Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Radley, K. and Tracey, A. S.(1989) 'Ion binding of the organic counterion methyl phosphonate in amphiphilic micellar nematic liquid crystals', Liquid Crystals, 6: 1, 75 — 81

To link to this Article: DOI: 10.1080/02678298908027324

URL: http://dx.doi.org/10.1080/02678298908027324

LIQUID CRYSTALS, 1989, VOL. 6, NO. 1, 75-81

Ion binding of the organic counterion methyl phosphonate in amphiphilic micellar nematic liquid crystals

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(*Received 25 January 1989; accepted 11 March 1989*)

The ^{1}H N.M.R. of the methyl phosphonate ion has been used as a probe in the investigation of the reversal of the diamagnetic anisotropy in amphiphilic nematic liquid crystals. Three classes of aromatic counterion substitution have been investigated involving sodium and ceasium decylsulphate and the aromatic counterions trimethylanalinium and analinium. It was found that, in the absence of diamagnetic anisotropy considerations, in the trimethylanalinium/ceasium decylsulphate system the signs of the ^{1}H N.M.R. dipolar couplings of the methyl phosphonate ion were reversed. This is explained in terms of ion binding and various degrees of protonation of the methyl phosphonate species.

1. Introduction

It has been suggested that the proton N.M.R. dipolar splittings of the methylphosphonate ion could be used as a probe to investigate the reversal of the diamagnetic anisotropy in amphiphilic nematic liquid crystals [1]. Indeed in the case investigated the ^{1}H N.M.R. of methyl phosphonate was an excellent probe. When a theoretical model for ion binding was described based on the alkali metal multi-binding site model reversal of the sign of the orientational order parameter of the methyl phosphonate was predicted not to be possible and this was born out by experimental results. The high resolution proton N.M.R. spectrum of the methyl phosphonate ion will consist of a doublet of triplets. The 1 : 2 : 1 triplet line separations are equal to $3\tilde{D}_{11}$. The dipolar coupling of the intra methyl hydrogen is

$$\tilde{D}_{11} = \frac{h\gamma_1^2}{8\pi r_{11}^3} S_{c_3},$$

where S_{c_3} is the orientational order parameter for the P–C axis with respect to the magnetic field and r_{11} is the distance between the methyl protons. Each triplet peak is split into a doublet with a separation

$$\tilde{A} = J_{12} + 2\tilde{D}_{12}.$$

The direct coupling is

$$\tilde{D}_{12} = \frac{h\gamma_1\gamma_2}{8\pi r_{12}^3}(3\cos^2\beta - 1)S_{c_3}$$

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where r_{12} is the distance between the phosphorus and the methyl protons and β is the angle between the P–H axis and the molecular symmetry axis [2]. Thus

$$\frac{\tilde{D}_{12}}{\tilde{D}_{11}} = -3^{3/2}\sin^3\beta(2 - 3\sin^2\beta)\frac{\gamma_2}{\gamma_1}.$$

The right hand side of this equation is negative since β is approximately 25° and $\gamma_2/\gamma_1 > 0$; hence $\tilde{D}_{12}$ and $\tilde{D}_{11}$ must have different signs. The sign and magnitude of J_{12} are known to be $-15{\cdot}85$ Hz from a previous study [3]. If the ratio $\tilde{D}_{12}/\tilde{D}_{11}$ is measured in a series of samples, using the known J_{12} the absolute sign of the order parameter S_{c_3} is determined unambiguously. The sign of the ^{1}H N.M.R. dipolar couplings in the methyl phosphonate is reversed when the diamagnetic anisotropy is reversed. The sign of the dipolar couplings is also reversed when the micellar shape changes, i.e. from cylinder to disk and vice versa. The micellar shape change also involves a change in the diamagnetic anisotropy. In this paper it will be shown that ion binding can induce changes in the sign of the dipolar coupling of the methyl phosphonate. The sign reversal of the diamagnetic anisotropy can also be induced by chemical substitution of either the hydrocarbons for fluorocarbon [4] or the metal counterion for an aromatic ion [5]. If the aromatic counterions are phenyl substituents this process is easily monitored using proton N.M.R. The spectrum appears to be complex but for phenyl ions the A_2B_2C spectra is easily analysed using a computer program. The program used is part of the software of the Aspect 2000 microcomputer which controls the Bruker spectrometers. If the isotropic Js are known or determined in isotropic solution the sign of the dipolar couplings and hence the sign of the order parameter can be determined [6]. The need for a separate probe such as the methyl phosphonate ion arises when the proton N.M.R. spectrum of the aromatic counterion is too complex for analysis as with trimethylanalinium.

2. Experimental

Sodium decylsulphate was prepared by the sulphonation of decanol as described previously [7]. Caesium decylsulphate was prepared starting with sodium decylsulphate solution in methanol which was passed through an ion exchange column to produce the free acid and then neutralized with Cs_2CO_3, as described previously [7]. Trimethylanalinium decylsulphate is formed as the result of the neutralization of the acid formed by ion exchange of sodium decylsulphate and trimethylanalinium hydroxide formed by the ion exchange of trimethylanalinium bromide using silver oxide in methanol solution. After evaporating to dryness the trimethyl-analinium decylsulphate was recrystallized twice from ethanol/petroleum ether and dried in a vacuum desicator. Analinium decylsulphate was formed as the result of the double decomposition of sodium decylsulphate and analinium chloride in chloroform. After filtering and evaporating to dryness the analinium decylsulphate was recrystallized twice from chloroform and petroleum ether and dried in a vacuum desicator [8].

Double distilled D_2O and H_2O and specially purified decanol were used throughout the investigation. Most of the N.M.R. spectra were obtained using a Brucker WP100 N.M.R. spectrometer. The ^{31}P N.M.R. spectra were obtained with a Bruker WP400 N.M.R. spectrometer. N.M.R. spectra was obtained at 22°C unless otherwise specified. Samples were weighed into a test tube with a constriction in the middle and heat sealed. The compositions are illustrated in tables 1, 2 and 3. The samples were homogeneously mixed by repeated centrifuging and heating. The test tubes were broken at the constriction and the samples of amphiphilic nematic liquid crystal were transferred to 5 mm N.M.R. tubes, which were heat sealed afterwards. The micellar structures were determined by inference from polarising micrographs. Planar textures imply cylinder shaped micelles while the pseudo-isotropic texture indicates that the sample has a disk shaped micellar structure. When samples are dried out, concentration gradients are formed around the edges. The two dimensionally orientated phase, with known structure, neighbouring the nematic phase, indicates the nematic micellar structure i.e. middlesoap/cylinder and lamellar/discs [9].

The sign of the diamagnetic anisotropy was determined by observing the evolution of the ^{2}D N.M.R. spectrum of D_2O with time. When the sample is first placed in the magnetic field the ^{2}D N.M.R. spectrum is a powder pattern; the line shapes then evolve with time. If a nematic phase has positive diamagnetic anisotropy a sharp doublet evolves from the wings whereas with negative diamagnetic anisotropy a sharp doublet evolves from the centre.

3. Results and discussion

The micellar shape in all of the samples of the amphiphilic nematic liquid crystals used in this investigation was shown to be disc shaped by using polarising microscopy. There were three counterion substitution classes in the investigation, i.e. (i) analinium/sodium decylsulphate; (ii) trimethylanalinium/sodium decylsulphate; (iii) trimethylanalinium/ceasium decylsulphate. Cases (i) and (ii) produced results which were expected. The sign of the dipolar splittings in the methyl phosphonate ion was reversed at given concentrations of the aromatic counterion substitution. In case (ii) where the aromatic counterion was trimethylanalinium the concentration at which the diamagnetism was reversed was much higher than in case (i) where the aromatic counterion was analinium. This is probably due to the relative solubility of the aromatic counterion in the interstitial aqueous region. The trimethylanalinium ion is much more soluble in D_2O than the analinium ion. The less soluble analinium ion is more easily incorporated in the oriented micelle surface. The order parameters determined from the proton N.M.R., for the aromatic counterions will be published elsewhere. These orientational order parameters showed abrupt changes at the same concentration as the methyl phosphonate dipolar splittings. The methyl phosphonate dipolar splittings changed by a factor of $-1/2$; this is illustrated in figure 1. In both of these cases (i) and (ii) the ratio $\tilde{D}_{12}/\tilde{D}_{11}$ remained constant within experimental error across this transition.

The time evolution of the ^{2}D N.M.R. spectrum was used to determine the sign of the diamagnetic anisotropy in these samples. At the low aromatic counterion concentrations before the transition, the samples were found to have a negative diamagnetic anisotropy while at higher concentrations of the aromatic counterion above the transition the diamagnetic anisotropy was found to be positive. The diamagnetic anisotropy for hydrocarbon chains is negative, whereas for aromatic rings it is positive [10]. If the diamagnetism of the constituent molecules dominates the diamagnetic properties of the amphiphilic nematic liquid crystal and not the inherent shape diamagnetism of the micelle, increasing amounts of aromatic counterions will make the negative diamagnetic anisotropy increase and become positive, as observed. The stationary ^{2}D N.M.R. spectrum is also interesting. As well as the D_2O doublet the ^{2}D N.M.R. spectrum of the ammonium ion appears as two sets of triplets. In both D_2O and ND_4^+ the ^{2}D N.M.R. quadrupolar splittings decreased quite rapidly

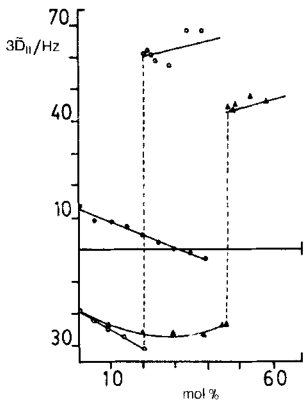

Figure 1. The dipolar coupling $3\tilde{D}_{11}$ for the methyl phosphonate ion measured using proton N.M.R., as a function of the % mole fraction of the substituted aromatic counterion. The data given in this figure and in figure 2 are contained in four tables comprising six pages which have been deposited with the British Library Lending Division; copies of this Supplementary Publication may be obtained from the British Library by using the procedure described at the end of this issue and quoting the number SUP 16513. Data cases (i) ○; (ii) ▲; and (iii) ●.

with the aromatic counterion substitution and increased by a factor of two when the diamagnetism changed from negative to positive. When the methyl phosphonate ion dipolar splittings in cases (i) and (ii) were subjected to a root mean square fit to find J_{PH}, it was found to be $-16{\cdot}68$ Hz compared to $-15{\cdot}85$ Hz in a previous study [3]. Two samples of the isotropic phase with similar compositions to the nematic phase samples were made and their ^{31}P N.M.R. spectra and pH were determined. In the first sample with composition 187 mg trimethylanalinium decyl sulphate, 187 mg sodium decylsulphate, 40 mg decanol and 600 mg D_2O the pH was found to be 2·38. The second sample with composition 132 mg analinium decylsulphate, 162 mg sodium decylsulphate and 500 mg D_2O the pH was found to be 2·11. The J_{PH} determined using ^{31}P N.M.R. was found to be $-16{\cdot}80$ Hz in each sample. It can be concluded therefore that the differences in J_{pH} in this and the previous study is not due to J anisotropy. Both of these systems used sodium decylsulphate and a D_2O solution of $(NH_4)_2SO_4$ which might be expected to produce a low pH in the samples.

The N.M.R. results of the aromatic substitution case (iii) trimethyl analinium/ceasium decylsulphate are different in many respects. The methyl phosphonate dipolar splittings still change sign at a specific aromatic counterion substitution. The corresponding ratios $\tilde{D}_{12}/\tilde{D}_{11}$ were still constant ($0{\cdot}26 \pm 0{\cdot}02$) within experimental error despite a sign change in the individual dipolar couplings. When the sign of the methyl phosphate dipolar splittings changed the corresponding magnitudes did not change abruptly as in cases (i) and (ii). The magnitudes of the ^{2}D N.M.R. quadrupolar splittings in D_2O did not change abruptly in corresponding samples. The sign of the diamagnetic anisotropy for the amphiphilic nematic liquid crystal before and after the change were both found to be negative. This is illustrated in figure 2 where $3\tilde{D}_{11}$ is plotted against $2\tilde{D}_{12} + J$. A similar change in sign for the methyl phosphonate was also observed during a temperature study of the 30 per cent class (i) sample. These results are incorporated in figure 2. When the data in figure 2 was subjected to an RMS fit to calculate J_{PH}, it was found to be $-16{\cdot}32$ Hz. An isotropic sample was made up with similar composition 149 mg trimethyl analinium decylsulphate, 222 mg

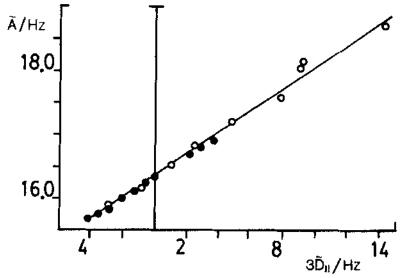

Figure 2. The dipolar coupling $3\tilde{D}_{11}$ for the methyl phosphonate ion, as a function of the dipolar coupling of the methyl phosphonate ion $\tilde{A} = 2\tilde{D}_{12} + J_{12}$. Data cases (iii) ○; and temperature data 30 per cent sample ●.

caesium decylsulphate, 40 mg decanol and 600 mg D_2O. The J_{PH} was determined using ^{31}P N.M.R. to be $-16{\cdot}32$ Hz. This is the same as for the nematic samples within experimental error. This is therefore the second case of a variable J_{PH} and it is not in anyway connected with J anisotropy. The pH of this solution was determined to be 6·71, i.e. slightly less than neutral. The pH of a nematic sample solution with composition of 500 mg caesium decylsulphate, 50 mg decanol and 600 mg D_2O was found to be 7·28, slightly greater than neutral. The major difference in the N.M.R. spectra of case (iii) to cases (i) and (ii) is that the dipolar couplings of methyl phosphonate have opposite signs for 0 per cent substitution of aromatic counterion. The difference in the counterion binding must be due to changes in pH. Variable J couplings in N.M.R. are very rare. Two cases come to mind, BF_4^- [11] and methylated tin [12] complexes, where the J variation is thought to be due to solvent induced changes in coordination. CH_3Sn^{3+} and $(CH_3)_2Sn^{2+}$ in micellar solution show exceptional high J couplings [13, 14]. These differences in the J_{PH} of the methyl phosphonate ion must be due to small structural changes induced by pH changes.

In alkali metal ions the nucleus is surrounded by a hydration sheath. Each hydration molecule sets up an electric field gradient but they have high symmetry coordination on average and so the electrical field gradient is zero. Hence the heavy nuclear N.M.R. quadrupolar splitting would be expected to be zero. When the small ion is embedded in the surface of a micelle the interaction between the surface and the ion cause a small distortion in the water sheath and hence the electric field gradient is non-zero resulting in an N.M.R. quadrupolar splitting [15]. It has been suggested that in a mixed detergent system at least, the interactions at two sites were needed to describe the quadrupolar splitting as a function of concentration. Site I involves multi-coordination bridges of the ion between several first amphiphilic species described by coordination numbers. In this case the quadrupolar splitting is negative. Site II is formed when site I starts to break up after the second amphiphile is substituted for the first amphiphile. Site II has mono coordination numbers and the quadrupolar splitting is positive [16]. There could be a third site where the second amphiphile is nearly 100 per cent substituted. With small asymmetric organic ions such as methyl phosphonate the picture is completely different. It was suggested previously that if the two site model was applied to the methyl phosphonate ion the dipolar coupling would not change sign. This was observed experimentally in two mixed detergent systems [1].

This two site model will not adequately describe the present experimental results. The mechanism by which N.M.R. parameters are determined for the highly symmetrical alkali metals and the asymmetric organic ion are very different. The N.M.R.

quadrupolar splittings from the alkali metals result from the distortion of the electric field gradient surrounding the ion nucleus. This is a direct measure of the interaction of the ion with the micellar surface. The dipolar splitting of small asymmetric ions, such as methyl phosphonate, is a function of the ion structure and order and environmental distortion is unimportant. Methyl phosphoric acid is a weak dibasic acid in aqueous solution. As a function of pH it will form at least three different species of various degrees of protonation. In the previous study [3] when $J = -15{\cdot}85$ Hz there is no real indication of the pH value but the solution was probably alkaline with the pH equal to approximately 10. When $J = -16{\cdot}80$ Hz as for cases (i) and (ii), where the measured pH was approximately 2, i.e. very acid when the methyl phosphonate species would probably be $CH_3PO_3H_2$. When $J = -16{\cdot}32$ Hz as for case (iii) where the measured pH was approximately 7 the methyl phosphonate species would be the intermediate monoprotonated $CH_3PO_3H^-$ species. The acid diprotonated species $CH_3PO_3H_2$ present at low pH can probably form a bridge between two amphiphiles via hydrogen bonding. In this case the C–P axis of the $CH_3PO_3H_2$ molecule is parallel to the normal of the micellar surface. The orientational order of this C–P axis has the same sign as the degree of order of the disc shaped micellar axis. At higher pHs at about neutral the dominant methyl phosphonate species will be $CH_3PO_3H^-$, therefore only one hydrogen bridge is possible with one amphiphile. The C–P axis of the $CH_3PO_3H^-$ is no longer parallel to the micellar surface normal but precesses around the normal. The angle of precession is greater than the magic angle so the order parameter of the C–P axis has a different sign than the order parameter of the micellar surface normal. This is what was found experimentally when the neutral class (iii) phases produced methyl phosphonate dipolar couplings with the opposite sign to those in the acidic class (i) and (ii). When trimethylanalinium is substituted in class (iii) the pH is lowered by one unit and the sign of the methyl phosphonate dipolar coupling is eventually reversed. This complication prohibited the investigation of the diamagnetic anisotropy sign reversal using methyl phosphonate as a probe.

4. Conclusion

The interaction of organic ions and alkali metal ions at micellar surfaces are quite different. Different N.M.R. methods are required for each type of interactions. The alkali metal ion-amphiphile interactions can be monitored using N.M.R. quadrupolar splitting. The lowering of the symmetry of the electric field gradients at the nucleus gives rise to quadrupolar splittings via the ion-amphiphile interaction distortion of the hydration sheath. The ^{1}H N.M.R. dipolar splitting of the low symmetry organic ions are determined from structural and orientational order considerations. The simple multi-site model used to describe alkali metal ion binding is not suitable for organic ions such as the methyl phosphonate ion and comparisons should not be made. The interactions can be much more complex and for methyl phosphonate the reversal in the sign of the ^{1}H N.M.R. dipolar coupling is explained in terms of the protonation of the methyl phosphate species as a function of pH.

Thanks are gratefully extended to the Natural Science and Engineering Research Council of Canada for its financial support of this work through operating grants to A.S.T. Thanks to Mrs. Lynn Cook for the word processing of the manuscript.

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