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Study of the liquid crystalline phases of benzopurpurin in water

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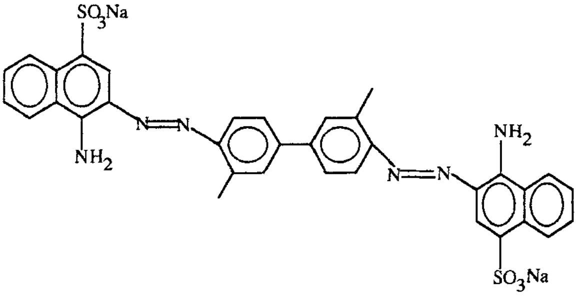
We report the NMR study of the liquid crystalline phases of aqueous solutions of the dye benzopurpurin (BP-4B). Upon changing dye concentration, the system exhibits a phase transition between two ordered phases at about 3·5 wt%. The structure of these phases was not determined but the evidence suggests that they consist of columns or helically twisted columns of stacked dye molecules which are randomly oriented, similar to nematic phases.

1. Introduction

Some ionic organic dyes and drugs produce liquid crystalline phases with water [1, 7]. These lyotropic systems are of special interest because the structure of the organic component differs remarkably from that which we find in conventional amphiphiles. In the latter these molecules consist of a polar group bound to a flexible aliphatic chain, while the dyes (or drugs) are sulphonic or carboxylic salts of aromatic or heterocyclic molecules. Folic acid [8] and some cyclic dinucleotides [9] may also belong to this class. The lyomesophases produced by these materials are often denoted as 'chromonic phases' and were studied through a variety of techniques. Very often two (or more) ordered phases were observed and are believed to consist of columns made of dimers or tetramers of the organic molecules. These columns can be randomly oriented (lyotropic nematics or 'N' phase), or arranged in an hexagonal pattern (hexagonal or 'M' phase).

In this communication we present deuterium and oxygen-17 NMR measurements in an aqueous solution of one particular dye: disodium-*o*-tolidinediazo-bis(1-naphthylamine-4-sulphonate), commercially named benzopurpurin (BP-4B). The chemical structure of the material is shown below:



A Spartan 2.1 Tripos force field computer simulation *of the acid* shows that the molecular shape is helical; each of the naphthyl rings is tilted by 27° with respect to

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the phenyl rings of the central biphenyl group, and the phenyl rings in the biphenyl group are tilted by 42° with respect to each other. The methyl, sulphonate and amine groups are in the *trans*-configuration and the overall length of the molecule is about 2·58 nm.

Thermodynamic and some NMR relaxation measurements of aqueous solutions of the Cs salt of BP-4B were reported recently by Bykov *et al.* [10]. These authors concluded, on the basis of thermodynamic and spin relaxation measurements, that two different ordered phases exist below and above about 3·5 wt %. Our NMR results support this conclusion. It may be of interest to note that we failed to observe ordered phases with another dye, Congo Red, in water, although its structure is very close to that of BP-4B. The only difference between Congo Red and BP-4B is the absence of two methyl groups on the biphenyl rings. The hydrophobic character of the methyl groups may play an important role in the clustering tendency of the dye molecules to dimers or tetramers [11] and consequently in the formation of ordered phases.

2. Experimental

Benzopurpurin, as the sodium salt, was obtained from Sigma. The material was separated from some additives through extraction with ethanol in a soxhlet apparatus for about 8 h. The remaining material was then dried under vacuum. IR spectra matched those which appear in the Aldrich Library of FT–IR spectra (1985, Vol. 2, p. 994). Proton NMR spectra of a dilute solution in D_2O corresponded well with the structure of BP-4B.

In aqueous solutions of BP-4B, especially at high concentrations, solid aggregates may precipitate from the solution after some time and thereby destroy the ordered phases. These aggregates should not be confused with the 'molecular aggregates' (dimers or tetramers), which according to Berg and Haxby [1] are responsible for the formation of liquid crystalline phases in similar systems. The samples should therefore be thoroughly shaken before the measurements. It should be noted that the ordered phases, in the NMR tubes, are stable for weeks and that aggregation occurred only after several months. This aggregation is much faster (within hours) in small X-ray capillaries or in thin flat cells which may indicate that this process is enhanced by the surface.

NMR spectra were taken on a Bruker WH400wb spectrometer operating at 61·4 MHz for deuterium. Temperature accuracy and precision are estimated at ± 0·5 K. Small angle X-ray scattering measurements were performed, using CuK_α radiation, with a compact Kratky camera having a temperature controlled sample holder (A. Paar Co.) and a linear position sensitive detector system (Raytech). The sample to detector distance was 26·4 cm.

3. Results and discussion

The deuterium NMR spectra of solutions of BP-4B in D_2O are well resolved doublets and the oxygen spectra quintuplets in the concentration and temperature range of the ordered phases. The observed quadrupolar splitting is proportional to elements of the quadrupole couplings and order parameter tensors [12]. The lowest concentration above which an ordered phase is observed, at room temperature, is 0·4 wt %. This is a remarkably low concentration for the formation of a liquid crystalline phase, noting that the molecular weight of the material is 724·7. The highest concentration which we studied was about 5 wt %, above which the solutions become too viscous. The spectral lines broaden with increasing concentration, which is attributed to the increased viscosity, but they *do not* show any notable variation in shape throughout the entire concentration and temperature ranges studied. The NMR spectra of neither ^{23}Na or ^{14}N show any quadrupolar splitting in the liquid crystalline range. This differs from observations on some other chromones where ^{23}Na spectra exhibited triplets due to the quadrupolar interaction [6]. Considering the small deuterium or oxygen quadrupolar splittings which were observed for D_2O (up to 70 Hz and 350 Hz, respectively) and the small concentration of the dye, it is likely that the sodium and nitrogen splittings are small and obscured by the linewidths. A narrow biphasic temperature range exists between the ordered and isotropic phases where a doublet (for deuterium), or a quintuplet (for oxygen), and a singlet are observed simultaneously.

Measurements of the quadrupolar splittings of deuterium as a function of the temperature for various dye concentrations are presented in figure 1. Similar behaviour is observed for oxygen. The concentration dependence of the splittings can be visualized better when the splittings are plotted as a function of the concentration, at a constant temperature. Such plots, for deuterium and oxygen, respectively, are presented in figures 2 and 3. The following conclusions can be drawn from an inspection of the data presented in these figures:

(i) The quadrupolar splittings are small as compared to those observed in most other aqueous lyotropic systems. This indicates a very small degree of ordering of the water molecules which may be attributed to the low ratio of dye to water molecules in our system. The splittings, as expected, decreases monotonously with the temperature but exhibit a more complex behaviour as a function of the concentration.

(ii) In general the splittings increase with the concentration of the dye. However, at about 3·5 wt % we observe a sharp drop of the quadrupolar splitting of D or ^{17}O. This abrupt change in the splitting was observed at all temperatures measured. We suggest that this drop, at about 3·5 wt % of BP-4B, suggests a transition between two differently ordered phases which occurs over a *very* narrow concentration range (a cusp in the phase diagram). This transition, between the two ordered phases, is also evident from the measurements of the transition temperatures, to biphasic and isotropic phases, as a function of the concentration, which are presented in figure 4. This figure is part of the phase diagram of BP-4B in water and ought to be compared to figure 3 of [10]. These results are in general agreement with those reported by Bykov *et al.* [10].

We have also performed accurate proton spin relaxation times (T_1 and T_2) measurements of H_2O in aqueous solutions of BP-4B at 297 K as a function of the concentration, between 2·5 and 4·2 wt %. T_1 was measured by the inversion recovery technique and T_2 by the CPMG technique. The error in the measurements of T_1 and T_2 is estimated to be about 2 per cent. The values of T_1 and T_2, as a function of the concentration at 295 K, are shown in figure 5. The results indicate clearly that there are *no* significant changes in the molecular dynamics of the water in this system upon the transition from one ordered phase to the other. We could not find any evidence to support the two-site (bound and free) model for water molecules which was suggested by Bykov *et al.* [10].

The major problem left is the structural identification of the phases. As evident from the results presented above, both phases seem to differ very slightly in their structure. We performed one further NMR experiment in an attempt to shed more light on this question: A small sample was placed vertically in the magnetic field (inside a 20 mm o.d. tube) and subsequently changed to an horizontal position. The deuterium spectrum

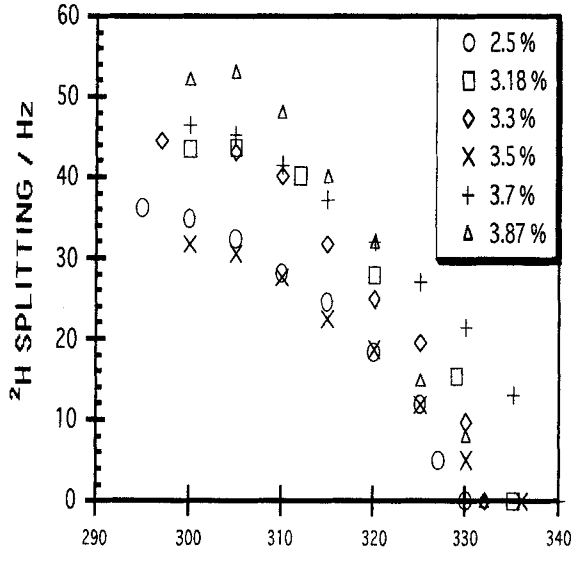

Figure 1. Deuterium quadrupolar splittings of BP-4B/D_2O solutions as a function of the temperature.

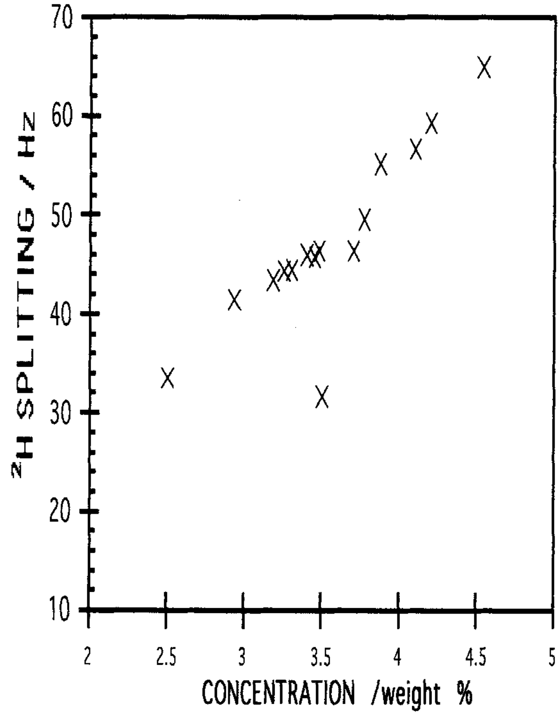

Figure 2. Deuterium quadrupolar splittings of BP-4B/D_2O solutions as a function of the concentration at 297 K.

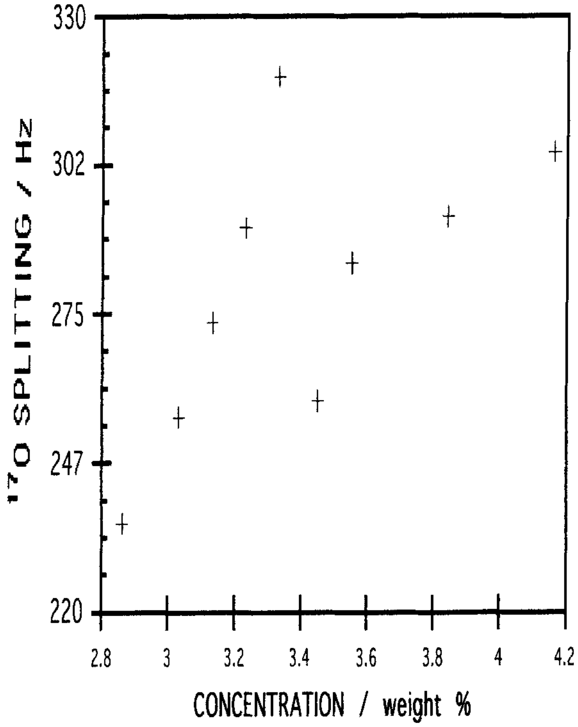

Figure 3. Oxygen-17 quadrupolar splittings of BP-4B/D_2O solutions as a function of the concentration at 297 K.

(a doublet), was measured in the vertical sample and re-measured after the sample was moved to an horizontal position. Within a few minutes, after the orientation of the sample was changed, the same doublet separation was observed. The experiment was performed with both the high and low concentration samples, with identical results. This result clearly shows that the reorientation of the director is relatively fast in the magnetic field. This behaviour is characteristic of nematic lyotropies.

We have also performed small angle X-ray measurements in sealed 0·1 mm capillaries and in thin flat cells [13]. The results, for both phases (above and below 3·5 wt %), show a single diffraction at 3·88 nm which varied little with the temperature. The quality of the spectra hardly improved upon prolonged exposure. We believe that the reason for this behaviour is the formation, within a few hours, of an isotropic solution and solid aggregates. We were thus unable to obtain the phase structure from these measurements.

Optical polarized microscopy of thin samples [13] did not provide definitive evidence about the structure although it confirmed that two different ordered phases exist below and above the transition concentration. Also, the textures observed in the low concentration phase bear some resemblance to those reported in cholesteric phases.

We are thus left to suggest the structures for the two phases without presenting conclusive evidence: We propose that both phases consist of columns made of molecular dimers or tetramers similarly to the structure suggested for most chromonic phases (cf. figure 7 in [4]). We believe that in the low concentration phase the columns have a helical twist which originates from the shape of the dye molecules. The random ordering of these columns must be similar to that which occurs in nematic phases.

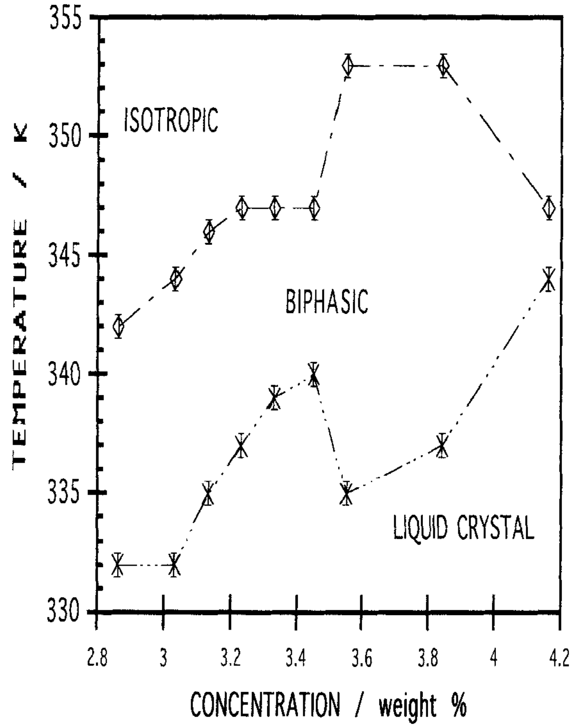

Figure 4. Transition temperatures to the biphasic and isotropic phases in BP-4B solutions as a function of the concentration.

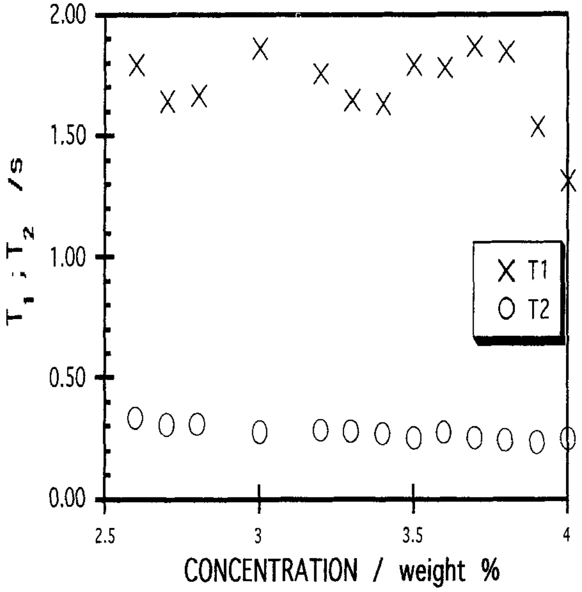

Figure 5. T_1 and T_2 values of BP-4B/H_2O solutions as a function of the concentration at 297 K.

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References

[1] Berg, R. A., and Haxby, B. A., 1970, *Molec. Crystals liq. Crystals*, **12,** 93.
[2] Atwood, T. K., and Lydon, J. E., 1984, *Molec. Crystals liq. Crystals*, **108,** 349.
[3] Atwood, T. K., and Lydon, J. E., 1986, *Molec. Crystals liq. Crystals Lett.*, **4,** 9.
[4] Atwood, T. K., Lydon, J. E., and Jones, F., 1986, *Liq. Crystals*, **1,** 499.
[5] Sadler, D. E., Shannon, M. D., Tollin, P., Young, D. W., Edmonson, M., and Rainsford, P., 1986, *Liq. Crystals*, **1,** 509.
[6] Perahia, D., Luz., Wachtel, E. J., and Zimmermann, H., 1987, *Liq. Crystals*, **2,** 473.
[7] Perahia, D., Wachtel, E. J., and Luz, Z., 1991, *Liq. Crystals*, **9,** 479.
[8] cf. Bonazzi, S., DeMorais, M. M., Gottarelli, G., Mariani, P., and Spada, G. P., 1993, *Angew. Chem. Int. Ed.*, **32,** 248, and references cited therein.
[9] Bonazzi, S., DeMorais, M. M., Garbesi, A., Gottarelli, G., Mariani, P., and Spada, G. P., 1991, *Liq. Crystals*, **4,** 495.
[10] Bykov, V. A., Sharimanov, Yu. G., Mrevlishvili, G. M., Mdzinarashvili, T. D., Metreveli, N. O., and Kakabadze, G. R., 1992, *Molec. Mater.* (*Molec. Crystals liq. Crystals. Science and Technology, Section C*), **1,** 73.
[11] Scheibe, G., Wörz, O., Haimerl, F., Seiffert, W., and Winkler, J., 1968, *J. Chim. phys.*, **65,** 146.
[12] Emsley, J. W., and Lindon, J. C., 1975, *NMR Spectroscopy Using Liquid Crystal Solvents* (Pergamon Press).
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