Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 20 Apr 2011.

To cite this article: Bruce J. Forrest & Leonard W. Reeves (1983): Motion Profiles of Deuteriocarbon Chains in Lamellar and Type II DM Nematic Phases, Molecular Crystals and Liquid Crystals, 90:3-4, 323-333

To link to this article: http://dx.doi.org/10.1080/00268948308072458

Mol. Cryst. Liq. Cryst., 1983, Vol. 90, pp. 323–333
0026-8941/83/9004–0323$18.50/0

Printed in the United States of America

Motion Profiles of Deuteriocarbon Chains in Lamellar and Type II DM Nematic Phases

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(*Received June 21, 1982*)

A binary system decylammonium—*d*-21 chloride water and a ternary system with a small amount of ammonium chloride have been studied over a wide range of water content by deuterium magnetic resonance. For the binary system a lamellar phase is formed, which on dilution becomes a two phase system lamellar/type II DM nematic. There is a large isotope effect in the composition, at which the two phase region occurs. The ternary system passes directly from the lamellar phase to a nematic system at a phase transition. The segmental motions in the deuteriocarbon chains are independent of the mesophase formed and of the electrolyte content. Large contributions to the degree of order of segments arise from co-operative motions of the whole bilayer and these are significantly different in the lamellar and type II DM, with and without electrolyte.

INTRODUCTION

The effect of added electrolytes on the formation of lyotropic nematic systems was investigated by Chen, Fujiwara and Reeves[1] prior to an understanding of their structure.[2–8] The case of the binary system 1-decylammonium chloride water and the related ternary system with added electrolyte, provides an example of a binary mesophase which is lamellar at low water contents.[9] The binary system[1,10] is lamellar up to 51%[1] D_2O by weight and the deuterium magnetic resonance spectrum

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is a powder pattern.[7] There is a linear decrease in the powder splitting with weight % water in the lamellar region.

A second phase appears at 51.1 wgt.% water of higher specific gravity and it is stable in thermodynamic equilibrium with the lamellar phase over a small range of 1.1 wgt.% change in water content. The lower phase has been shown to be a type II DM nematic phase.[4,10] This nematic phase and the co-existent lamellar phase in equilibrium both align in a magnetic field with the director perpendicular to the field direction. ($\Delta\chi = 0$). The alignment of the lamellar phase may be achieved by a cycle of warming to a single isotropic phase and allowing the system to cool to ambient temperature in the magnetic field. The alignment of the lamellar phase does not occur unless there is a co-existent nematic phase. The relationship between these two phases has been used as evidence for the structural similarities of the lamellar and finite disk micelle nematic mesophases.[2,4,7,10]

The addition of a small amount of a third electrolyte component eliminates the region of 2 phase equilibrium and dilution with water produces a phase change between a single lamellar and a single nematic phase at a higher concentration of water than the two phase region of the binary system.[1] A recent study[10] of the region of thermodynamic equilibrium between the type II DM and lamellar phases has shown that the degree of order profile obtained from deuterium quadrupole splittings in the —CH_2— segments of the deuteriohydrocarbon chains can be derived for the type II DM nematic phase from that of the lamellar phase by multiplying by 0.38 at each segment. The hydrocarbon chains are therefore in planar bilayers of identical internal ordering but the overall degree of order of the chain is reduced at each segment by the same factor because of the motion of finite micelles in the nematic phase.

The present study is an important extension of the previous results covering the systematic investigation of the degree of order of all segments in 1-decylammonium *d*-21 chloride for both the binary and ternary systems over a large range of water contents. The aim of this investigation is to provide a better description of chain order in the related mesophases.

EXPERIMENTAL

Decylammonium chloride-d_{21} was synthesized and purified as reported previously.[10] Mesophases were prepared with the following initial

composition by weight: A. DACL-d_{21}, 70.1; H_2O containing 5% D_2O, pH = 1 (HCL), 29.9. B. DACL-d_{21}, 59.67; NH_4Cl, 1.27; H_2O containing 5% D_2O, pH = 1 (HCL), 39.06. All ^2H NMR measurements were made at 24°C on a Bruker SXP spectrometer operating at 9.2 MHz. The deuterium magnetic spectra were registered for the above compositions, then small amounts of water were successively added and after rehomogenising and equilibrating the sample, a deuterium spectrum was retaken at each water addition.

RESULTS

(a) Binary Phases

The deuterium quadrupole splittings for all positions —CD_2— and CD_3— in the decylammonium chain as a function of H_2O are plotted in Figure 1 from 30 to 45 wgt.%. The single lamellar phase remains stable up to a water content 44.05 wgt.% at which composition a second more dense nematic phase separates in equilibrium with the lamel-

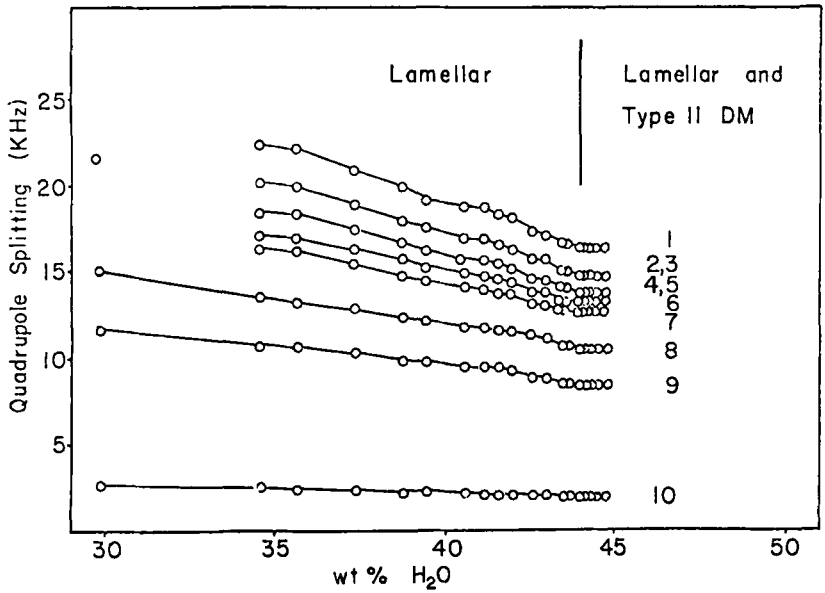

FIGURE 1 Quadrupole splittings of decylammonium chloride chains in the binary lamellar phase vs. water content. The lone point at approximately 30% water is the average quadrupole splitting for positions 1–7 which are not individually resolved at this composition.

lar phase. For the composition range 44.05 to 44.75 wgt.% water the lamellar and nematic phases co-exist. The two co-existent phases have already been determined to have negative diamagnetic susceptibility anisotropy and the lower phase is type II DM.[1,11]

Very interesting is the rather large change in composition at which the two phase system separates. Using D_2O and natural abundance *n*-decylammonium chloride the two phase region occurs between 51.1 (91.01 mole % D_2O) and 52.3 wgt.% water[1] but with H_2O and *n*-decylammonium-*d*-21 chloride the two phase region spans 44.05 (89.45 Mole % H_2O) to 44.75 wgt.% water. Isotope effects at the molecular level have already been reported for similar lyotropic nematic systems.[12]

The deuterium quadrupole splittings decrease in a linear fashion with the weight % of water until the two phase region separates, at which point two sets of splittings occur, one for each phase, and these both remain constant over the range of co-existence. The smaller of these pairs of splittings is 0.38 times the larger for all segments and is assigned to the type II DM nematic phase.[10] The largest quadrupole splitting for the CD_2-group of the *n*-decyl chain at 30 wgt.% water is 25.4 kHz (extropolated). The assymmetry parameter of the deuterium quadrupole coupling in deuteriated chains is usually neglected as very small[5,7] and consequently a good approximation to the degree of order 'S_D' of the C—D bond at the α position along the director at 90° to this bond is given by:

$$S_D = \frac{4\Delta\nu}{3\nu_Q} = 7.61 \times 10^{-3}\Delta\nu \qquad (1)$$

where ν_Q is the quadrupole coupling constant of a C—D bond in a hydrocarbon chain. This is taken as 175 kHz. $\Delta\nu$ is the measured quadrupole splitting in the mesophase. The factor 7.61×10^{-3} may be used with $\Delta\nu$ in kHz, giving a degree of order for the CD_2 along the director as +0.194. The positive sign is attributed because the axis of the pseudo-extended chain has a mean direction along the director. At the composition where the two phases separate, the degree of order of the —CD_2— is +0.124 in the lamellar phase and +0.047 in the type II DM nematic phase. The degree of order at the α segment position is much lower than in lamellar phases prepared using phospholipids at lower water contents ($S_D = 0.45$–0.6).[13,14] A corresponding increase in motional freedom of the anchoring —NH_3— group is indicated as well as other motions such as wave-like distortions in the planar bilayers. These additional motions in the 1-decylammonium chloride bilayers

increase in amplitude over the single lamellar phase region as further water is added. The large decrease in degree of order from the lamellar to the nematic phase in their co-existent range has been explained as motion of the finite micelles in the nematic phase.[10] In any aligned bilayer system the motion of the chains as a whole can be separated from that of the segmental motion since they contribute in product form to the experimental degree of order 'S_D'.[7,10,13,14]

$$S_D = S_{chain} \cdot S_{t/g} \tag{2}$$

S_{chain} = degree of water associated with whole body motions of the pseudo-extended chain.

$S_{t/g}$ = degree of order associated with segmental motions within the chain.

Using the ratio of degrees of orders of segment 'i' divided by that of the —CD_3 group on carbon 10.[7]

$$\frac{(S_D)_i}{(S_D)_{10}} = \frac{(S_{t/g})_i}{(S_{t/g})_{10}} \tag{3}$$

Such degree of order ratios become independent of the whole body motions of chains. These are plotted in Figure 2 for the binary system. The two co-existent phases now give only one set of points because one set is just 0.38 as large as the other. This confirms that the lamellar and nematic phases in equilibrium have identical segmental chain motions. In the one phase region from 30 to 44.05 wgt.% water the appreciable decrease in absolute quadrupole splittings is accompanied by very small changes in the segmental ratios of splittings, and no discontinuity is found at the one phase/two phase boundary. The hydrocarbon chains in the bilayers are thus insensitive to the phase change. This can only be so if the bilayer has the same symmetry[15] and the disk-micelles in the nematic phase are large enough to render the effects of amphiphiles at the disk-edge negligible. The quadrupole coupling constant ν_Q 175 kHz. can vary with the state of matter because of intermolecular force field effects[16] but since all deuteriocarbon chains observed here are in nearly identical environments in a defined bilayer structure, absolute changes in value over the range of systems investigated is negligible and consequently differential changes from one segment to another are even more so. Any change in the value of a quadrupole splitting is safely interpreted in terms of 'S' the degree of order change rather than 'ν_Q' a quadrupole coupling constant change.

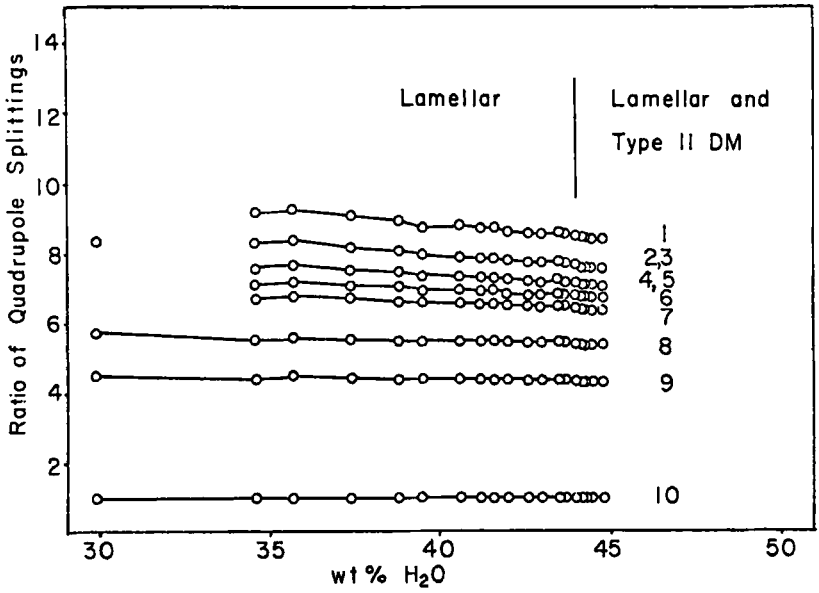

FIGURE 2 Ratios of the quadrupole splittings of the various positions of the decylammonium chains relative to that of the terminal methyl group vs. water content for the binary lamellar phase. The lone point at approximately 30% water is the average value for positions 1–7 which are not individually resolved at this composition.

(b) The ternary system containing electrolyte

Mesophase B from the experimental section, containing 1.27 wgt.% ammonium chloride behaves in a different manner with addition of water. The absolute values of deuterium quadrupole splittings are plotted as a function of water content in Figure 3. In the range 38.5 to 46.5 wgt.% water there is a linear decrease in quadrupole splitting for all segments in the single phase system. Over the overlapping region of water content 38.5 to 44.05 wgt.% the quadrupole splittings in Figure 3 are always larger for any segment than in Figure 1. This comparison is best expressed by a linear regression fit to a straight line for both Figures 1 and 3 for the lamellar region. The fact that the single phase below 46.5 wgt.% water for the ternary system is a lamellar phase will be argued on the basis of analogy in the discussion section. In Table I the least squares parameters to the straight lines for binary and ternary systems are compared. The intercept corresponds to the extrapolated state of 0% water which reflects the value at the origin rather than having any physical significance.

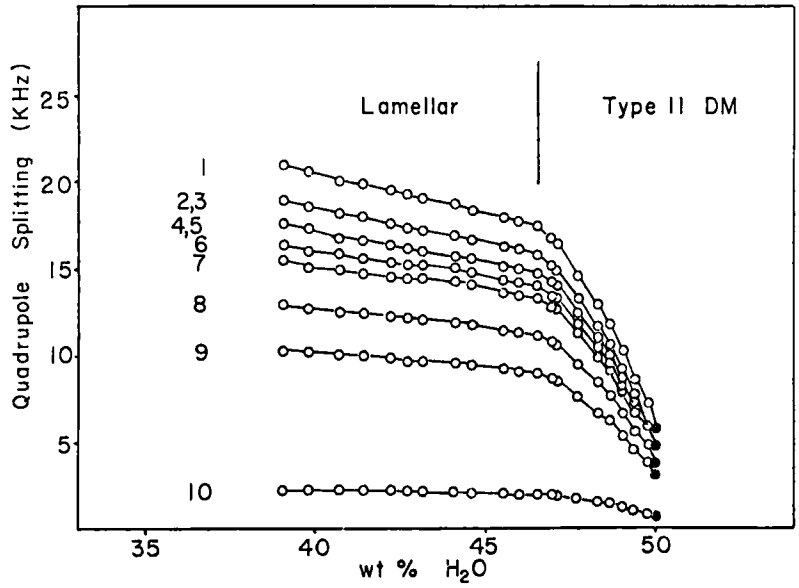

FIGURE 3 Quadrupole splittings of the decylammonium chloride chains in the ternary lamellar and Type II DM phase vs. water content. The filled points represent an equilibrium between the disk micelle phase and an isotropic phase.

Above 46.5 wgt.% water the ternary system undergoes a discontinuity in the linear slope. The more rapid decrease in quadrupole splitting with increased water content has been explained by a decrease in the mean micelle size as water is added,[7,15] to a type II DM nematic phase. The single type II DM nematic phase was confirmed by standard methods.[11] In Figure 4 the ratio of quadrupole splittings is plotted against water content for the ternary system. The splitting ratios are again insensitive to the phase transition, lamellar → type II DM but more interestingly the slight linear decrease and the values of the ratios are the same in Figures 2 and 4 over the considerable region of overlap. In order to avoid a confusion of which points belong to each system Figures 2 and 4 are plotted separately but in fact all 8 segments which are resolved fall on their own characteristic segmental linear plot.

DISCUSSION

Seelig and Seelig[13] have pointed out that bilayer fluidity is not measured from the degree of order since fluidity is more aptly related to

TABLE I

Line fitting parameters for the decrease in quadrupole splitting with increasing water content for; (a) decylammonium chloride/water binary lamellar phase. (b) decylammonium chloride/ammonium chloride/water ternary lamellar phase.

(a) The slope has units kHz $(wgt.\%)^{-1}$

Position	Slope	Intercept (kHz)	No. of pts.	Correlation
1	−0.6276	44.1239	12	0.988
2,3	−0.5679	39.9146	12	0.991
4,5	−0.4949	35.7246	12	0.988
6	−0.4368	32.4784	12	0.982
7	−0.4101	30.6388	12	0.987
8	−0.2931	23.5851	13	0.986
9	−0.2238	18.4431	13	0.981
10	−0.0458	3.9864	13	0.972

(b)

Position	Slope	Intercept (kHz)	No. of pts.	Correlation
1	−0.4581	38.7856	11	0.995
2,3	−0.4047	34.6491	11	0.984
4,5	−0.3719	32.0496	11	0.989
6	−0.3061	28.2910	11	0.983
7	−0.2741	26.1499	11	0.960
8	−0.2208	21.5290	11	0.989
9	−0.1701	16.9609	11	0.981
10	−0.0328	3.6073	11	0.957

local dynamics and microviscosity. The lamellar phases prepared in this study contain at the lowest water contents of 30 wgt.% for the binary system about the same mole % as those previously used for model membrane studies. For Dipalmitoyl lecithin bilayers, the α segment has a degree of order 0.4 with a microviscosity estimated at 10 times that of a corresponding dodecanoate/decanol bilayer but the latter has an α—CD_2— degree of order of 0.6. The degree of order is influenced by all motions which occur on a time scale less than 10^{-4} seconds. This includes relatively slow motions which are not generally ascribed to microviscosity effects. One such motion in the type II DM nematic systems is the oscillation of the large finite micelles, which are at least partly inherent in local director fluctuations. This slower motion will be a part of the macroviscosity but it is not a local microviscosity effect. The micelle oscillation does not contribute significantly to the nu-

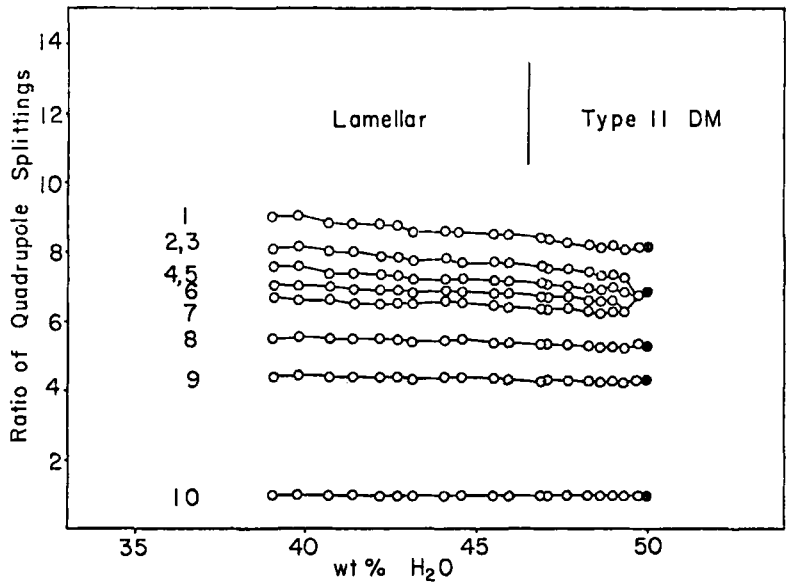

FIGURE 4 Ratios of the quadrupole splittings of the various positions of the decylammonium chains relative to that of the terminal methyl group vs. water content for the ternary lamellar and Type II DM phases. The filled points represent the co-existence of the disk micelle phase and an isotropic phase.

clear spin relaxation time T_1 but it has clearly been detected in the angular dependence of $T_{1\rho}$.[17] The much smaller degrees of order of the lamellar binary and ternary systems based on decylammonium chloride (0.124 to 0.194) must arise because of co-operative motions connected with the whole bilayer. The segmental motion of the chains, which is separated in segmental order ratios, is quite independent of phase changes and the addition of electrolyte.

A multi-lamellar system has both the co-operative wave motions available to membrane modes and some independent modes which affect only a single bilayer. The degree of order of phospholipid and dodecanoate lamellar phases[13,14,18] has been explained in this way. The large changes in degrees of order with water content measured from the quadrupole splittings in the present system, since they occur independently of the segmental chain motions, are assigned to the same origin. The large decrease in degree of order between the lamellar and finite micelle systems occurs because of another degree of motional freedom of the finite micelles which is not available if the bilayers are essentially infinite.

When the micelle in the nematic phases changes shape at a transition type I CM → type II DM,[15] there are significant changes in relative segmental order near the ionic head group at the micelle interface. No such segmental order changes occur here (Figures 2 and 4). The chains are therefore, by analogy, all embedded in a planar bilayer, showing that only lamellar and disk-micelle phases are present. Relative to the terminal methyl group the ratios of order of all segments decrease by 10% from the low water content binary system to the high/water content nematic system formed in the ternary mixture. This is a very minor adjustment of the trans/gauche interconversion probabilities for such a range of water contents and for electrolyte additions. The phase changes are therefore controlled at the micelle interface rather than from the micelle interior. These subtle interface effects do not influence such parameters as area per head group[19] a great deal, because changes in head group area are known to affect the segmental defects in the chain.[5]

The large fall in degree of order in the ternary system over the range of type II DM behaviour are evidently associated with some whole body motions of the chains which do not occur in lamellar phases. A decrease in micelle size with added water[15] and additional consequent motional freedom would be a logical origin for this effect.[10]

Acknowledgment

The operating funds provided by the National Science and Engineering Research Council of Canada to LWR are gratefully acknowledged.

References

1. D. M. Chen, F. Y. Fujiwara and L. W. Reeves, *Can. J. Chem.*, **55**, 2396 (1977).
2. F. Y. Fujiwara, L. W. Reeves, M. Suzuki and J. A. Vanin in "Solution Chemistry of Surfactants," **1**, 63 (1979), Ed. K. L. Mittal Pub. Plenium. Press.
3. L. Queiroz do Amaral, C. F. Pimentel, M. R. Tavares and J. A. Vanin, *J. Chem. Phys.*, **71**, 2940 (1979).
4. F. Y. Fujiwara and L. W. Reeves, *J. Phys. Chem.*, **84**, 653 (1980).
5. Y. Hendrix and J. Charvolin, *J. Physique*, **42**, 1427 (1981).
6. L. J. Yu and A. Saupe, *J. Am. Chem. Soc.*, **102**, 4879 (1980).
7. B. J. Forrest and L. W. Reeves, *Chem. Revs.*, **1**, 1 (1981).
8. A. M. Figuredo Neto., Ph.D. Dissertation, Institute of Physics, University of Sao Paulo, Brazil (1981).
9. P. A. Winsor, *Chem. Revs.*, **68**, 1 (1968).
10. B. J. Forrest and L. W. Reeves, *Mol. Cryst. Liqu. Cryst.*, **58**, 233 (1980).
11. F. Y. Fujiwara and L. W. Reeves, *Can. J. Chem.*, **56**, 2178 (1978).
12. F. Y. Fujiwara and L. W. Reeves, *Can. J. Chem.*, **57**, 478 (1979).

13. A. Seelig and T. Seelig, *Biochemistry*, **13**, 4839 (1974).
14. J. Seelig and A. Niederberger, *Biochemistry*, **13**, 1585 (1974).
15. B. J. Forrest and L. W. Reeves, *J. Am. Chem. Soc.*, **103**, 1641 (1981).
16. E. A. C. Lucken, Nuclear quadrupole coupling constants, Acad. Press. London, New York (1969).
17. M. I. Burgar, R. Blinc, M. M. Pintar and L. W. Reeves, *Mol. Cryst. Liqu. Cryst.*, **84**, 245 (1982).
18. J. Seelig and W. Niederberger, *J. Am. Chem. Soc.*, **96**, 2069 (1974).
19. S. Marcelja, *Biochim. Biophys. Acta.*, **367**, 165 (1974).