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Proton NMR ion binding studies of ethanol and the ethylammonium ion partially oriented in an amphiphilic nematic liquid crystal

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The proton NMR spectra of ethanol and the ethylammonium ion have been investigated in an amphiphilic nematic liquid crystal mixed detergent system KDDG/TDTMABr. The binding of ethanol was found to be as equally strong with the cationic as with the anionic detergent. The ion binding for the ethylammonium ion was found to be the weakest with the cationic detergent. A multi-site ion binding model is suggested for the ethylammonium ion where the sites originate from orientational order rather than multicoordination. pH measurements eliminated the multi-species model and the continuous site model is eliminated because the three dipolar couplings of the ethyl ammonium ion do not move through zero simultaneously.

1. Introduction

Amphiphilic nematic liquid crystals are ideal orientation matrices for NMR ion binding studies of both alkali metal ions and organic ammonium and acid ions embedded in the electrical double layer of a micelle surface [1, 2]. They align homogenously in the magnetic field of NMR spectrometers and give rise to high resolution spectra. In the NMR of alkali metal ions ($I>\frac{1}{2}$) quadrupolar splittings are allowed because the ion-amphiphile interactions distort the hydration sheath, which lowers the symmetry of the electrical field gradient at the nucleus [3]. The ^{1}H NMR ($I=\frac{1}{2}$) dipolar splittings of the low symmetry organic ions are determined by structural and orientational ordering considerations [4]. The ^{1}H NMR spectra of small solute molecules or ions with five protons such as the ethyl groups in the ethyl ammonium ion or ethanol molecule are usually first order and hence simple to analyse to produce dipolar splittings which are easily reduced to dipolar coupling constants. If the nuclei i and j belong to the same rigid part of the molecule and the director of the nematic phase is parallel to the magnetic field, the dipolar coupling constant $\tilde{D}_{ij}$ is given by

$$\tilde{D}_{ij}=\frac{-h\gamma_i\gamma_j}{4\pi^2 r_{ij}^3}S_{ij},$$

where S_{ij} is the degree of orientation of the axis passing through i and j, assuming the distance between nuclei i and j r_{ij} is constant (i.e. neglecting the influence of the vibrational motion) and γ is the magnetogyric ratio [5]. Precise information is obtained from such studies, concerning the sign and magnitude of the direct (dipolar) coupling constants and the degree of orientational order (S_{zz}), if the sign and magnitude of the indirect coupling constants J are known.

Micelle structure combined with the sign of the diamagnetism and to a lesser extent the ion binding influence the sign of the order parameters of small molecules and ions embedded in the electrical double layer of a micelle surface [6]. It has been found in a mixed detergent system, where the positively charged head group is replaced by a negatively charged head group and vice versa, the quadrupolar splittings and sometimes the dipolar couplings appear to move through zero and to change sign [4, 7]. The quadrupolar splittings have been adequately described using a multi-site model for ion binding, but this model is inadequate for dipolar couplings [6–8]. Preliminary work with the methyl phosphonate ion would suggest a multi-species model would be better where the dipolar coupling seems to be pH dependent [9]. The proton NMR spectra of 2-aminoethanol has been studied previously in a mixed detergent amphiphilic nematic liquid crystal system. [10]. The resulting dipole coupling constants were interpreted in terms of a solute bridge between two detergent head groups in the anionic detergent samples giving way to a single –OH group interacting with one detergent head group in the cationic detergent samples. It would now be interesting to study the interaction of the –OH and $-NH_2$ groups with the micellar surface separately using the ethylammonium ion and ethanol. There has been an earlier proton NMR study of ethanol in an amphiphilic nematic liquid crystal by Flautt and Lawson in 1969 [1].

2. Experimental

The samples were prepared from the mixed detergent, potassium-dodecanoylglycinate (KDDG)/tetradecyltrimethylammonium bromide (TDTABr) system. The detergents were prepared as described previously [4, 5, 7, 8, 10]. The mixed detergent system has been developed over the years. In each sample the electrolyte has a constant ratio with respect to the total number of moles of the anionic and cationic detergents, and the decanol concentration is varied until a nematic phase sample is obtained [4, 7]. In the systems previously investigated, the decanol concentration does not have a pronounced effect on the quadrupolar splittings from the inorganic ion or of the deuterium atoms on the hydrocarbon chains, in the absence of a micellar shape change or a reversal in the diamagnetic anisotropy [7, 8]. The sample compositions are presented in tables 1 and 2. Double distilled D_2O and specially purified *n*-decanol were used throughout. The samples were homogeneously mixed by repeated heating and centrifuging. The samples were placed in 5 mm NMR tubes and these tubes were heat sealed.

The micellar shape of the phase in each sample was determined as previously described. Small quantities were sucked into a CAM LAB microslide. Samples with disc-shaped micelles give rise to polar micrographs with pseudo-isotropic textures, while samples with cylindrical shaped micelles give polar micrographs with planar textures [11]. The time evolved ^2D NMR spectra of D_2O was used to determine the diamagnetic anisotropy of the phase in each sample. Initially when placed in the magnetic field the ^2D NMR spectra was a powder pattern. As the lineshape evolves with time, the nematic phase sample has positive diamagnetic anisotropy if a sharp doublet evolves from the wings whereas with negative diamagnetic anisotropy a sharp doublet evolves from the centre [12].

NMR spectra were obtained at 22°C using Bruker 400 MHz and 270 MHz spectrometers. In the superconducting magnets of the Bruker high field NMR spectrometers the sample spinning axis corresponds to the magnetic field direction. In such NMR spectrometers nematic phase samples can be routinely spun without regard to the sign of the diamagnetic anisotropy to produce high resolution spectra. pH was measured on the samples in table 2 and recorded using a Russell combination pH electrode.

The present studies were initiated using the samples listed in table 1. The NMR studies were to include the ion binding of alkali metal ions, hence the exotic cocktail of ions. Later this was abandoned in favour of a proton NMR study of the organic solutes. The 400 MHz proton NMR was of inferior quality particularly in the ethylammonium ion where at the transition the small splittings were not resolved. The 270 MHz proton NMR spectra were run on the second set of samples described in table 2. The auto shimming allowed the small couplings to be resolved turning a minor study into a major study. A part of the data in the first study is illustrated in table 1 in order to compliment the data of the second study in table 2.

3. Results and discussion

The isotropic spectra of the ethyl groups in ethanol and the ethylammonium ion in water was first order, a chemically shifted quartet and triplet. The lower field quartet is due to the methylene (2) group and the higher field triplet is due to the methyl (1) group. The peak separation is due to the intermolecular indirect J coupling between the methylene and methyl protons of the ethyl group. J was measured as 7·0 Hz for ethanol and 7·5 Hz for the ethylammonium ion. The anisotropic spectra of these ethyl groups was still first order but now included intra- and inter-molecular dipolar couplings. The methyl protons were now a triplet of triplets and the methylene protons were now a doublet of quartets arising from the intra-molecular dipolar splitting $3\tilde{D}_{11}$ and $3\tilde{D}_{22}$, respectively. The new intermolecular coupling also includes a dipolar splitting where the line separation is now $2\tilde{D}_{12}+J$.

The micellar structure in all of the samples in the investigation, using polar microscopy was inferred to be disc-shaped. The diamagnetic anisotropy of the phases in all of the samples was found to be always negative, using time evolved ^{2}D NMR.

There were two sets of amphiphilic nematic liquid crystal samples in this investigation. The first set was restricted to five samples which were made up from D_2O in which ethanol and many inorganic salts had been dissolved, see table 1. In this set the NMR spectra was taken using a 400 MHz spectrometer. This included the recording of the ^{2}D NMR of D_2O. In these ^{2}D spectra of D_2O the quadrupolar splittings moved toward zero when the samples began to contain more cationic than anionic detergent. The behaviour of the ^{2}D NMR is similar to that which has been observed previously in a mixed cationic–anionic detergent amphiphilic nematic liquid crystal system [7, 8]. The proton coupling for the $-CH_2-$ in the glycinate headgroup was also recorded. Its average splitting was found to be $3{\cdot}20 \pm 0{\cdot}2$ kHz, which was constant within the experimental error. This indicates the change in the micelle surface charge, induced by interchanging the anionic detergent for the cationic detergent and vice versa, does not involve a change in the orientation of the micelle surface.

There are two main approaches to the investigation of ion binding using NMR spectroscopy. First quadrupolar distortions, where the quadrupolar splittings [3] result directly from the amphiphile–ion interactions. The interaction creates an asymmetric hydration sheath, which distorts the electrical field gradient at the quadrupolar nucleus. Secondly dipolar-orientation, where the NMR dipolar splittings do not result directly from the amphiphile–ion interactions but from structure and orientational order. Many small organic solute molecules and ions interact with the micellar surface via hydrogen bonding. The presence of these protons can be controlled by pH [9].

If the organic ion has two or less planes of symmetry S_{xx}/S_{zz} measurements give information concerning the spatial distribution of the ion. The sign of S_{zz}, the

Table 1. Mesophase compositions and the ¹H NMR parameters for the solute ethanol in the mixed detergent system KDDG/TDTABr.

Composition				NMR parameters				
Mol% KDDG	KDDG†	TDTABr†	Decanol†	ν_{D-2}‡ D_2O Hz	Detergent§ head group $-CH_2-$ kHz	Intramolecular dipolar splitting $3\tilde{D}_{11}$ Hz	$3\tilde{D}_{22}$ Hz	Intergroup dipolar splitting $(2\tilde{D}_{12}+J)$/Hz
10	29	302	35	13·6	3·02	1·89	314·3	26·4
30	89	235	25	50·1	3·28	3·7	315·8	27·0
50	148	134	15	116·4	3·24	4·5	283·1	22·6
70	207	101	28	199·5	3·46	11·6	270·4	17·0
90	266	34	65	274·8	3·01	8·4	254·5	12·3

† Concentration of decanol in mg together with molar mg quantities of KDDG and TDTABr made up with 700 mg of D_2O containing 0·5 per cent LiCl, 0·5 per cent Na_2CO_3, 0·5 per cent K_2CO_3, 0·5 per cent $RbNO_3$, 0·5 per cent Cs_2CO_3, 0·5 per cent $C_2H_5NH_3Cl$, 0·1 per cent CH_3NH_3Cl, 0·15 per cent ethanol by weight.

‡ Quadrupolar splitting.

§ Dipolar splitting.

Table 2. Mesophase compositions, pH measurements and the ^1H NMR for the ethylammonium ion in the mixed detergent system KDDG/TDTABr.

Composition				Proton NMR parameters			
				Intramolecular dipolar splitting		Intergroup dipolar splitting	
Mol% TDTABr	KDDG†	TDTABr†	Decanol†	CH_3– $3\tilde{D}_{11}$/Hz	–CH_2– $3\tilde{D}_{22}$/Hz	$(2\tilde{D}_{12}+J)$/Hz	pH
0	295	0	70	—	—	—	7·6
10	266	34	60	+86·5	+344·3	+10·6	7·7
20	236	67	40	+56·0	+214·2	+9·6	7·6
30	207	101	25	+46·6	+165·5	+9·4	7·4
40	177	134	16	+28·5	+88·3	+9·0	7·5
50	148	168	15	+20·0	+49·7	+8·8	7·5
60	118	202	20	+11·5	+20·8	+8·5	7·5
70	89	235	25	+7·6	+5·5	+8·2	7·2
80	59	269	30	+1·8	−4·6	+7·5	6·9
90	29	302	35	−1·1	−7·3	+6·8	6·9
100	0	336	50	−5·5	−12·1	+6·1	6·5

† Concentration of decanol in mg together with molar mg quantities of KDDG and TDTABr made up with 700 mg D_2O containing 2 per cent ethylammonium chloride by weight.

orientational order parameter, determines the orthogonality of the major molecular axis after allowances have been made for micellar structure and diamagnetic anisotropy. The S_{xx}/S_{zz} biaxiality [13] of the orientational order has been investigated in aromatic ions and was found to be dependent on the micellar shape and hence the curvature of the micellar surface. These aromatic ions were primarily investigated because of their ability to induce changes in the diamagnetic anisotropy. The benzenesulphonate ion gave rise to smaller values of S_{zz} than the benzoate and anilinium ions but its biaxiality was stronger. It was concluded that the reduction of S_{zz} for benzenesulphonate was due to its greater solubility in the aqueous region while the biaxiality was dependent upon the interaction of individual ions with the micellar surface.

The ethylammonium ion and the ethanol molecule have only one plane of symmetry and no axis of symmetry i.e. C_s group symmetry. The lack of axial symmetry makes the biaxiality S_{xx}/S_{zz} difficult if not impossible to determine. The dipole coupling $\tilde{D}_{22}$ would seem to be proportional to the orientation of the C–N (C–O) bond and should give some insight into the $-\overset{+}{N}H_3$ (–OH) group–amphiphile interaction. The methyl group of the ethyl group is unanchored, so the motion of the methyl group is less restricted than the motion of the methylene group, and large deviations in both $\tilde{D}_{11}$ and $\tilde{D}_{12}$ would be expected. Any restrictions in the motion of the ethyl group, other than the anchoring at the micellar surface of the $-\overset{+}{N}H_3$ (–OH) group would be imposed by the environment in the neighbourhood of the ethyl group. The sign of the dipolar couplings and hence the sign of the order parameters gives information concerning the orthogonality of the ion orientation. In the present study only the ethylammonium ion $\tilde{D}_{12}$ sign could be determined with any certainty. The ethylammonium ion $\tilde{D}_{12}$ changes sign so it would be reasonable for the corresponding $\tilde{D}_{11}$ and $\tilde{D}_{22}$ to change sign as well. The assignment of the absolute sign for these $\tilde{D}_{11}$ and $\tilde{D}_{22}$ signs was mainly for convenience during the construction of the figure.

In the present proton NMR results for ethanol in a mixed detergent amphiphilic nematic, $\tilde{D}_{22}$ shows that the –OH group of the ethanol interacts with the surface of the micelle as strongly in the sample with the anionic detergent as in the sample with the cationic detergent, while the –OH group in the ethanol appears to be anchored in the micellar surface the wide deviation in the $3\tilde{D}_{22}/3\tilde{D}_{11}$ ratios (30–150) suggests that the ethyl group has a fairly unrestricted sphere of movement. The ethyl segment of the ethanol could be more than likely situated outside the micelle rather than in the restricted sphere of movement of the micellar interior.

Ion binding has been successfully described for alkali metal ion NMR quadrupolar splittings in a mixed detergent amphiphilic nematic liquid crystal system using a multisite model [7]. The unexpected non-zero quadrupolar splitting is derived from the asymmetry of the water sheath, which produces an electric field gradient at the ion nucleus as a result of the ion–amphiphile interaction, where the ions are embedded in the electrical double layer at the micellar surface [3]. At least two sites are needed to explain the movement of the quadrupolar splittings through zero when the anionic detergent is replaced by the cationic detergent. Site I involves multicoordination bridges formed by the ion between several first amphiphile 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 no coordination number and the quadrupolar splitting is positive [7, 8]. With small ions such as methyl phosphate $CH_3PO_3^{2-}$, where molecular distortion is less important and orientational order produces NMR dipolar couplings, if the two site model was applied in such cases the dipolar couplings would not change sign [6]. This was observed experimentally with the methyl phosphonate ion in two mixed detergent systems. Sign changes in the NMR parameters for the methyl phosphonate ion were observed when pH control was imposed by the chemical composition of the amphiphilic nematic mixtures [9]. These observations might be better described by a multispecies model where a greater protonated species is in equilibrium with a less protonated species.

The NMR $\tilde{D}_{22}$ dipolar coupling of the ethylammonium ion in the amphiphilic nematic mixed detergent system, showed a fairly strong interaction between the ethylammonium ion and the anionic detergent. When the cationic detergent replaced the anionic detergent, the values of $\tilde{D}_{22}$ became smaller and moved through zero. This suggests that the cationic detergent amphiphile–ion interaction is much weaker than the anionic detergent amphiphile–ion interaction for the ethylammonium ion. This seems to fit in with the previous NMR observations for 2-aminoethanol [10]. In the anionic detergent phases the $-NH_2$ and $-OH$ groups seemed to interact equally with the head groups of the detergents, probably forming a bridge between the two detergent head groups. When the anionic detergent is replaced by the cationic detergent there is a dramatic change in the order of the 2-aminoethanol. It could be that with increasing amounts of cationic detergent the solute bridge is broken down and only the $-OH$ group will now have a strong interaction with the cationic detergent head group, while the $-NH_2$ group has a much weaker interaction. In the present study the OH and NH_2 groups interactions with a micellar surface have been studied separately in the presence of ethyl segments. The conclusions concerning the OH and NH_2 groups interactions with the micellar surface are similar in the present study for ethanol and the ethylammonium ion as well as in the previous 2-aminoethanol study.

The pH of each of the second set of samples in the present study were measured and are listed in Table 2. The pH imposed by the chemistry of the system only changed by about 1 unit around seven i.e. neutral. It has been found previously that the signs of the NMR parameters of the methyl phosphonate ion were pH dependent in various amphiphilic nematic mixtures [9]. This would suggest a multi-species ion binding model for methyl phosphonate ion rather than a multi-site model. In the present study for the ethylammonium ion, the pH measurements, which were about 7, do not support the multi-species ion binding model. The pK of ethylamine is 10·97 which suggests that if the reversal in the signs of the NMR parameters, was due to the protonation of ethylamine, the pH in the amphiphilic nematic sample would have to move correspondingly between 10 and 12. The experimental values of pH were between 6·5 and 7·5 which rules out the multi-species ion binding model.

An alternative to the multi-site model for ion binding is the continuous site model. In this model there is a continuous change between two sites [14]. The first site is the oppositely charged amphiphile and ion situation, where the interaction is normal to the micellar surface (i.e. a positive quadrupolar splitting). The second site is the same charged amphiphile and ion situation, where the interaction is parallel to the micellar surface (i.e. a negative quadrupolar splitting). It is difficult with alkali metal ions NMR to eliminate this continuous site model because only one NMR parameter, the quadrupolar splitting is measured. With the ethylammonium ion in a mixed detergent system, if the continuous site model applied, it would be expected that the NMR dipolar couplings would pass through zero simultaneously. In the present study the dipolar splittings of the ethylammonium ion pass through zero at three different detergent ratios i.e. $3\tilde{D}_{11}$ between 10–20 per cent KDDG, $3\tilde{D}_{22}$ between 20–30 per cent and $2\tilde{D}_{12}$ close to 20 per cent KDDG (see the figure). The present results for zero

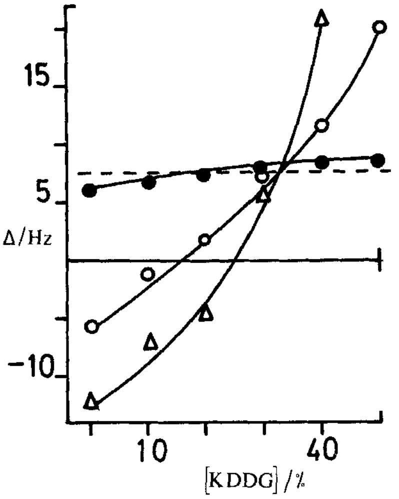

Figure. Plot of the dipolar splitting Δ from the proton NMR for the ethylammonium ion measured in an amphiphilic nematic where TDTABr is substituted for KDDG as a function of the molar % KDDG of the total detergent. (●) are the inter dipolar couplings $2\tilde{D}_{12}+J$ and (○) and (△) are the intra dipolar coupling $3\tilde{D}_{11}$ and $3D_{22}$, respectively; the broken line --- represents the J coupling.

dipolar couplings are similar to the findings with the dimethylammonium ion [4]. These favour a multi-site model where the sites are order and not coordination dependent. If more than one organic group as with the 2-aminoethanol is involved, multicoordination or bridging could be more important.

If the freedom of movement of the ethyl group is expressed by $\tilde{D}_{11}/\tilde{D}_{22}$ the results suggest that the ethyl group on the ethylammonium ion has a much smaller freedom of movement than the ethyl group in the ethanol solute. This suggests that the ethyl group of the ethylammonium ion is more likely to be situated inside the micelle of the anionic detergent rather than on the outside as for ethanol.

4. Conclusion

It has been found in the present study that ethanol interacts with the micellar surface with similar strength both in presence of a negative and a positive charged head group. In contrast the ethylammonium ion shows a two fold decrease in the degree of orientational order between the cationic detergent and the anionic detergent. An ion binding model is suggested based on multi-site binding, where the sites are determined more by order than multicoordination. Careful inspection of the various dipolar couplings, leads to the conclusion that ethanol is probably situated outside the micelle, while the ethylammonium ion is situated mainly inside the micelle. The ion binding sites for the ethylammonium ion could be determined by which side of the electric double layer the ethyl group is situated, that is in the restricted environment of the interior or in the unrestricted environment outside near the micellar surface.

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