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THE AQUEOUS LYOTROPIC ANALOGUES OF THERMOTROPIC NEMATICS AND CHOLESTERICS.

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The motional non-equivalence in a deuteriated $-CD_2-$ segment of a hydrocarbon chain near a chiral carbon atom has been investigated in a series of nematic and cholesteric phases. The deuterium nuclear magnetic resonance signals show the number of non-equivalent motions as equal to the number of different quadrupole doublet splittings. It is shown that a necessary but not sufficient condition for motional non-equivalence is the presence of a chiral carbon. The chiral carbon is not sufficient because in some cases the two quadrupole doublets may accidentally overlap. The composition of a number of nematic and cholesteric mesophases has been located and recorded.The non-equivalence is affected to a large extent by the protonation of the chiral head group, showing that head group anchoring is changed in this chemical modification.

Mixtures of amphiphilic compounds, electrolytes and water in a concentrated regime, form aqueous lyotropic liquid crystals (1). The most common forms are the lamellar or neat phases which contain positionally ordered bilayer leaflets interspersed with water layers, and the hexagonal phase in which the bilayer leaflets converge on an axis giving a cylindrical form to the bilayer micelle, these

micelle rods then take up a hexagonal arrangement of the circular cross-section in the plane perpendicular to the rod axes (2). These positionally ordered 'Infinite' micelle sytems are not nematic and have no direct correspondence with thermotropic liquid crystals except a symmetry relationship between smectic phases and lamellar liquid crystals of the lyotropic type. Neither lamellar or hexagonal phases are aligned by the application of magnetic fields.

Mesophases discovered by Lawson and Flautt (3) which are aligned by magnetic fields have since been shown to be nematic (4-6,7). These nematic forms occur with finite cylindrical and finite disc shaped micelles (8). For the cases where surfactants have simple aliphatic hydrocarbon chains, the cylindrical micelle nematics have positive diamagnetic anisotropy, and therefore align with the director and field axis parallel while on the other hand the disc shaped micelle nematic phases have negative diamagnetic anisotropy and align with the mesophase director perpendicular to the magnetic field (8,9). The susceptibility anisotropy sign may be reversed, without causing a phase change from disks to rods or vice versa, by adding surfactants with an aromatic ring such as p-alkoyl-benzoates (10). We have adopted the nomencature type I CM mesophases for cylindrical micelles (CM) with positive anisotropy, type II CM for mesophases with cylindrical micelles of negative diamagnetic anisotropy. The disc micelle nematics also can be synthesized with both signs of diamagnetic anisotropy to give type I DM and type II DM nematic (10) mesophases.

Cholesteric and nematic micellar mesophases may be studied in the same context because a nematic phase occurs for a racemic mixture of an optically active surfactant while any unbalanced mixture of optical forms leads to the creation of a cholesteric phase in the same mixture (11).

There is considerable biological interest in examining the motion of optical isomers of amino acids which reside at the micelle interfaces or in the aqueous layers. A previous study of l and d Alanine has been made (12). The amino acid solute in racemic and other mixtures, clearly showed different average motion for the d and l forms in a mesophase which would subsequently have been recognized as cholesteric. The mesophase was based on sodium decyl sulphate, a guest of resolved 2 methyl sodium decyl sulphate, sodium sulphate and water. It can be regarded as an induced cholesteric mesophase (13) obtained by adding an optically active compound to the nematic phase originally made by Lawson and Flautt (3).

The present study utilises the special relationship between nematic (racemic) forms and corresponding cholesteric liquid crystals (non-racemic mixtures of single centre optically active surfactants) to investigate non-equivalence in motion of (17) components of those mesophases.

1. EXPERIMENTAL

α-d_2 Potassium laurate was prepared by base exchanging with D_2O at an elevated temperature. A single deuteriation step with an excess of D_2O 500 ml per 300 g of potassium laurate was sufficient to obtain a greater than

75% replacement of hydrogen with deuterium in the α position. The conditions were 4 gms. sodium peroxide, 300 g of potassium laurate, and 500 gr. of D_2O placed in a stainless steel bomb at 160°C for 4 days. The bomb contents were cooled and transferred to a beaker and were treated with excess 12 molar hydrochloric acid. The deuteriated lauric acid was extracted with hexane and recrystallised twice from ethanol. Proton and deuterium NMR spectra were used to show a 75% replacement of α-protons with no other position in the chain affected.

Optically resolved surfactants were synthesised by acoylating optically active amino acids. The acoylation procedure was the standard reaction of the acoyl chloride with an amino acid salt. For the acid chloride preparation, α-d_2 deuteriated lauric acid or merely lauric acid was allowed to react with a 20 mole % excess of thionyl chloride under reduced pressure and reflux for 3 hours. Lauroyl chloride was distilled under reduced pressure at ≈ 120°C from the reacted mixture. Potassium N lauroyl amino acids, either deuterated in the αd_2 position or in natural abundance were prepared by the Schotten-Bauman reaction (14). Yields varied between 40 and 75%, and purities of the acid forms were verified through melting points, thin layer chromatography and NMR spectra. The following α-deuterated surfactants were prepared: L-potassium N-2-2-d_2 lauroyl alaninate (L-2,2-d_2-LAK), L-potassium N-2,2-d_2-lauroyl-valinate (L-2,2-d_2-LVK), L-potassium N-2,2-d_2-lauroyl-serinate (L-2,2-d_2-LSK) and potassim N-2,2-d_2-lauroyl glycinate (2,2-d_2-LGK). Other surfactants, such as n-decylaminonium chloride and deuterated derivatives were obtained from our laboratory stock, the preparation

and purification having been described in our previous papers (15). CTAB or hexadecyl trimethyl ammonium bromide was a recrystallised reagent grade material. A laboratory stock of this detergent with all N-methyl groups per-deuteriated was also used (16, 18).

Deuterium magnetic resonance spectra were obtained at approximately 61 MHz on the WH 400 Bruker spectrometer available at the South West Ontario NMR centre at the University of Guelph.

A series of nematic and cholesteric mesophases were prepared and small quantities (~0.5 weight %) of a deuterated guest amphiphile was incorporated for investigation by deuterium NMR spectroscopy. The mesophase compositions are summarized in Table I.

Results

Non-equivalence in the motion of amphiphile solutes in lyotropic nematics and cholesterics

Recent studies have shown that nematic mesophases in the micellar lytotropic category can be directly related to cholesteric mesophases merely by using the same molar concentration of all components with the exception that a principal amphiphile is utilised in an unbalanced mixture of D and L optical forms rather than the racemic mixture (11) in order to create the cholesteric form.

The composition of a series of nematic and cholesteric mesophases is summarized in Table I. The racemic forms of all mesophases correspond to the disc micelle type II behaviour for nematics (7). The guest amphiphiles present in small amounts ~0.53-0.47 weight % were designed to cover the following possibilities:

1. Racemic mixtures of an optically active detergent.

e.g. DL-LAK deuterated in the α position of the lauroyl chain or DL LSK also similarly deuterated.

2. α deuteriated amphiphiles which are not optically active such as 22-d_2-KC12 (α,α dideutero potassium laurate) or teradeutero decanol in the 1,1,2,2 or 33,44 positions.
3. Optically resolved forms of optically active detergents e.g. 2,2,L-ADE the αα deuterated lauryl ester of alanine in the α Levo form, or 2,2,d_2-L-LSK the αα deuteriated lauryl serinate of potassium in the pure levo form.

The column under deuteriated guests follows the compound abbreviations given in the legend to the Table.

Tracey and Diehl (12) showed that the diastereomers of alanine dissolved in the aqueous interface area of a mesophase, which today would be called an induced cholesteric phase, have different degrees of order for the internuclear vectors between the methyl and CH proton at the assymmetric carbon of alanine. This study has not been followed up although it raises several important questions about chiral recognition in pseudo membrane systems. The first part of the present study addresses some of these questions. The object of deuteriating the α position of the lauroyl chain of a guest amphiphile is to study the deuterum magnetic resonance and to use the partially averaged quadrupole splitting as a sensitive indicator of degree of order at the α position to the head group of the individual C-D bonds (7).

Fig. 1 is an illustration of a deuterium magnetic resonance study in a purely nematic system, of a non optically active guest amphiphile. The disk nematic system

type II DM is based on the amphiphile CTAB or hexadecyltrimethyl ammonium bromide. The mesophase composition was deionized neutral water of pH = 7.2. In Figure 1A the Glycinate amphiphile is protonated to the carboxylic acid while the sample which gave rise to figure 1B has the glycine head group in the carboxylate form. Only one quadrupole doublet is observed for the two α C-D bonds, but this doublet changes considerably in relative splitting as the carboxyl group of the glycinate head group is deprotonated to the carboxylate form.

In Figure 2 the deuterium magnetic resonance spectrum of a CTAB mesophase with potassium $\alpha\alpha' d_2$ lauroyl -L-alaninate as a guest is illustrated. The spectrum 2B corresponds to a mesophase prepared using neutral water at pH ~ 7 while 2A corresponds to a mesophase prepared from ~1 normal hydrochloric acid solution. The first contrasting feature to Figure 1 is the appearance of two different deuterium quadrupole splittings for the one stereoisomer. A mixture of stereoisomers in the racemate with D and L alaninate gives exactly the same spectra at the same mesophase composition. The spectra of D and L amphiphiles are therefore the same at the αα' position. The spectra are best interpreted by assuming that the two C-D bonds in the α-CD_2-group are rendered motionally inequivalent by the lack of symmetry in the alanine or alaninate head group. The degree of order along the different -C-D-bonds becomes distinct and two different quadrupole splittings result as in the figure. The superimposition of spectra for the D and L form headgroups is

the result of the minor image relation of a given -C-D bond in the L and D forms.

In figure 3 the deuterium magnetic resonance spectra correspond to a CTAB type II DM nematic mesophase with a small amount of potassium $\alpha\alpha$-d_2 lauroyl-L-valinate (0.5 wgt %) as a guest. When prepared from 1 normal hydrochloric acid (upper spectrum) the two -C-D bonds in the α carbon are apparently motionally equivalent and are only one outer quadrupole doublet occurs with a splitting 9KHz. In the carboxylate form the motional inequivalence is revealed in two quadrupole doublets of splitting 11 and 5.5 kHz for the $-C-D_2-$group showing once again that the individual -C-D bonds on the same carbon segment have different degress of order. In all cases the use of racemic mixtures of the α deuteriated lauroyl-alaninate, serinate or valinate for the guest amphiphiles leads to identical spectra of those shown in figure 1, 2 and 3. The D forms of the α deuteriated guests give the exact mirror image spectra of the L forms.

Discussion

A rather simple explanation of the non-equivalence of motion in individual C-D bonds on the same $-CD_2-$segment can be given. It is well known that in isotropic organic liquids the methylene groups adjacent to an optically active carbon contain magnetically non-equivalent protons. The amphiphiles in nematic and cholesteric mesophases are members of finite bilayer structures (19, 20). In such bilayers the aligned liquid crystalline order in magnetic fields leads to structures where the pseudo extended hydrocarbon chains are perpendicular to the magnetic field. The degree of order profile of a 10-16 segment

chain is known to exhibit a plateau region of nearly uniform order near the polar or ionic head group for 4 to 6 segments and a strong decrease in degree of order toward the non-polar tail (7). The qualitative nature of the form of the order profile is understood in terms of intramolecular motions connected with the rotations about carbon-carbon bonds. Near the head group at the interface, the principal deviations from an all trans chain are kinks and jogs. A kink is an arrangement gauche$^+$ trans guache$^-$ or equally probably gauche$^-$ trans guache$^+$ in three successive segments. While a jog has more than one intervening trans segment between the gauche rotations. Near the non polar tail of the hydrocarbon chain, single isolated gauche rotations become increasingly probable leading to a fall off in degree of order as the methyl group of the non polar tail is approached.

The inclusion of an amphiphile in a bilayer structure where the head group has an optically active carbon causes, as a result of the dissymetry of the head group the two possible configurations of a kink g^+tg^- and g^-tg^+ to be of unequal probability. With respect to the bilayer normal, the degree of order of a C-H bond direction is $-\frac{1}{2}$ in one combination of 'gtg' and $+\frac{1}{2}$ in the other. If both configurations are equally probable there is on the average no contribution in kinks to the overall degree of order of the C-H bond. If the two configurations do not have the same probability there is a contribution to the degree of order, which is not the same for g^+tg^- and g^-tg^+. In simple terms, if g^+tg^- has a probability p^+, and g^-tg^+ a probability p^- then contributions to the degree of order are $\frac{1}{2}(p^+-p^-)$ for one C-D bond and $\frac{1}{2}(p^--p^+)$

for the other C-D bond where $p^+ + p^- = 1$.

In Table II a complete summary is made for all the guests in all the mesophases measured. Examination of Table II shows that non-equivalence of motion in the $-\alpha CD_2-$ groups of amphiphiles is a consequence of optical activity in the head group but that this latter condition although necessary is not sufficient to predict non-equivalence. We must therefore accept that apparent equivalence can occur in the presence of optical activity by accidentally small differences in p^+ and p^-. It is also clear that non-equivalence at the level of a $-CD_2-$ segment is not induced into a segment if the mesophase becomes a cholesteric phase but it is an intrinsic property of a chiral molecule and its motions in both nematic and cholesteric phases.

Acknowledgements

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TABLE I

MESOPHASE	HOST AMPHIPHILE	DECANOL	ELECTROLYTE	WATER	DEUTERIATED GUESTS
DL-LAK	DL-LAK (33.03)	(6.20)	Na_2SO_4 (4.24)	0.1 wt% D_2O/h_2O (55.99)	2,2-d_2-DL-LAK (0.53)
"	" "	"	" "	" "	2,2-d_2-DL-LSK "
"	" "	"	" "	" "	2,2-d_2-KC12 "
"	" "	"	" "	" "	2,2-d_2-L-ADE "
"	(33.56)	(5.67)	" "	" "	1,1,2,2-d_4-DEOH "
"	" "	"	" "	" "	3,3,4,4-d_4-DEOH "
L-LAK	L-LAK (33.03)	(6.20)	Na_2SO_4 (4.24)	0.1 wt% D_2O/H_2O (55.99)	
L-LAK	L-LAK (33.03)	(6.20)	Na_2SO_4 (4.24)	0.1 wt% D_2O/H_2O (55.99)	2,2-d_2-L-LAK (0.53)
"	" "	"	" "	" "	2,2-d_2-L-LSK "
"	" "	"	" "	" "	2,2-d_2-KC12 "
"	" "	"	" "	" "	1,1-d_2-L-ADE "
"	" (33.56)	(5.67)	" "	" "	1,1,2,2-d_4-DEOH "
"	" "	"	" "	" "	3,3,4,4-d_4-DEOH "
KC12	KC12 (32.50)	(7.10)	KKCl (2.10)	0.1 wt% D_2O/H_2O (57.80)	2,2-d_2-L-LAK (0.50)
"	" "	"	" "	" "	2,2-d_2-DL-LAK "
DL-LAK	DL-LSK (34.18)	(6.10)	Na_2SO_4 (4.17)	0.1 wt% D_2O/H_2O (55.03)	2,2-d_2-DL-LAK (0.52)
"	" "	"	" "	" "	
L-LSK	L-LSK (34.18)	(6.10)	Na_2SO_4 (4.17)	0.1 wt% D_2O/H_2O (55.03)	2,2-d_2-L-LAK (0.52)
"	" "	"	" "	" "	
HDTMABr	HDTMABr (29.06)	(5.27)	NaCl (2.12)	H_2O (62.91)	2,2-d_2-L-LAK (0.47)
"	" "	"	" "	" "	2,2-d_2-L-LVK "
"	" "	"	" "	" "	2,2-d_2-L-LSK "
"	" "	"	" "	" "	2,2-d_2-LGK "
"	" "	"	" "	" "	1,1-d_2-L-ADE "
SDS	SDS (34.41)	(6.07)	Na_2SO_4 (5.67)	H_2O (53.34)	2,2-d_2-L-LAK (0.51)
"	" "	"	" "	" "	2,2-d_2-L-LSK "
"	" "	"	" "	" "	2,2-d_2-L-LVK "

Legends

Table I

Compositions of the nematic and cholesteric mesophases studied in this work. The chemical compounds are abbreviated in their naming according to the following scheme. These abbreviations are also used in the text.

KCl2 = Potassium Laurate

DeOH = n-decanol

SDS = Sodium decyl sulphate

ADE = The ammonium chloride ester of alamine with n-decanol

LAK = Postassium lauroyl alaminate. This is prepared either as a racemic mixture D/L-LAK or as resolved optical forms D-LAK and L-LAK.

LSK = potassium lauroyl serinate. Also prepared as Racemic D/L or in optically resolved forms D and L.

LVK = potassium lauroyl valinate

LGK = potassium lauroyl glycinate

NaCl = sodium chloride

Na_2SO_4 = sodium sulphate

HDTMA Br = CTAB = hexadecyl trimethyl ammonium bromide

The first column names, under mesophase, the principal amphiphile used in mesophase preparation (the host amphiphile). In the second column under host amphiphile the weight percentage in the mesophases is given in parenthesis e.g. (33.03). The weight percentage of decanol (DeOH) is given in the third column. In the fourth

Legends (cont'd)

column, the electrolyte is named and the weight percent used placed in parenthesis. The fifth column gives the weight % of water (0.1 wgt % D_2O in H_2O) used to prepare the mesophase. In the last column the small weight % of a deuteriated amphiphile guest is given. The composition of any mesophase can be obtained by reading across the columns at the appropriate level. Mesophases based on resolved surfactants L-LAK and L-LSK are necessarily cholesteric mesophases while those based on racemic detergents DL = LAK and DL-LSK are nematic phases. Mesophases based on HDTMABr, SDS and KCl_2 are also nematic. All nematic phases were verified as disk-micelle mesophases with negative diamagnetic anisotropy.

TABLE 2

HOST MESOPHASE	MESOPHASE TYPE	GUEST AMPHIPHILE	INEQUIVALENCE (pH)
DL-LAK	TYPE II D.M.	2,2-d_2-DL-LAK	YES (7)
"	"	2,2-d_2-DL-LSK	NO (7)
"	"	1,1-d_2-L-ADE	NO (7)
"	"	2,2-d_2-KC12	NO (7)
"	"	1,1,2,2-d_4-DEOH	NO (7)
"	"	3,3,4,4-d_4-DEOH	NO (7)
L-LAK	CHOLESTERIC	2,2-d_2-L-LAK	YES (7)
"	"	2,2-d_2-L-LSK	NO (7)
"	"	2,2-d_2-KC12	NO (7)
"	"	1,1-d_2-L-ADE	NO (7)
"	"	1,1,2,2-d_4-DEOH	NO (7)
"	"	3,3,4,4-d_4-DEOH	NO (7)
KC12	TYPE II D.M.	2,2-d_2-DL-LAK	YES (7)
"	"	2,2-d_2-L-LAK	YES (7)
DL-LSK	TYPE II D.M.	2,2-d_2-DL-LAK	YES (7)
"	"	2,2-d_2-DL-LSK	NO (7)
L-LSK	CHOLESTERIC	2,2-d_2-L-LAK	YES (7)
"	"	2,2-d_2-L-LSK	NO (7)
HDTMABr	TYPE II D.M.	2,2-d_2-L-LAK	YES(1),YES(7),YES(12)
"	"	2,2-d_2-L-LSK	YES(1),NO (7),NO (12)
"	"	2,2-d_2-L-LVK	NO (1),YES(7),YES(12)
"	"	1,1-d_2-L-ADE	NO (1),NO (7),NO (12)
"	"	2,2-d_2-LGK	NO (1),NO (7),NO (12)
SDS	TYPE II D.M.	2,2-d_2-L-LAK	YES(1),YES(7),YES(12)
"	"	2,2-d_2-LGK	NO (1),NO (7),NO (12)

TABLE II

The observations of non-equivalent motions in methylene $-CD_2-$groups in lyotropic micellar mesophases. The mesophases correspond in order to those listed in Table I and are named according to the principal amphiphile present in the mixture. The second column classifies the mesophase according to the nomenclature previously published (10). The third column lists the deuteriated guest amphiphile present as listed in the last column of Table I. The last two columns on the right give a simple yes or no answer to the question 'Is inequivalence observed in the $-CD_2-$group and the bracketed number (7), (1), and (12), etc. lists the pH of the water used to prepare the mesophase and thus the state of protonation of the carboxyl head group.

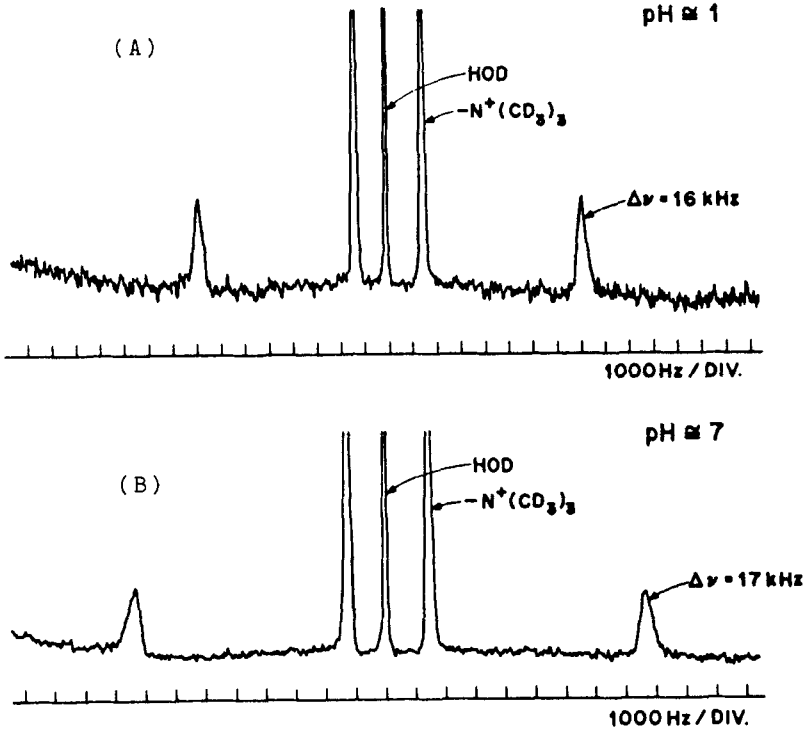

Figure 1

Figure 1

Deuterium magnetic resonance spectra of mesophase components with small concentrations of specifically deuteriated positions. Spectra were taken at South Western Ontario NMR facility at Guelph University at ~ 60 MHz. The mesophase was a nematic disk micelle type II DM system formed with CTAB, decanol, sodium sulphate and H_2O. The guest amphiphile was potassium $\alpha\alpha'$-d_2-lauroyl glycinate at ~0.5 wgt% in the phase. In the upper spectrum (A) the mesophase was prepared from 1 normal hydrochloric acid with a small amount of D_2O added (0.1% by wgt). There are three quadrupole doublets: The outer one with splitting 16 kHz is assigned to the $\alpha\alpha'$-d_2-lauroyl glycinate ion, the intense doublet with splitting of ~3KHz is associated with the headgroup $-N(CD_3)_3^+$ present as a highly diluted mixture in the host detergent CTAB. The strong central peak is actually the quadrupole doublet of the ~0.1% D_2O present as DOH. The splitting is never greater than a few Hz because the water is only weakly bound by the head groups at the micelle interface.

The lower spectrum (B) corresponds to a mesophase with the same composition but prepared from neutral water at pH ~7. The quadrupole doublets are similarly assigned. The largest with $\Delta\nu$ = 17 KHz is from the $\alpha\alpha' d_2$-glycinate guest ion, and the others are marked as in the upper spectrum from the $-N(CD_3)_3^+$ head group and HOD.

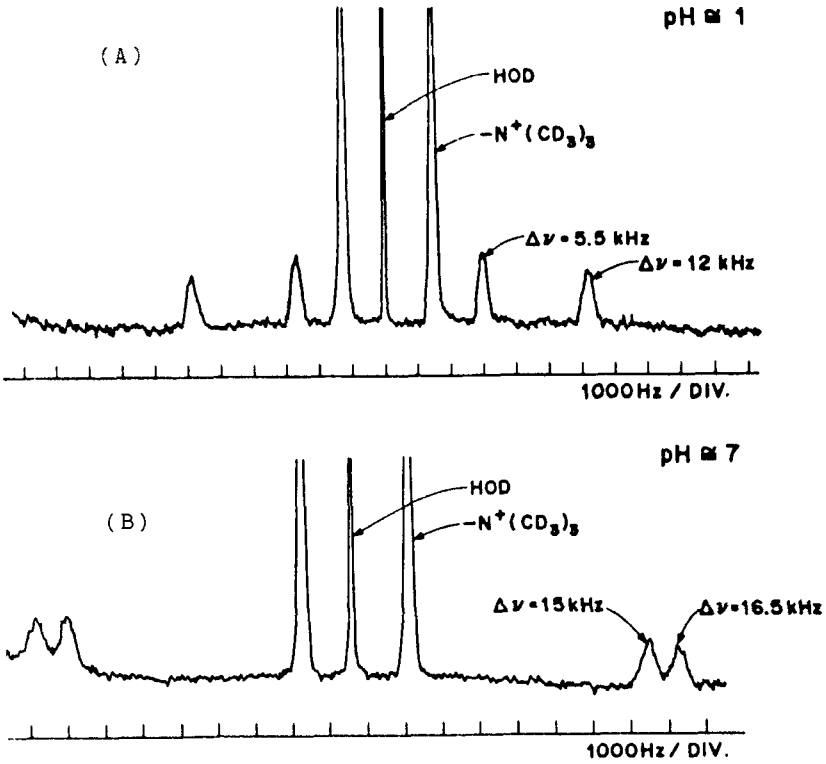

Figure 2

Figure 2

The upper deuterium magnetic resonance spectrum arises from a nematic disk-micelle phase prepared from CTAB, decanol, sodium sulphate and 1 Normal hydrochloric acid with LEVO potassium L-$\alpha\alpha'$-d_2-lauroyl alaninate as a guest. The α and α' deuterium nuclei on the same carbon position become motionally inequivalent and unlike Figure 1 there are two quadrupole doublets associated with the chain $-CD_2-$group at 5.5 and 12 KHz. The $-N(CD_3)_{3+}$ and HOD quadrupole doublets are not appreciably changed from those of Figure 1.

The lower spectrum was obtained from a mesophase of the same composition but prepared from neutral water with 0.1% D_2O added. Two quadrupole doublets are observed for the same $-CD_2-$group as in the upper spectrum but there are large changes in the quadrupole splittings as is indicated by the values on the figure.

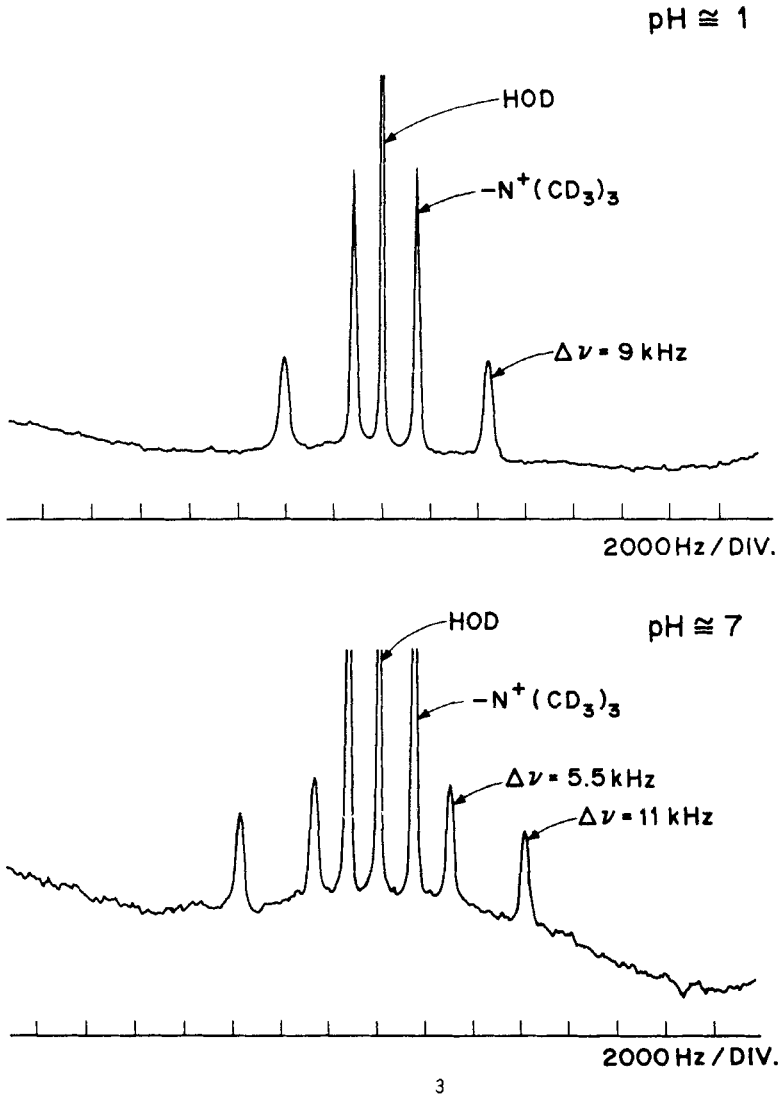

Figure 3

Spectra of alpha-deuteriated potassium lauroyl L-valinate in the CTBA nematic mesophase. Upper spectrum in acid at ph:1 and lower spectrum in a neutral mesophase (water at ph-7). See text for further description.

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