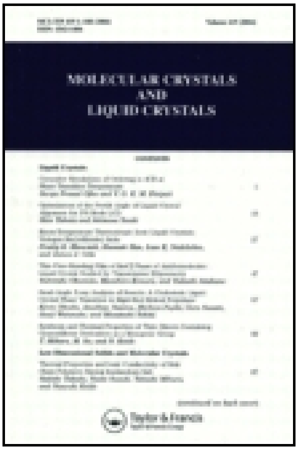

Molecular Crystals and Liquid Crystals

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

Conformational Studies of a Carboxylic Acid Incorporated into Lyotropic Liquid Crystalline Systems. A Deuterium Nuclear Magnetic Resonance Investigation

Bruce J. Forrest [a] , Laura Hecker [a] & Leonard W. Reeves [a]

[a] Chemistry Department, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G2

Version of record first published: 20 Apr 2011.

To cite this article: Bruce J. Forrest , Laura Hecker & Leonard W. Reeves (1980): Conformational Studies of a Carboxylic Acid Incorporated into Lyotropic Liquid Crystalline Systems. A Deuterium Nuclear Magnetic Resonance Investigation, Molecular Crystals and Liquid Crystals, 58:3-4, 223-232

To link to this article: http://dx.doi.org/10.1080/00268948008082123

Mol. Cryst. Liq. Cryst., 1980, Vol. 58, pp. 223–232
0026-8941/80/5803-0223$04.50/0

Printed in the U.S.A.

Conformational Studies of a Carboxylic Acid Incorporated into Lyotropic Liquid Crystalline Systems

A Deuterium Nuclear Magnetic Resonance Investigation

BRUCE J. FORREST, LAURA HECKER, and LEONARD W. REEVES
Chemistry Department, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G2

(*Received June 25, 1979*)

Butanoic acid-d_7 and its corresponding anion have been incorporated into two Type II disc micelle lyotropic liquid crystalline systems based on hexadecyltrimethylammonium bromide, and on sodium decylsulfate. The order parameter profiles for the perdeuteriated guests have been determined. Calculations based on these order profiles have been performed in order to describe the conformation of the guest carboxylic acid present in the bilayer micelle. These calculations indicate that two conformations predominate, one an all trans arrangement (63%), and the second possessing a single gauche rotation about the α-β C—C bond (37%). The model used was based on two possible methods of anchoring the polar group at the aqueous interface.

INTRODUCTION

One important question in the field of colloid and interface science concerns the equilibrium conformations of hydrocarbon chains which are incorporated as components of a bilayer. Many such systems have been investigated by deuterium nuclear magnetic resonance.[1–5] Analyses of the deuterium quadrupole splittings in deuteriated hydrocarbon chains lead to determination of order parameters of the C—D bond vectors, and some estimation of the number of gauche rotamers along the lipid chains.[1,2] However, determination of the average conformation for component amphiphiles from the observed order parameters for long chains is not possible because of the large numbers of conformations, which must be considered. The detailed equilibrium populations of conformers for phospholipids or fatty acids is always ambiguous. In addition, information concerning the anchoring of individual amphiphiles at the hydrophobic-hydrophilic interface is of great importance, since it is this anchoring which determines to a large extent, the differing order parameter profiles of chemically unique bilayer constituents.[6]

Lyotropic liquid crystals which spontaneously align when placed in an applied magnetic field have been classified into two main types, Type I, and Type II, depending on whether the mesophase director is aligned parallel, or perpendicular, respectively, with respect to the magnetic field.[7,8]

Recent low-angle X-ray diffraction experiments have been most useful in elucidating the structure of these novel liquid crystals.[9] These studies have shown that the Type II system based on mixtures of sodium decylsulfate (SDS)/decanol/H_2O/Na_2SO_4 is composed of disc-shaped micelles of bilayer thickness of 38 Å, which are dispersed in a water matrix of average thickness of 90 Å. These micelles which are greater than 1,000 Å in diameter, possess no positional order of their centres of gravity in the mesophase.[9] In this sense these liquid crystals may be called nematic. The classical Lα mesophase can co-exist with the Type II disc micelles (DM), and nucleates from it by gaining two positional degrees of order.[15]

A previous report has been published of the degrees of order of the α C—D bond axes of a series of carboxylic acids and carboxylates, of chain length two to sixteen carbons, aligned in a Type II DM mesophase based on sodium decylsulfate.[10] At this α position the degree of order increases with increasing chain length, reaching a constant value at a length close to that of the host decylsulfate chains. The increase in order was found to be linear with intermediate chain lengths, while deviations from linearity occurred at small chain lengths because of partitioning of the guests between the interstitial aqueous compartment and the disc-like micelles.

The results presented here are an extension of this work. Butanoic acid-d_7 and its corresponding anion have been incorporated into Type II DM mesophases in order to determine the complete order parameter profile. The possible conformations of this carboxylic acid (carboxylate) are much more restricted in number than with the long chains. An attempt has been made to relate the measured order parameter profile to conformation and head group anchoring.

EXPERIMENTAL

Butanoic acid-d_7 was prepared as described previously.[11] Deuteriation was greater than 90% as indicated by ^{1}H NMR. The product was distilled prior to use. Specifically labelled hexadecyltrimethylammonium bromide (HDTMABr) and sodium decysulfate (SDS) were prepared also as described previously.[11,12] HDTMABr and SDS were obtained from standard sources, recrystallized approximately 4 times and dried exhaustively under vacuum before use. Mesophases were based on either SDS or HDTMABr amphiphiles.[7,11] The formation of the butanoic acid as the guests in the bilayer, was assured by using water, pH ≈ 2(0.5% D_2O) for the liquid crystal preparation. The DOH deuterium resonance was used to verify the water degree of order, in the mesophases. Butanoate anion was included as a guest by maintaining the water of the liquid crystal at pH ≈ 12.

Mesophase compositions by weight were as follows:

a) HDTMABr (may contain a small amount of HDTMABr-d_9, deuterium substituted at the *N*-methyl positions) 33.70%, Na_2SO_4 3.18%, decanol 4.55%, H_2O 55.84%, butanoic acid-d_7 2.73%.

b) SDS (may contain a small amount of SDS-9.10-d_2) 34.19%, Na_2SO_4 5.66%, decanol 5.97%, H_2O 52.58%, butanoic acid-d_7 1.60%.

All ^2H NMR spectra were determined on a Bruker SXP spectrometer operating at 9.2 MHz. Reasonable signal to noise was achieved by the accumulation of 1000–2000 transients. The operating temperature was 31.1 ± 0.2°C, unless otherwise specified. The resonance of the α position of butanoic acid has been assigned previously,[10] while β and γ (terminal methyl) resonances were assigned through a consideration of their relative intensities.

RESULTS

A representative deuterium NMR spectrum of the butanoate ion as a guest in a HDTMABr Type II DM liquid crystal is shown in Figure 1. The quadrupole splittings of the α, β and terminal methyl positions of butanoic acid-d_7 and the corresponding anion are shown in Table I for both HDTMABr and SDS mesophases. In accordance with previous studies of guest carboxylic acids and carboxylates, the quadrupole splittings were observed to decrease as the terminal methyl group is approached, indicating an anchoring of the guest head group at the interface by the carboxyl (carboxylate) moiety.[6,10] In the case of the SDS liquid crystal, the value of the quadrupole splitting of the α-CD_2 fragment decreases upon ionization of the carboxyl group from a value of ~6830 Hz to ~4280 Hz (~40%) in agreement with the previous work.[10] Indeed, the splittings of the β-CD_2 fragment and γ methyl group decrease proportionately, so that the ratio of the quadrupole splittings remain essentially constant. Although in the HDTMABr liquid crystal the magnitudes of the quadrupole splittings of the butanoic fragments are not lowered as dramatically (~3%) upon ionization, as in the case of the SDS mesophase, the ratios of the quadrupole splittings are again essentially

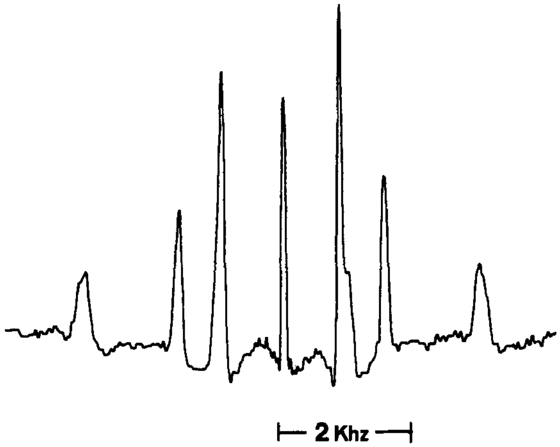

FIGURE 1 Deuterium magnetic resonance spectrum of the butanoate ion aligned in a hexadecyltrimethylammonium DM liquid crystalline phase. The quadrupole splitting of the central peak due to HOD (< 10 Hz) is not resolved.

constant. Indeed, the ratios of the quadrupole splittings appear to be very similar whether the butanoic acid is present as a guest in the SDS DM liquid crystal, or the HDTMABr DM liquid crystal. In other words, it is the anchoring of the butanoic acid or butanoate ion at the interface by its headgroup, which is chemically distinct from that of the host detergent which determines the relative order profile of the chain.

The temperature dependence of the chain profile was also investigated. Decreasing the temperature to approximately 15°C caused an increase in

TABLE I

Quadrupole splittings for butanoic acid and the butanoate ion incorporated into HDTMABr and SDS mesophases. Ratios of the quadrupole splittings $\Delta\nu cx$ relative to that of the α position, $\Delta\nu c2$, are also given.

	Acid		Anion	
HDTMABr mesophase Position	Quadrupole splitting[a] (Hz)	$\Delta\nu cx/\Delta\nu c2$	Quadrupole splitting (Hz)	$\Delta\nu cx/\Delta\nu c2$
α	6079	1	5911	1
β	3119	0.53	3036	0.51
CH_3	1776	0.29	1717	0.29
SDS mesophase				
α	6827	1	4277	1
β	3588	0.53	2089	0.49
CH_3	1877	0.27	1074	0.25

[a] Error is less than 1%.

the quadrupole splittings of 15–25% for all fragments of butanoic acid or the butanoate anion in the HDTMABr DM liquid crystal, indicating that the order parameters for the α-CD_2, β-CD_2 and terminal methyl group are of the same sign.[13]

DISCUSSION

The observed deuterium quadrupole splitting is proportional to the degree of order of each CD_2 or CD_3 fragment which is isotopically labeled and is given by

$$\Delta\nu = \tfrac{3}{2}QS_{\mathrm{CD}}\tfrac{1}{2}(3\cos^2\Omega - 1) \tag{1}$$

where $\Delta\nu$ is the quadrupole splitting of the deuterium magnetic resonance spectrum, Q is the quadrupole coupling constant, and Ω is the angle between the mesophase director and the applied magnetic field. All mesophases studied here are of Type II DM (negative diamagnetic anisotropy), that is, the phase director axis which is coincident with the bilayer normal in this case is perpendicular to the applied magnetic field (i.e. $\Omega = 90°$). The order parameter of a carbon-deuterium bond axis is given by:

$$S_{\mathrm{CD}} = \tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle \tag{2}$$

where S_{CD} is the degree of order of an individual C—D bond axis, and θ is the angle between that axis and the mesophase director. Thus,

$$\Delta\nu = -\tfrac{3}{4}Q\tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle \tag{3}$$

In a relatively crude approximation, it has been proposed that there exist on the average two orientations for the anchoring of a carboxylate group at the hydrophobic-hydrophilic interface due to lipid-water structuring effects.[5] In the first of these, (a) the internuclear vector of the two $O^{1/2-}$ atoms is perpendicular to the bilayer normal, so that for an extended all trans chain, the chain long axis would be at an angle of 35.25° to the bilayer normal. In the second of these (b) the internuclear vector of the two $O^{1/2-}$ atoms is at an angle of 35.25° to the bilayer normal, and thus the chain long axis of an extended all trans carboxylate will be parallel to the bilayer normal. This model of the interface suggests that the lipid/water interactions alone impose order on the region of the polar head. Previous studies have indicated a participation of the counter ion hydration in ordering the head polar group.[12,14] The degree of order of sodium ions in a Type II DM liquid crystal based on the mixed detergent system of potassium dodecanoate/hexadecyltrimethylammonium bromide has been interpreted in terms of a three site model of the binding of these ions at the interface.[14] There does exist therefore a layer of counter ions at the interface which interact with the detergent amphiphiles and affect their order profile. We shall as a first approximation, neglect the presence of counter ions. It is theoretically possible to calculate the degree of order of the C—D bond axes of a carboxylate assuming that the conformation of the molecule is known. Alternatively, given the experimental values for the quadrupole splittings it should be possible to calculate the average molecular conformation. This relationship of degree of order to conformation is generally ambiguous because of the large number of conformations possible for a long chain fatty acid. In the case of the short butanoate chain the number of possible conformations is quite limited. With the carboxylate anchored at the interface, and given the free rotation of the terminal γ methyl group, the conformation of the butanoate ion in the bilayer depends *only* upon the rotation about the α-β C—C bond (i.e. whether the molecule is in the all-trans conformation, or whether there exists a gauche ± conformation about the α-β C—C bond). Thus for both types of anchoring of the carboxylate, there exist two conformations for the butanoate ion (trans, or gauche ±) giving a total of four possible independent arrangements.

Assuming that all C—C—C and C—C—D angles are tetrahedral, and using conformer rotations of 120°, it is possible to calculate S_{CD} for each C—D bond of the four possible conformations. These values are given in Table II. For type A(trans), both methylenes and the methyl group yield an order parameter of $-\frac{1}{3}$, and a single quadrupole splitting would be predicted for the DMR spectrum. For type A (gauche ±) two splittings would be

TABLE II

Order parameters of the C—D bond vectors of butanoic acid calculated using Eq. (2).

		Position	S_{CD}
Orientation A			
	All *trans*	α	−1/3
		β	−1/3
		γ	−1/3
	Gauche $\pm(\alpha - \beta)$	α	−1/3
		β	+1/3
		γ	+1/9
Orientation B			
	All *trans*	α	−1/2
		β	−1/2
		γ	−1/6
	Gauche $\pm(\alpha\ \beta)$	α	−1/2
		β	0
		γ	+1/6

TABLE III

Ratios of experimental quadrupole splittings for butanoic acid and its corresponding anion in hexadecyltrimethylammonium bromide and sodium decylsulfate type II DM liquid crystals.

HDTMABr mesophase	Ratio of quadrupole splitting	Acid	Anion
	α/β	1.89	1.95
	β/β	1.00	1
	γ/β	0.55	0.57
SDS mesophase	α/β	1.90	2.05
	β/β	1	1
	γ/β	0.52	0.51

expected with relative magnitude of 3:1. Similar predictions may be made for type B (*trans*), and type B (gauche ±).

The experimental ratios of the quadrupole splittings of butanoic acid and the butanoate ion in HDTMABr and SDS mesophases are shown in Table III. These ratios do not depend on the mesophase solvent and therefore the case of butanoic acid in a HDTMABr mesophase will be used for a sample calculation. The experimental ratios of the quadrupole splittings in this case are 1.89:1.00:0.55 (α/β, β/β, and γ/β). Since these ratios do not agree well with those calculated for the four possible conformations, it appears that contributions to the observed order parameter come from a time average of different molecular conformations. It follows, therefore, that there are six possible binary combinations of the four conformations. Using the experimental ratio of the α/β splitting it is possible to calculate the relative contribution of each conformation in a pair set of conformers, and subsequently predict the ratio of the quadrupole splitting which would be expected for β/γ. The pair sets, which yield real physical solutions are given in Table IV. From examination of this table, it is clear that best binary combinations are that of 63 % A(*trans*), 37 % B(gauche ±) and that of 31 % A(gauche ±), 69 % B(*trans*) which yield β/γ ratios of 0.70 and 0.34, respectively. The experimental

TABLE IV

Calculated ratios $\Delta\nu\gamma/\Delta\gamma\beta$ for binary combinations of conformations. The experimental value is 0.55.

Conformations	% *trans* ($\alpha - \beta$)	$\Delta\nu\gamma/\Delta\nu\beta$ (calculated)
A(*trans*), A(gauche ±)	77 %	1.29
A(*trans*), B(gauche ±)	63 %	0.70
B(*trans*), A(gauche ±)	69 %	0.34
B(*trans*), B(gauche ±)	54 %	0.06

value is 0.55. First of all, it is seen that both of the above combinations are composed of two conformations which have a different anchoring of the carboxyl group at the interface, and secondly that both are a combination of approximately 60–70% *trans* and 30–40% gauche ±.

For the conformation A(gauche ±), there exists a gauche rotation of the α-β bond and the carboxylate plane is perpendicular to the normal of the bilayer. Therefore the chain long axis extends nearly perpendicularly to the bilayer normal. Such a situation does not lead to efficient packing of the guest with adjacent detergent molecules. The combination of 63% A(*trans*), 37% B(gauche ±) better maximizes the Van-der-Waals forces between adjacent chains, and therefore it is reasonable to assume that this binary combination best reflects the conformation of butanoic acid intercalated in the Type II DM liquid crystal. It has previously been shown that the degree of order of the α CD_2 group of a series of carboxylic acid guests in a SDS Type II DM mesophase increases linearly with chain length over the region between 3 and 8 carbon atoms.[10] As the chain length increases, more constraints are placed upon the conformational motions in order to maximize attractive forces between adjacent chains. Based on the model of the interface region presented here, an increased order parameter of the α CD_2 moiety with increasing chain length is compatible with increasing population of B(gauche ±) conformations about the α-β C—C bond. This conformation results in the chain-long axis being parallel to the bilayer normal.

CONCLUSION

The conformation of a carboxylic acid, butanoic acid, and the corresponding butanoate ion, present in bilayer disc micelle lyotropic liquid crystals have been investigated. Based on two probable orientations of the carboxyl (carboxylate) group at the interface, it was found that the ratios of the experimental deuterium quadrupole splittings could not be satisfactorily explained by a single molecular conformation. Rather a time average of two conformations is necessary. The first of these is the all *trans* conformation (63%) while the second possesses a gauche rotation of the α-β C—C bond (37%). As well, it was found that the orientation of the headgroup differs for these two conformations. These results, therefore, are also informative of the nature of the anchoring of amphiphiles at hydrophobic-hydrophilic interfaces.

Acknowledgement

The financial support of this work through an operating grant from the National Research Council of Canada to L.W.R. is gratefully acknowledged.

References

1. J. Seelig and W. Niederberger, *Biochemistry*, **13**, 1585 (1974).
2. A. Seelig and J. Seelig, *Biochemistry*, **13**, 4839 (1974).
3. J. Charvolin, P. Manneville, and B. Deloche, *Chem. Phys. Lett.*, **23**, 345 (1973).
4. B. Mely, J. Charvolin, and P. Keller, *Chem. Phys. Lipids*, **15**, 161 (1975).
5. K. Abdolall, E. E. Burnell, and M. I. Valic, *Chem. Phys. Lipids*, **20**, 115 (1977).
6. B. J. Forrest and L. W. Reeves, *Chem. Phys. Lipids*, **24**, 183 (1979).
7. K. Radley, L. W. Reeves, and A. S. Tracey, *J. Phys. Chem.*, **80**, 174 (1976).
8. D. M. Chen, F. Y. Fujiwara, and L. W. Reeves, *Can. J. Chem.*, **55**, 2396 (1977).
9. Lia Quieroz de Amaral, C. Pimentel, and M. Travares. Private Communication (1977). M. Travares, M.Sc. Dissertation, University of Sao Paulo (1978). *Suppl. to Acta Cryst.*, **A34**: S188 (1978). *J. Chem. Phys.*, **71**, 2940 (1979).
10. D. M. Chen, F. Y. Fujiwara, and L. W. Reeves, *Can. J. Chem.*, **55**, 2404 (1977).
11. L. W. Reeves, A. S. Tracey, and M. M. Tracey, *Can. J. Chem.*, **57**, 747 (1979).
12. Y. Lee, L. W. Reeves, and A. S. Tracey, *Can. J. Chem.*, (in Press).
13. G. Lindblom, B. Lindman, and G. T. T. Tiddy, *Acta Chem. Scand.*, **A29**, 876 (1975).
14. L. Hecker, L. W. Reeves, and A. S. Tracey, *Mol. Cryst. Liq. Cryst.*, **53**, 77 (1979).
15. F. Y. Fujiwara and L. W. Reeves, *J. Phys. Chem.*, (submitted).