SOME NOVEL NMR INVESTIGATIONS IN THERMOTROPIC LIQUID CRYSTALS: METAL ION-LIGAND INTERACTIONS AND THE COEXISTENCE OF THE NEMATIC-SMECTIC PHASES

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ABSTRACT

Some salts such as alkali metal and silver per chlorates, cobalt chloride and their complexes with ligands such as acetone, acetonitrile, dimethylsulphoxide, pyridine, and N-methyl and N,N dimethyl formamides dissolve in thermotropic nematic liquid crystals providing information on the metal-ion ligand interactions. The ^{1}H, ^{2}H and the metal ion resonances have been used to derive the information.

An eutectic ternary mixture of bicyclohexylcarbonitriles and mixtures of nematic liquid crystals such as N-(p-ethoxy (or methoxy)benzylidene)-p-n-butylaniline with trans-4-pentyl-4(4-cyanophenyl)cyclohexanes or a mixture of three phenyl cyclohexanes and one biphenyl cyclohexane have been shown to exhibit "induced" smectic phases over certain ranges of composition and temperature.

I. INTRODUCTION

The use of NMR to study the metal ion - ligand interactions has so far been restricted to lyotropic liquid crystals and isotropic solutions. Though the information derived from the systems oriented in lyotropic media is extremely useful from the biological and chemical points of views, it is invariably on the hydrated species due to the presence of large amounts of water in the media (1). On the other hand, the results obtained from the isotropic solutions are based on the line shape and line position analyses and do not provide precise quantitative structural/geometrical information on the ions and their complexes with the ligands. The use of thermotropic liquid crystals for such purposes appears promising and some such results are presented in this communication. During the course of such investigations, it was observed that mixtures of certain nematic liquid crystals exhibit "induced" smectic phases over certain ranges of temperature and composition. Coexistence of the nematic and "induced" smectic phases has been observed by NMR and such results are also reported herein.

II. EXPERIMENTAL

The salts used were, lithium, sodium, potassium and silver perchlorates and cobalt chloride. The solvents employed were:

(1) N- (p- methoxy (or ethoxy)) benzylidene)-p-n-butylaniline (MBBA or EBBA) and their deuterated ($-d_2$) analogues with deuterium substituted at positions ortho to the -N= group in the butylaniline ring.
(2) Trans-4-pentyl-4(4-cyanophenyl) cyclohexane (S-1114)

(3) An eutectic mixture of propyl, pentyl and heptyl bicyclohexyl carbonitrile (ZLI-1167)
(4) A mixture of three phenylcyclohexanes and one biphenylcyclohexane (TNC - 1132)

The ligands were acetone, aceto-nitrile, dimethylsulphoxide, pyridine and N-methyl and N,N- dimethyl formamides and their deuterated analogues.

About 10 - 20 mole per cent solutions of the ligands were studied in the liquid crystals with and without the addition of the salts. About 2 - 5 weight per cent solutions of the solutes were also studied in ZLI-1167, in 20 : 80 weight ratios of TNC-1132 : EBBA and 16:84 weight ratios of $S_2$1114 : EBBA-d_2. The ^{1}H and the ^{2}H -NMR spectra were recorded on a WH-270 FT-NMR spectrometer. Nearly 100 and 500 Free Induction Decays (FID's) were accumulated for the proton and the deuterium spectra respectively and Fourier transformed with the help of the dedicated Aspect-2000 Computer. The metal ion spectra such as those of the ^{7}Li were recorded on MSL-300 spectrometer and nearly 3000 FID's with a delay of about 0.2s between the various scans were accumulated and Fourier transformed with the help of an Aspect-3000 computer. Typical ^{2}H spectra of pyridine-d_5 with and without $LiClO_4$ and ^{1}H spectra of acetonitrile in ZLI-1167 as a function of temperature are shown in figures 1 and 2.

III. RESULTS AND DISCUSSION

(a) Metal-ion ligand interactions:

As soon as the salt is added to the solution of the ligand in the liquid crystals, the sample shows the "coexistence" of two spectra, one corresponding to the oriented species and the other to the "isotropic" like form (marked * in figure 1). With time, a phase separation occurs in the sample resulting in slow changes of the spectra. The bottom of the sample shows droplets of an "isotropic" liquid and the spectra of the sample at the bottom correspond to those of the "isotropic" like ligand and those at the top to essentially "oriented" species. Similar behaviour was observed for the metal ion spectra. The ^{2}H NMR of the deuterated solvent shows the normal spectra of oriented nematic liquid crystal with the dipolar and the quadrupolar splittings 10 per cent larger on addition of the salt than without the salts. These results correspond to an increase of the degree of order of the liquid crystal by about 10 per cent on addition of the salt (saturated solution). The fact that the spectrum is like that of a normal nematic liquid crystal indicates the formation of a novel metal-ion liquid crystal.

In addition to the normal spectra of the solutes, the proton NMR spectra showed a doublet for the oriented water present in the solvent. It was found that the degree of order of H-H axis of water drastically reduces on addition of the salts. The value with salt ($LiClO_4$) reduces to 3 per cent of the value without the salt for acetonitrile dissolved in EBBA (2). This is interpreted in terms of the removal of water from the liquid crystal and the formation of a distorted tetrahedral complex with the ions. The studies provide a method for the investigation of the deformation of the molecular structure as a result of the complex formation.

(b) "Induced" smectic phases in mixtures of nematics:

The proton NMR spectra of 4.5 weight per cent of CH_3CN oriented in ZLI-1167 were studied in the

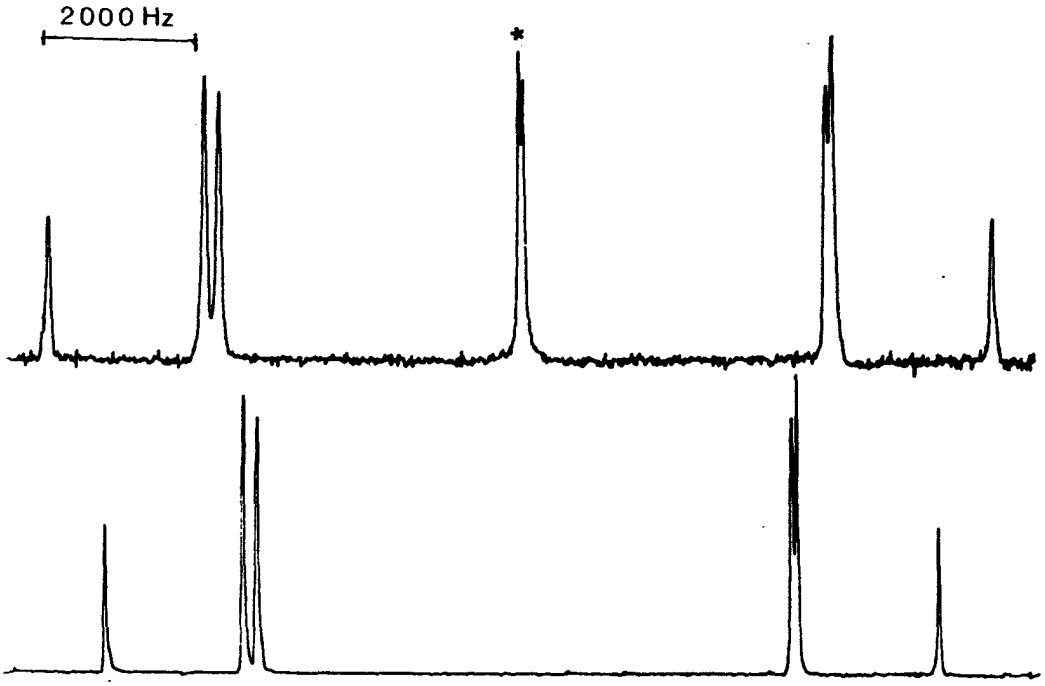

Fig. 1: ^{2}H - NMR spectra at 41.46 MHz of 10 mole per cent pyridine-d_5 oriented in the nematic phase of EBBA at 293 K. Upper trace is with $LiClO_4$ (saturated solution) immediately after the addition of the salt. The lines marked(*) arise from the "isotropic like" phase. The lower trace is without the salt.

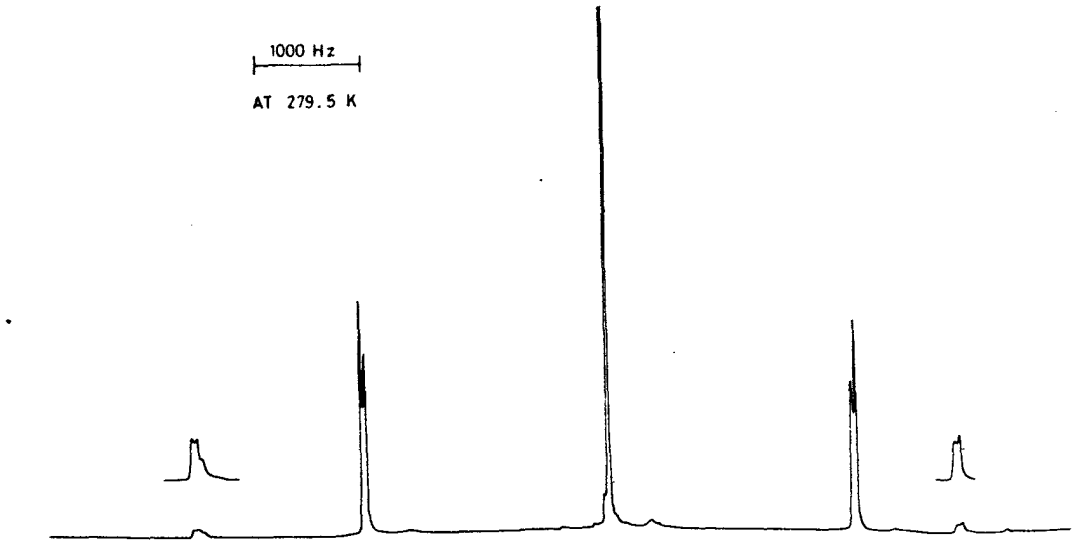

Fig. 2 : Proton NMR spectrum at 270 MHz of 4.5 weight per cent acetonitrile oriented in ZLI-1167 at 279.5 K.

entire temperature range from isotropic to solid phase (357 - 258 K). The spectrum in the nematic phase showed a triplet with the separation between the components of the triplet reducing with the increase of temperature as expected for a solution in the nematic phase. This is observed in the nematic phase just below the isotropic phase upto 280 K. At 279.5 K, a coexistence of three types of triplets was observed as shown in figure 2. The two triplets have nearly equal separations with their central lines overlapping. The third triplet has a slightly different chemical shift and the separation is considerably larger. Below 279 K, the triplet with larger separation becomes more prominent and the other two triplets overlap to provide a single triplet. At 269 K, only the triplet with larger separation is present. A study of the textures of the solution under a polarizing microscope as a function of temperature indicates the coexistence of the nematic and "induced" smectic phases at 279.5 K. A similar behaviour has been observed for CD_3CN oriented in a 20:80 weight of mixture of TNC-1132 and EBBA as well as in a 16:84 weight ratio of S-1114 and EBBA-d_2 (3). Polarizing microscope studies indicate the appearance of the induced smectic A as well as smectic B phases in these mixtures. Though mixtures of nematic liquid crystals with strongly polar end groups (such as cyano) and nonpolar compounds are known to show "induced" smectic A phase over certain ranges of composition and temperature by other techniques (4), the appearance of the induced smectic B phases does not seem to have been reported to the best of our knowledge. Further, from the NMR experiments, the relative intensities of the spectral lines in the various phases provide the ratios of the concentrations of the phases. In the 16:84 mixture of S-1114 : EBBA-d_2, about 45:55 ratio of nematic to "induced" smectic A phases has thus been estimated.

IV. CONCLUSIONS

The experiments reported herein provide the following information:

(1) Studies of the metal -ion ligand complexes can be undertaken in thermotropic liquid crystals.
(2) Deformation of the molecular structure as a result of complex formation can in principle be investigated. However, due to the low concentrations of the ions that can go into the solution and the rapid exchange between the complexed and the uncomplexed species, derivation of such an information precisely may present practical difficulties.
(3) Variation in the order parameter as well as the chemical shift may be used to identify the site of complexation.
(4) Ions may be used to remove the traces of the water present in liquid crystals.
(5) The formation of a novel metal ion - liquid crystal compound with liquid crystalline properties has been detected.
(6) Mixtures of certain nematics show the appearance of induced smectic phases over certain concentration and temperature ranges.

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