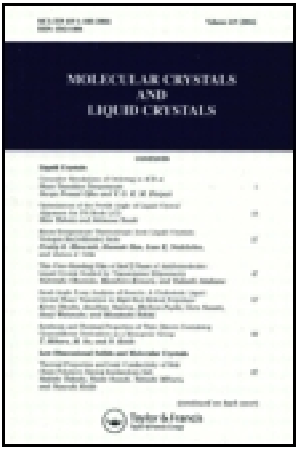

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Molecular Dynamics in MBBA With Chiral Impurity

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MOLECULAR DYNAMICS IN MBBA WITH CHIRAL IMPURITY

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Abstract The temperature dependence of the proton spin-lattice relaxation time has been investigated in the nematic and induced cholesteric phases of MBBA with chiral impurity. In cholesteric phase the activation energy was found to increase with the impurity concentration increasing while in unwound by magnetic field nematic the activation energy is lower and equal to that for pure MBBA.

INTRODUCTION

Nuclear spin-lattice relaxation is a convenient tool in studing of molecular motion, phase transitions and pretransitional phenomena in liquid crystals. Whereas the nature of spin-lattice relaxation processes for nematic liquid crystals is sufficiently well studied[1,2], the relaxation processes in cholesteric liquid crystals with helical submolecular structure are known relatively little. Such structure may be observed both in pure cholesterics (cholesteryl esters) and in induced one, where helical structure arises due to little amount of chiral impurity both mesogenic (any pure cholesteric) or nonmesogenic (optically active substances).

The investigations of spin-lattice interactions, which had been carried out so far concerned basically with pure cholesterics. For cholesteryl-oleyl-carbonate[3] it was concluded that relaxation is dominated by molecular self-diffusion in high frequency region and by order director fluctuations - at low frequencies. The investigations of spin relaxation in induced cholesterics performed so far[4,5] have only shown that relaxation mechanism remains the same as in the nematic matrix. In this connection it was interesting to investigate the relaxation mechanisms in induced cholesterics as well as study the influence of helicoid pitch that is concentration of chiral addition on the relaxation processes in liquid crystal.

EXPERIMENTAL RESULTS AND DISCUSSION

The temperature dependence of the proton spin-lattice relaxation time T_1 has been investigated in liquid crystal MBBA with small amount of chiral nonmesogenic 2-(4'-methoxybenzyliden)-p-mentan-3-one with concentrations c=0.2, 0.3 and 0.33% and in pure MBBA. Relaxation times T_1 were measured with standard pulse techniques using conventional 90°-τ-90° pulse sequence. The measurement was carried out at two values of external magnetic field for every sample : 5.4kG for all and 7.5, 10.6 and 12.2kG for c=0.2, 0.3 and 0.33% respectively. Such values of magnetic field were chosen due to possibility of the nematic-cholesteric phase transition in induced cholesterics. The critical field H_c, needed to unwind helicoid, is given by[6]

$$H_c = (\pi^2/p)(K_{22}/\Delta\chi)^{1/2},$$

where K_{22} is the Frank elastic constant, p is pitch and $\Delta\chi$ - the anisotropic part of the diamagnetic susceptibility.

The value of critical magnetic field was defined by the shape of free induction decay. In fields $H > H_c$

unwinding of helicoid takes place and homogeneous orientation arranges. In this case free induction decay has characteristic beatings which are caused by dipole splitting of NMR line. In fields $H < H_c$ helical twist averages dipole interaction and free induction decay has an exponential shape. The values of critical field defined in such way are: $H_c = 6.5$, 9.5 and 11 kG for c=0.2, 0.3 and 0.33% respectively.

Figure 1 represents the experimental results of the spin-lattice relaxation rate T_1^{-1} plotted against the reciprocal temperature for sample with impurity concentration c=0.2% in fields 7.6kG ($H > H_c$) and 5.3kG ($H < H_c$), that is in nematic and cholesteric phases.

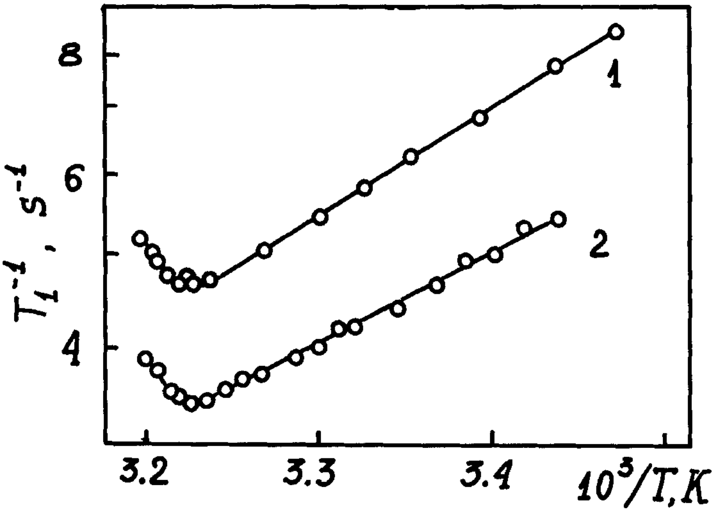

FIGURE 1. The temperature dependence of T_1^{-1} for c=0.2%. 1 - $H < H_c$, 2 - $H > H_c$

Both dependences have typical for the mechanism of translation diffusion thermally activated character excluding the region near the phase transition to isotropic phase. This is evidence of the preservation of the relaxation mechanism in induced cholesteric, inherent to nematic matrix. At the same time activation energy values, defined by the slope of the temperature dependence graphs, are somewhat different and are: E=4.4 and 4.95 kcal/mol for unwound and twisted samples respectively.

For other concentrations of chiral impurity the temperature dependences of T_1^{-1} are the same. It was found thus, that in strong external fields activation energy is independent on impurity concentration and equal to 4.4 kcal/mol. This coincides with the received value for pure MBBA. In week fields activation energies are somewhat higher and increase with increasing concentration: E=4.95, 5.5 and 5.7 kcal/mol for c=0.2, 0.3 and 0.33% respectively. This monotonous increase of E is square-law of the impurity concentration in the range, where it changes from 0 up to 0.33% and is well discribed by the expression:

$$E = (1.22 \cdot 10^4 c^2 + 4.4)\ \text{kcal/mol}.$$

Unfortunately, to observe this dependence for higher concentrations is not a success so far as for c=0.5 and 0.7% it is impossible to define unambiguously the activation energy. At these concentrations samples did not reacted upon the applied orienting field $H > H_c$ in spite of careful mixing and heat treatment. It is probably connected with the strong interaction between the impurity molecules, that results in the formation of impurity clusters in nematic matrix.

Regular increase of E with increasing of the impurity concentration is explained by arising of the elastic deformation fields in nematic which raise at $H < H_c$ barrier for translational motion of matrix molecules. The result received shows that the mechanism of induced twisting of the nematic is caused by the interaction of chiral additives via the matrix orientational order.

Figure 1 also shows that the temperature dependence of T_1^{-1} changes near the temperature of phase transition to isotropic liquid. This is caused by the rise of the pretransitional liquid-like fluctuations in the liquid crystal phase at these temperatures. In this case T_1^{-1} is defined by the superposition of two contributions: self-diffusion and pretransitional liquid-like molecular motion:

$$T_1^{-1} = T_{1D}^{-1} + T_{1L}^{-1} .$$

The values of T_{1L}^{-1} can be evaluated by extrapolating of the diffusion contribution into high temperature range and subtracting the extrapolation values of T_{1D}^{-1} from experimental T_1^{-1}. Calculated values of T_{1L}^{-1} both for the induced cholesteric and for unwound nematic turned out to be equal in the whole pretransitional range and exponentially increase with temperature increase. Thus, addition of the little amount of chiral impurity does not lead to visible change of dynamic properties of induced cholesteric in pretransitional region as compared with initial nematic. By this average orientational states of molecules probably must not change.

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