

Chemical Reviews

Volume 81, Number 1

February 1981

New Lyotropic Liquid Crystals Composed of Finite Nonspherical Micelles

BRUCE J. FORREST and LEONARD W. REEVES*

Chemistry Department, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Received July 16, 1980

Historical Background

Amphiphile molecules and ions, in low concentrations in water disperse individually, then above a critical micelle concentration, form micelles.^{1,2} These micelles are agglomerations of amphiphiles which spontaneously form a hydrophobic core and an interfacial polar region within the aqueous solvent.² This hydrophobic effect is paramount in the formation of lyotropic liquid crystals,³ solubilization of organic compounds,⁴ and acceleration or retardation of the rates of some chemical reactions,⁵ and principally it is the cornerstone of the life process, namely the biological membrane matrix.⁶ It is the lipid bilayer in the living state supporting peripheral and integral membrane proteins which provide for the dynamics of life.

In general, the geometries of the hydrophobic cores of micellar units are many and varied, as is the ability of amphiphiles to accommodate to varied interface curvature. For want of a better term, we shall refer to all agglomerations of amphiphiles as micellar structures regardless of size or shape. Since the existence of rod-like micelles is accepted,¹ the definition becomes a question of symmetry in the sense that micelles might possess a point of symmetry and be spherical, an axis of symmetry and be rodlike or cylindrical, or a plane of symmetry and be composed of a planar bilayer of amphiphiles. The most common local symmetry of the biological membrane is certainly that of an infinitely extended planar bilayer micelle, but this, as we have indicated, is interrupted by protein inclusions.

The occurrence of lyotropic liquid crystalline forms based on the hydrophobic effect depends on the long-range repulsive forces between micellar interfaces. Repeating micellar units in a positional array form the well-characterized L_{α} lamellar mesophase and the H_{α} hexagonal phase which have planes and axes of repeating order, respectively.⁷ It is important to understand that the building blocks of the structures are very well ordered in these cases, but that the interior of the building blocks which contain hydrocarbon chains are not as well ordered. The amount of disorder and some description of it inside the micellar structures are very important in discussing any process at a molecular level. Fortunately, the ordered array of micellar superstruc-



Bruce J. Forrest, Research Associate, Chemistry Department, University of Waterloo, graduated with a Ph.D. in 1978 from Simon Fraser University where he worked on nuclear magnetic resonance studies of model membranes. In 1978, he became a research associate of Dr. L. W. Reeves at the University of Waterloo and joined the investigation of lyotropic liquid crystalline systems. Effective July 1981, he will be an NSERC Research Fellow at Dalhousie University, Halifax, Nova Scotia.



Leonard W. Reeves, Professor of Chemistry, University of Waterloo, graduated with a Ph.D. in 1954 from the University of Bristol and became a research associate of Professor Joel H. Hildebrand at University of California, Berkeley, 1954–1956. After postdoctoral work with W. G. Schneider at NRC, 1956–1957, he became assistant professor at the University of British Columbia and rose to the rank of Professor in 1965. In 1969 he became Professor at the University of Waterloo. He has maintained a laboratory at the University of Scio Paulo since 1967 as a Visiting Professor. Since working with W. G. Schneider, he has continued work with nuclear magnetic resonance in chemistry, at first as a developing technique and more recently as a tool. In the last 10 years he has become interested in new lyotropic liquid crystals the subject of this article. He is a Fellow of the Royal Society of Canada.

tures is an excellently defined framework to position the amphiphiles in space while they are subjected to the

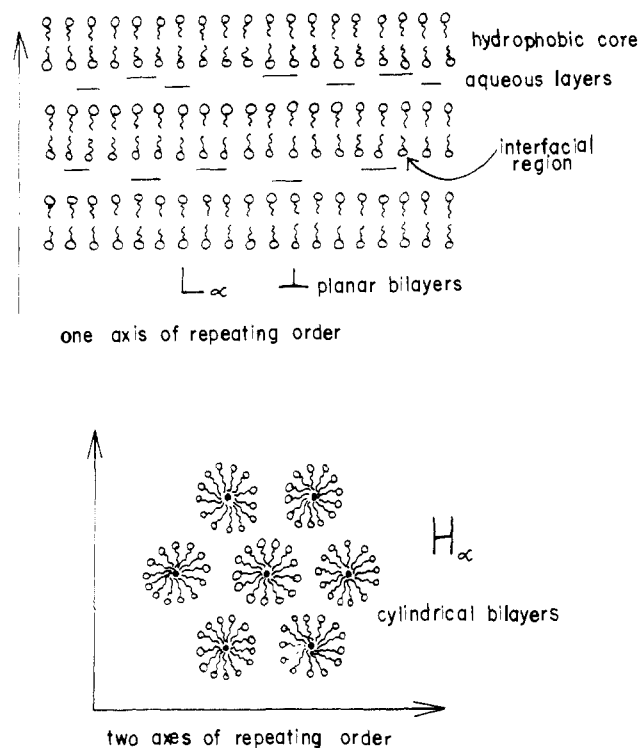


Figure 1. Top: Schematic representation of a lamellar phase composed of infinite long bilayers. The circles represent the polar head groups of the amphiphiles and the wavy lines the hydrocarbon tails. Bottom: Cross-sectional view of a hexagonal phase formed by infinitely long cylindrical micelles located at the centers of a two-dimensional hexagonal lattice.

modern array of such molecular tools as nuclear magnetic resonance (NMR).

In Figure 1, the representation of the H_α hexagonal and L_α lamellar mesophase structures which have repeating positional order is largely the result of the work of Luzzatti and co-workers.⁷ Several other structures have been confirmed or proposed within the liquid crystalline classification, but we shall limit our remarks to the L_α and H_α structures which are relevant to nematic lyotropic systems. In further discussion, we shall refer to micelles as the fundamental units of nematic lyotropic systems, while molecules are the corresponding unit in the case of thermotropic liquid crystals. Since the majority of X-ray diffraction studies have been confined to binary water/amphiphile systems which do not in general form lyotropic nematic phases, the latter had not been recognized as a distinct class of lyotropic crystals until after the recent work using nuclear magnetic resonance. The lyotropic systems have been labeled nematic, inferring an absence of positional order of the micellar units, although some repeating order has been recently discovered.⁸ These effects, however, are highly dependent on the size and nature of the sample container.

The Process of Magnetic Alignment of Liquid Crystals

The experiment which provided the motive for the investigation of lyotropic liquid crystals in magnetic fields was the discovery by Saupe and Englert⁹ that small solute molecules such as benzene were oriented and aligned by thermotropic liquid crystals. The proton magnetic resonance spectra of a relatively smaller number of spin $1/2$ nuclei, which are coupled by both

indirect pseudo-scalar coupling and through-space dipole-dipole coupling which is not completely averaged to zero, can be interpreted in terms of the motional constants of the anisotropic tumbling of the ordered solutes and the relative internuclear distances.¹⁰ This had become a widely used tool for molecular structure, and it was a natural question to seek a lyotropic liquid crystal that would spontaneously align in a magnetic field in a short time. Lawson and Flautt in 1967¹¹ described the first such aqueous lyotropic medium and furthermore proceeded to show that both polar and nonpolar molecules could be used as solutes.¹² The mesophase was based on the mixture sodium decyl sulfate/decanol/water and sodium sulfate.¹¹ The essential structural difference between the lyotropic liquid crystals of the H_α and L_α type and this new series reported first by Lawson and Flautt was not recognized, and it is the main subject of this review. Because the thermotropic liquid crystal solvents used up to 1967 for orienting and aligning small solutes were known to be nematic and were well characterized, it was customary to use the work nematic without further justification for the lyotropic variety though the definition of nematic behavior¹³ and structure is much more profound than just the property of spontaneous alignment in static magnetic fields.

When the discussion is restricted to uniaxial liquid crystals, two parameters describe the physical properties, the principal or optic axis value and the anisotropy or difference between measurements parallel and perpendicular to the optic axis or uniaxis. Selecting the important parameter of diamagnetic susceptibility, then the appropriate quantities are χ_{11} and $\Delta\chi = (\chi_{11} - \chi_{\perp})$. It is clear that $\Delta\chi$ may be zero, in which case the fluid is isotropic, at least as far as diamagnetism is concerned. $\Delta\chi > 0$ leads to a tendency for the principal axis to align parallel to a large static applied field. This we have named type I behavior.¹⁴ $\Delta\chi < 0$ results in a tendency to align the principal or optic axis of the mesophase in all directions in the perpendicular plane to the applied magnetic field (type II behavior). Lawson and Flautt¹¹ in the original communication did show that the liquid crystal prepared had $\Delta\chi < 0$; i.e., it was later classified as type II,¹⁴ but some experiments indicate that they also prepared a type I $\Delta\chi > 0$ but did not recognize or report it.

The alignment of the director or principal axis is subject to kinetic restrictions and may not perceptively occur in periods of up to 1 week because the process is so slow. In general, when a 2-day limit is taken, it is known that the H_α and L_α liquid crystals do not align in magnetic fields at temperatures of 20–35 °C. The magnetic torque and internal viscosity frictional forces have been treated by DeGennes,¹³ and some dynamical measurements on thermotropic type I nematic phases have been made by Luckhurst, Leslie, and Smith¹⁵ while type I and type II lyotropic nematic phases have been studied by Fujiwara and Reeves.¹⁶ For the lyotropic nematic liquid crystals, it was found that the velocity constant of alignment is inversely proportional to the radius of the sample tube for tubes of less than 5 mm in diameter. Although by now quite a few studies of oriented solute molecules have been made by using NMR methods in the so-called lyotropic nematic systems, systematic studies of the liquid crystals them-

selves have been almost completely limited to the studies made by Reeves and co-workers.¹⁷

The deuterium magnetic resonance signals as a function of time in the static field give an evolutionary picture of the alignment process from a completely random distribution of directors in space to one which is more favorable to the field direction. The spectrum expected from a random alignment involving a doublet determined by eq 1 has been called a powder spectrum. In eq 1, $g(\nu)$ is the line-shape function and $C = (3/2QS_{zz})$;

$$g(\nu) = \pm \frac{1}{2\sqrt{3}C} \left(1 \pm \frac{2\nu}{C} \right)^{-1/2} \quad (1)$$

$-C \leq \nu \leq C/2$ for the negative sign and $-C/2 \leq \nu \leq C$ for the positive sign. In discussing the line shapes encountered, the two-dimensional powder diagram is relevant, namely, the random alignment of directors in a plane through which the magnetic field passes.

The equation which describes such a line shape for a deuterium quadrupole doublet contains four asymptotes where, for resonances which have no line width, the intensity becomes infinite:

$$g(\nu) = \frac{1}{\sqrt{2}\pi C \left(1 \pm \frac{2\nu}{C} \right)^{1/2} \left(1 \mp \frac{\nu}{C} \right)^{1/2}} \quad (2)$$

If the sign combination in the denominator is "+-" for the parentheses as ordered, then ν takes the values $-C/2 \leq \nu \leq C$; if the other sign combination occurs "-+", then $-C \leq \nu \leq C/2$, where $C = (3/4QS_{zz})$. For the cases of a liquid crystal containing D_2O the line width of the deuterium doublet resonances is on the order of 1 Hz or somewhat less, while the overall width of the above powder spectra may be 250–1000 Hz; thus in determining the overall experimental spectrum the intrinsic line widths are negligible and eq 1 and 2 are valid except near the asymptotes. Figure 2 shows a theoretical spectrum for both cases for the situation in which C is assigned the value 1.

Experimental observations of line shapes of the D_2O deuterium magnetic resonance are characteristic of the sign of the diamagnetic anisotropy of the lyotropic mesophase and also reveals the effects of the liquid crystal/glass interface. This is illustrated in Figures 3–5. The effect of the liquid crystal/glass interface is most pronounced for type II systems, in which case the directors have a strong preference for director alignment perpendicular to the glass interface of an NMR tube. Such a result is illustrated in Figure 5. This is useful corroborative evidence with respect to the internal structure of these type II liquid crystals. Lamellar mesophases L_α similarly align with the director perpendicular to the glass interface.

In no case where a mesophase has been definitely characterized as L_α or H_α does spontaneous alignment of the directors occur around room temperature, and this, along with other evidence, suggests that there is a basic difference in these structures from the mesophases that do align in magnetic fields.

Chemical Flexibility of the Aligning Mesophases

The original lyotropic liquid crystal which Lawson and Flautt¹¹ observed to align in a static magnetic field contained two amphiphiles, water and an electrolyte.

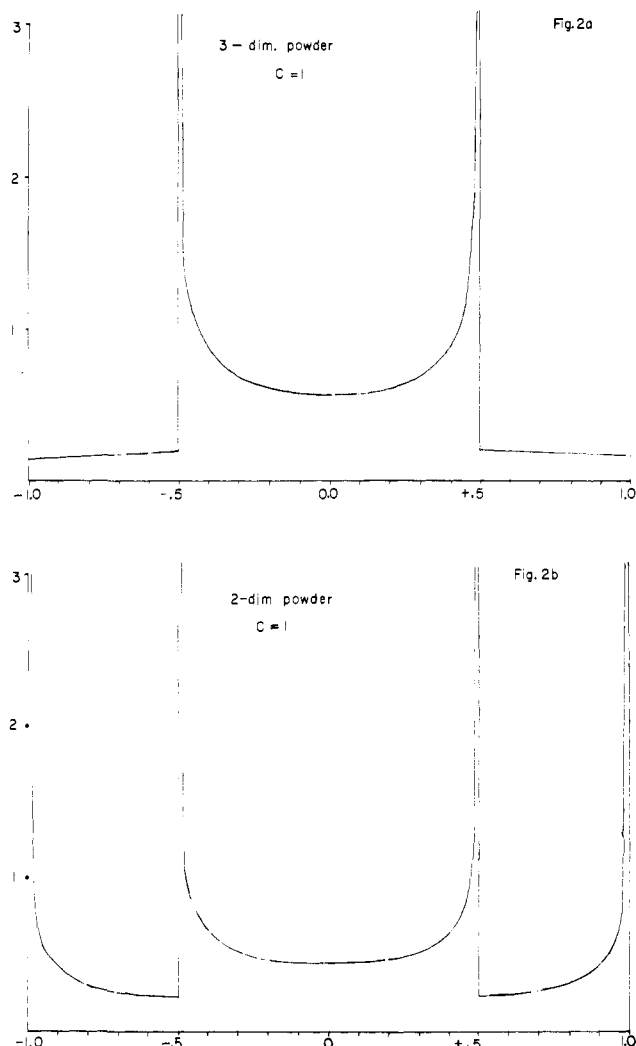


Figure 2. Top: Theoretical NMR line shape for a spin 1 system with random distribution of the directors in space. This shape is shown as a three-dimensional powder pattern. Bottom: Theoretical NMR line shape for spin 1 nuclei with random alignment of the directors in a plane through which the magnetic field passes. This shape is known as a two-dimensional powder pattern.

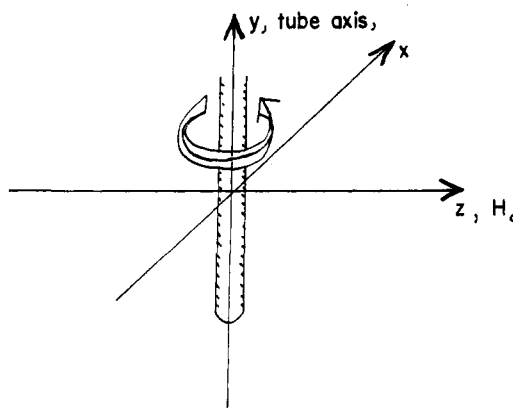


Figure 3. A reference frame for the alignment of the axis of the cylindrical sample tube, the directors in the sample, and the magnetic field. Use a right-handed Cartesian set with the z axis horizontal and the y axis vertical. The magnetic field is placed along the z axis, and the cylindrical sample tube is aligned along the y axis, which is also the axis of tube spinning for cases where spinning is used.

Since this is a new lyotropic liquid crystalline form, the question arises as to whether there are a large number of these new mesophases of varied chemical composi-

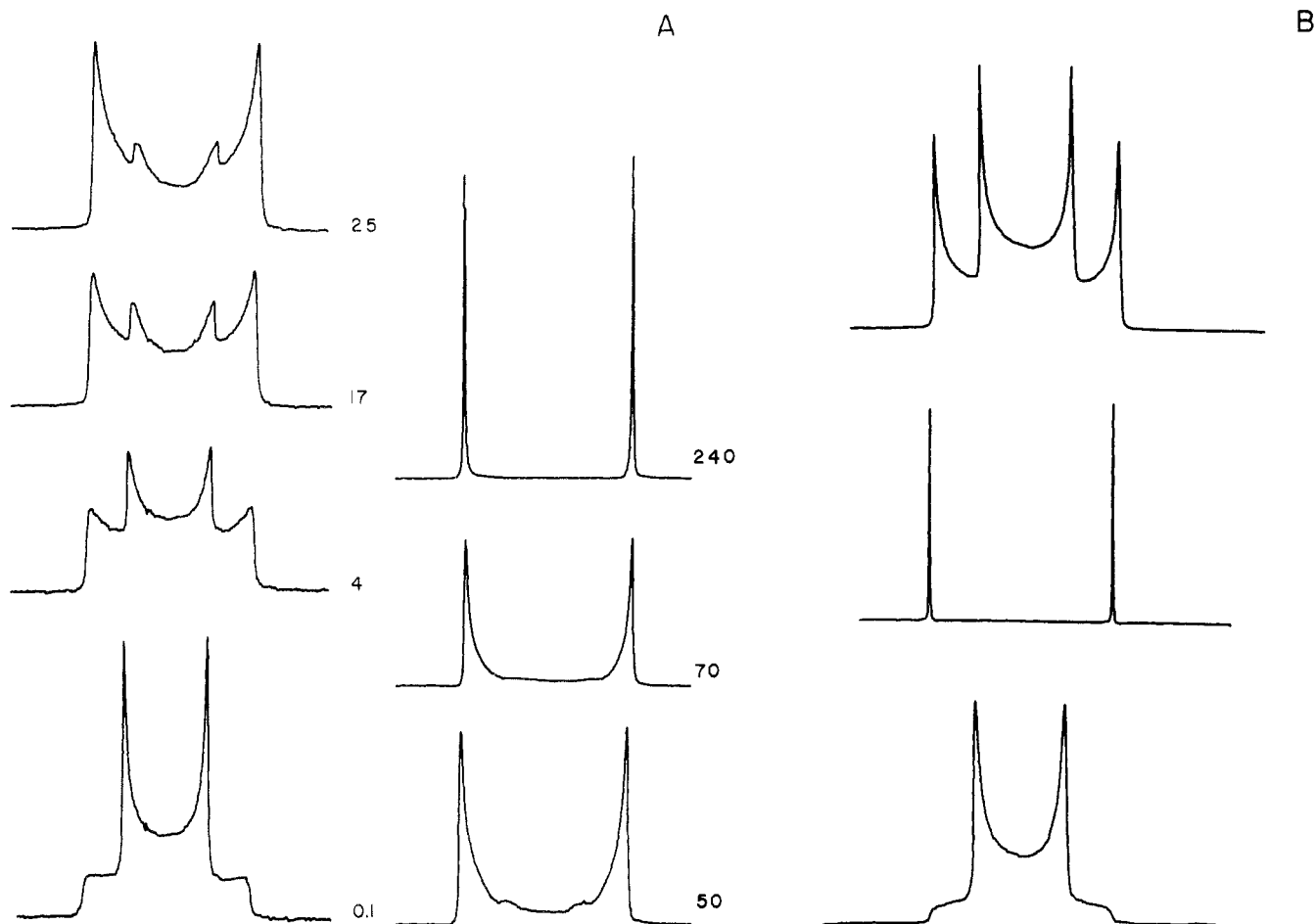


Figure 4. Director distribution from deuterium NMR: (A) Powder pattern, directors randomly distributed in space, shortly after placing a shaken sample in the magnet. Tube not spinning. The stationary sample after 17 min shows the preference for $\Omega = 0^\circ$ with growth of intensity in the wings. After 240 min, the sample is completely and uniformly aligned along the magnetic field or z axis, $\Omega = 0^\circ$, throughout the sample. The doublet separation for this case is 593 Hz at 30.6°C . Type I behavior. (B) After the directors are allowed to align as in (A), the tube is allowed to spin about the y axis for several hours at 5 Hz. When the tube is stopped and a pulse of radiofrequency is applied immediately, the spectrum is indicative of a random distribution of directors in the xz plane, i.e., perpendicular to the axis of the cylindrical sample tube.

tion. Amphiphiles are molecules or ions with a hydrophobic component, usually a hydrocarbon chain, and a polar or ionic group (headgroup) which is hydrophilic. Chemical variations have so far been restricted to the simple unbranched hydrocarbon chains with variation in the "head group". The amphiphile components may be varied in a regular manner by mixing two or more different chemical compounds in varying proportions to form a mesophase of the same structure. If the amphiphile is ionic, then a small counterion is involved, of appropriate charge. This counterion may be chemically varied, and it was such a variation, in the simplest possible manner, that led to the discovery of type I and type II mesophases.¹⁴ (See Figures 4 and 5.)

The mesophases, which do spontaneously align in magnetic fields, often contain electrolytes as did the first example prepared by Lawson and Flautt.¹¹ Variation of the chemical nature and concentration of this electrolyte does effect the type and properties of the lyotropic nematic phases rather profoundly.¹⁹ The mesophases all contain at least 50% water, which can be varied isotropically with deuterium substitution.¹⁴ The isotope effects of such a change are not yet well characterized, but they are often quite important.²⁰ Another means of chemically varying the lyotropic mesophase is to dissolve small quantities of guest molecules in the manner used for the study of structure

of oriented species by NMR spectroscopy. Such impurities can also affect the type of mesophase formed.

The first systematic studies¹⁴ of the chemical flexibility of aligning mesophases were quite important with respect to the discovery of type I and type II behavior. The Lawson and Flautt mesophase was first modified by omitting the added sodium sulfate and then further modified in a systematic manner by partial substitution of the sodium counterion for a variety of other monovalent ions, Li^+ , K^+ , Cs^+ , Rb^+ , NH_4^+ , etc. This change was achieved by maintaining the overall composition in mole terms, but using mixtures of sodium decyl sulfate/other ion decyl sulfate in varied proportions to prepare the mesophase.

These results not only illustrated the existence of the two magnetic types but also emphasized the important role of ions in provoking phase changes. Figure 6 illustrates the dependence of sodium-23 and deuterium quadrupole splitting on counterion.

A complete review of all the systematic chemical changes investigated up to now would lengthen this review without introducing new principles. A summary of all lyotropic nematic mesophases is contained in Table I along with the appropriate reference to the original literature. Variation of the following chemical factors: water content, pH of water, counterion, co-ions (added electrolytes), head groups, chain lengths of am-

SCHEME I

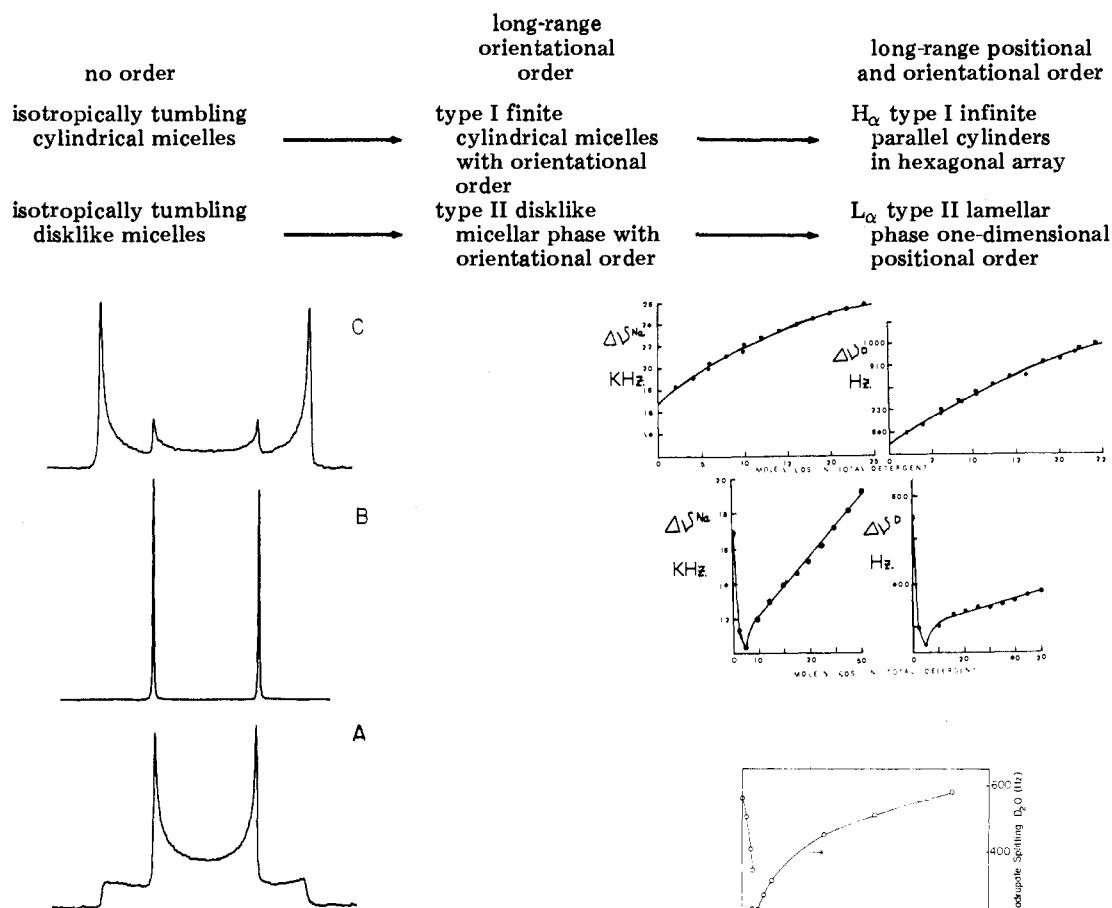


Figure 5. Director distribution for the alignment of a type II $\Delta\chi < 0$ sample. (a) Deuterium powder spectrum for the sample immediately after shaking and placing in the magnet. (b) After sample remained in the magnetic field so that alignment occurred along the perpendicular directions to the magnetic field in the xy plane. Final sharp doublet coincides with the principal peaks of the powder spectrum. (c) The sample tube is rotated by $\pi/2$ about the y axis; thus the xy plane is transformed to be the xy plane. The operation corresponds to a transformation

$$\begin{bmatrix} & & 1 \\ & & \\ -1 & & \end{bmatrix}$$

The magnetic field now passes through the plane containing the directors. The spectrum shows that the $\Omega = 0$ angles perpendicular to glass tube interface are favored.

phiphile, and added guests or impurity species, have led to the discovery of a whole array of lyotropic nematic systems of both magnetic types.

Structural Evidence

The study of nuclear magnetic resonance signals is probably the best way to probe phase diagrams; it is especially effective in establishing the presence of two or more coexistent phases from the number of D_2O deuterium quadrupole splittings. Although 2H NMR is not a direct structural tool, it is a useful but indirect approach to the structure of lyotropic nematics. Chemical variation of hexagonal H_α and lamellar L_α systems lead to mesophase transitions to type I and type II nematic systems, respectively, as water content is increased.^{20,21} The spontaneously aligning phase always has a lower measured degree of order than the classical H_α or L_α phase with which it is in thermodynamic equilibrium (see Figures 7 and 8). This strongly

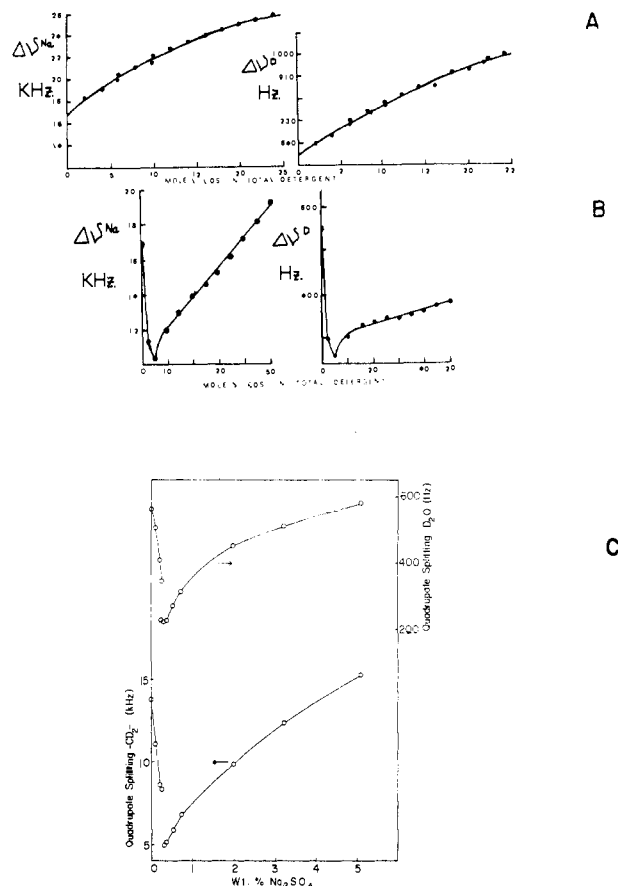


Figure 6. Effect of change of counterions and co-ions on the magnetic type of the mesophase formed. (A) Ternary mesophases prepared from 37 wt % sodium decyl sulfate, 7 wt % decanol and 56 wt % D_2O were modified by substituting lithium decyl sulfate on a mole for mole basis for sodium decyl sulfate up to 25 mol % in the total detergent. The splitting between the outer 3:4:3 quadrupole triplet for sodium-23 magnetic resonance signals $\Delta\nu^{Na}$ and the deuterium magnetic resonance doublet $\Delta\nu^D$ has been plotted against mole fraction of lithium decyl sulfate in the total detergent. The continuous curve with positive slope indicates no change in phase. The mesophases remain type I throughout. (B) Mesophase compositions as in (A), but with cesium decyl sulfate substituted for the sodium detergent. The addition of ~ 5 mol % cesium decyl sulfate causes a change in phase exemplified by the discontinuity in the dependence of NMR parameters on detergent composition. There is a phase change type I $\Delta\chi > 0 \rightarrow$ type II $\Delta\chi < 0$ at this point. (C) The addition of sodium sulfate to the ternary mesophase of composition similar to (A) causes a change in phase type I \rightarrow type II when 0.262 wt % sodium sulfate is reached in the phase. On the left of (C) the deuterium doublet of 19% sodium 3,3,4,4-tetradeuteriododecyl sulfate in the mixture is plotted against the added sodium sulfate, while in the right the deuterium doublet splitting from the 0.1% D_2O/H_2O is represented.

suggests the mesophase sequence given in Scheme I, with water content decreasing from left to right.

In fact, Reiss-Husson and Luzzati, in 1964, using an improved small-angle X-ray scattering technique,

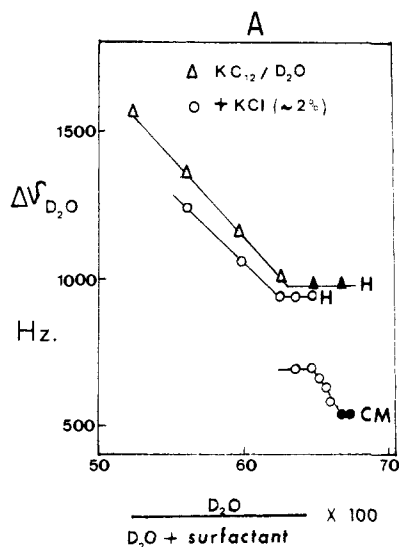


Figure 7. Deuterium quadrupole splitting of D_2O in binary mesophases potassium laurate/water and related ternary mesophases potassium laurate/water/KCl. The binary system is denoted by Δ and concentrations of water vary between 52 and 67 wt %. The ternary system is distinguished by \circ and the compositions may be described by the weight ratio potassium laurate/potassium chloride which is always 15.00. To this solid mixture was added D_2O to give 54.54 to 65.88 % by weight in the total mixture. In both cases the quadrupole splittings for D_2O are plotted vertically. For powder pattern spectra the quadrupole splitting is doubled in all cases before plotting. This procedure is justified by the type I behavior.

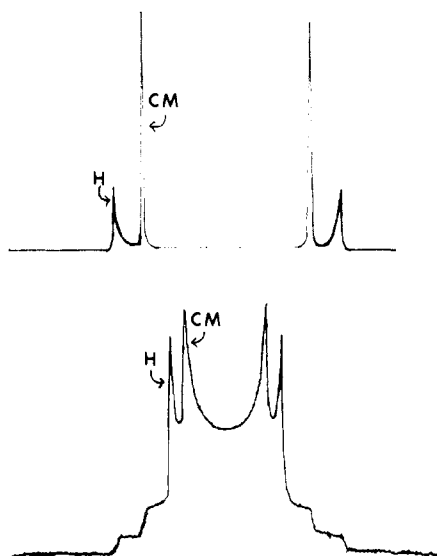


Figure 8. The lower spectrum of two coexisting phases was taken after 5 min in the magnetic field. The mesophases correspond to the region where the hexagonal phase and the denser intermediate mesophase are in equilibrium (cf. figure 7). The hexagonal phase has a D_2O deuterium powder spectrum with the larger splitting labeled H, while the powder spectrum of lower splitting is assigned to the denser "nematic" phase. After 1 week in the magnetic field, both birefringent phases have partly aligned, especially the "nematic" phase. Both are clearly type I $\Delta\chi > 0$ where the splitting of the aligned phase corresponds to the wings of the separate powder spectra below.

studied binary mixtures of a number of amphiphiles including sodium laurate from the isotropic to the liquid crystalline region.⁷⁰ These workers discovered, between the isotropic and hexagonal regions, an area of two phases, one a hexagonal phase with two-dimensional order as shown in Figure 1, and a structurally related second phase composed of rod-shaped micelles pos-

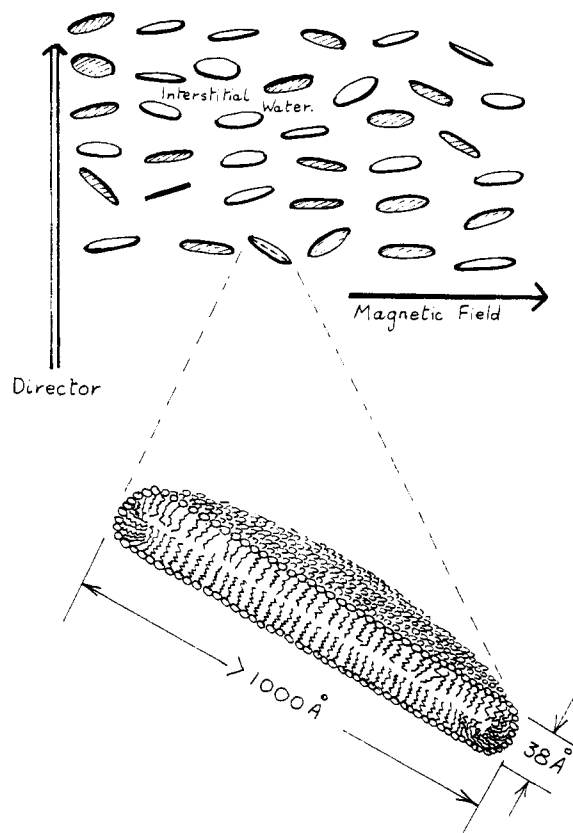


Figure 9. Schematic representation of a type II DM mesophase. The size distribution of the micelles is unknown, but average sizes are of the order indicated by the expanded diagram of an individual disk. The disks are free to move in the aqueous medium, but the mean direction of the normal to each disk is perpendicular to the applied magnetic field. For purposes of clarity, the intermicellar distance has been exaggerated and is in reality on the order of 100 Å.

sessing little positional order. Additional confirmation of these proposed sequences has come from recent light scattering experiments on an isotropic system of sodium decyl sulfate/electrolyte/water which showed the existence of rod-shaped micelles approximately 600 Å in length.²² The chemical composition of this system is that which would be obtained by dilution of a type I sodium decyl sulfate/electrolyte/water mesophase. In addition, the specific gravity of phases formed are in the order isotropic > type I nematic > hexagonal and isotropic > type II nematic > lamellar. In other words, the higher the water content of a phase, the higher is its specific gravity.

Recent low-angle X-ray diffraction experiments which are characteristic of structural arrangements in the colloidal range have shown that the original type II mesophase based on sodium decyl sulfate consists of finite disk-shaped micelles of bilayer thickness (~ 38 Å) which are greater than 1000 Å in diameter. There exists an intermicelle distance of, on the average, 90 Å. No positional order of the micellar units was detected.²³ However, subsequent experiments showed some evidence of a certain amount of positional order, although, as mentioned previously, this effect is dependent both on the size and nature of the container.^{23,24}

The structure of the type II mesophase is diagrammatically illustrated in Figure 9. Preliminary studies of a type I nematic based on potassium laurate showed the presence of finite cylindrical micelles of diameter 42 Å in an aqueous matrix of thickness 90–190 Å, which

again possesses no long-range positional order.²⁵

At this point it must be remembered that low-angle X-ray studies on lamellar and hexagonal systems give directly the repeating distance which includes one bilayer thickness and the thickness of one water layer. The bilayer thickness is then derived by using water and hydrocarbon densities to calculate indirectly the bilayer thickness. The low-angle X-ray diffraction of the lyotropic nematics gives a more direct measure of the bilayer thickness of the disks or cylinders, which includes, of course, the thickness of adsorbed water and counter ions. The inclusion of these adsorbed layers accounts for the rather large bilayer thicknesses of 38 and 43 Å for type II DM sodium decyl sulfate and type I CM potassium laurate systems. For example, a bilayer thickness of approximately 33 Å would be expected for the laurate cylinders when the amphiphile is in the all-trans conformation, and an even smaller value is expected for chains which are effectively shortened by the presence of kinks or jogs.

It is possible to use deuterium NMR order parameters to calculate the thickness of a bilayer whose amphiphiles are undergoing *trans/gauche* motion.²⁶ This motion lowers the observed order parameters and at the same time reduces the bilayer thickness. In the case of lyotropic nematics the observed quadrupole splittings and derived order parameters must be corrected for their reduction by rigid body and micelle motions.²⁷ One such case where both the extent of micelle motion and X-ray distances are known is for the type I CM potassium laurate mesophase. When a typical order parameter of 0.70 for rigid body motion is assumed, a bilayer thickness of approximately 23 Å may be calculated. This distance is much smaller than the X-ray dimension of 43 Å, which itself is much larger than the thickness expected for the extended all-trans conformation. The apparent discrepancy lies in the fact that the low-angle X-ray results for lyotropic nematics includes an annulus of water and ions which are adsorbed on the surface. The above calculations indicate that the thickness of the adsorbed layer is on the order of 10 Å across. It must be pointed out, however, that the calculation of bilayer thickness from ²H NMR data is not a very sensitive function of the observed order parameters. Laser light scattering has also been employed to study type II DM liquid crystals based on laurate and decyl sulfate amphiphiles.²⁸

The two main classes, type I CM and type II DM lyomesophases, suggest interesting new mesophases only some of which have been prepared. Of the nematic variety it should be possible to change the sign of the diamagnetic anisotropy of cylindrical and disklike micelles and so prepare type I DM and type II CM mesophases. [A type I DM phase has recently been prepared in this laboratory by partial substitution of potassium (heptyloxy)benzoate for sodium lauroylsarcosinate in a type II DM phase. An intermediate phase which does not align in a magnetic field ($\Delta\chi = 0$) has been observed and named type 0 DM.] This change in the determining diamagnetic anisotropy, namely that of the pseudo-extended hydrocarbon chains, should be feasible by substitution of aromatic rings constrained to rotate with the para axis perpendicular to the aqueous interface. A more interesting modification is the use of a resolved optically active

detergent to make up the micelles. Should such a detergent make up 100% of the micelle amphiphiles, then a cholesteric mesophase may result. It is known that no cooperative chiral effect is transferred from bilayer to bilayer across the aqueous barrier in L_α lamellar phases. There is, therefore, no lamellar phase with a screw axis. These cholesteric lyomesophases have been discovered by using the decyl ester of D- or L-alanine, with electrolyte and water.²⁹ At low water content, when the micelles are large, no twist axis can be detected, but there is a transition to a cholesteric phase at higher water contents as detected by polarized microscopy and NMR. Equal amounts of D and L mesophases combine to form a type II DM nematic phase, indicating that the chiral phases have a twist axis which aligns parallel to the static magnetic field.³⁰ A cholesteric lyomesophase derived from type I CM systems has also been prepared but has not yet been reported.³¹ It is possible to induce a twist axis into a normal nematic phase by adding chiral compounds as guests to nonoptically active detergents in making the phases. This has been done with cholesterol additions to a mesophase based on decyl ammonium chloride³² in a procedure earlier developed by Fujiwara and Reeves.³³ Brucine sulfate and tartaric acid also induce a twist axis. Tracey and Deihl detected two environments for D- and L-alanine in a mesophase based on decyl sulfate with an optically resolved amphiphile additive.³⁴

Bilayer Chemistry

The ²H NMR order parameter of a carbon-deuterium bond axis is given by

$$S_{CD} = \frac{1}{2}(3 \cos^2 \theta - 1) \quad (3)$$

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. The residual ²H NMR quadrupole splittings for an aligned anisotropic sample are given by³⁵

$$\Delta\nu = \frac{3}{2}QS_{CD} \times \frac{1}{2}(3 \cos^2 \Omega - 1) \quad (4)$$

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. In the case of type I CM nematics, $\Omega = 0^\circ$, while for type II DM liquid crystals, $\Omega = 90^\circ$. Since the experimentally observed quadrupole splittings are proportional to the order parameter of each C-D bond axis which can be isotropically labeled, ²H NMR provides quantitative information of the order and motional anisotropy of amphiphilic molecules without the perturbation introduced by a large reporter group. The variation of order with position along a hydrocarbon chain has been dubbed "the order profile".

Significant work has been done in binary lamellar and hexagonal soap/water systems as well as phospholipid water systems. However, these studies are limited in that little chemical variation of the system is possible, and the observations are limited in most cases to one chemical species. It should be emphasized in this regard that the use of any probe molecule to infer order profiles for a chemically distinct species is highly unsatisfactory. For example, for the original Lawson and Flautt type

TABLE I

amphiphile	counterion	electrolyte	guests	magnetic type	ref
A. Type II DM Lyomesophases					
decyl sulfate, decanol	Na ⁺	Na ₂ SO ₄	ethanol, formamide, carboxylic acids and carboxylates, ethylene carbonate, ethylene monothiocarbonate, furan thiophene, tetrafluoro-1,3-dithietane		11, 12, 21, 37, 41, 44, 54-57
decyl sulfate, decanol	Na ⁺	(NH ₄) ₂ SO ₄ , CH ₃ NH ₃ Cl, (CH ₃) ₃ NHCl, (CH ₃) ₄ NCl, [(CH ₃) ₄ N] ₂ SO ₄			36, 61
decyl sulfate, decanol	CH ₃ NH ₃ ⁺ (CH ₃) ₂ Sn ⁺ ND ₄ ⁺ , ND ₃ H ⁺ , NH ₄ ⁺ (CH ₃) ₂ NH ⁺ , (CH ₃) ₃ N ⁺	Na ₂ SO ₄	methanol		47, 58-61
decyl sulfate, decanol	Na ⁺ Na ⁺ /Me ₃ Pb ⁺	methylmercury nitrate, trimethyltin nitrate, NaNO ₃ , trimethyllead nitrate			62
octyl sulfate, octanol	Na ⁺	Na ₂ SO ₄			11
decanoate	Na ⁺ , K ⁺	KCl			28
decanoate, decanol	Na ⁺ , K ⁺	KCl			28
HDTMA, ^a	Br ⁻ , Cl ⁻ , NO ₃ ⁻	NaBr, NaCl, NaNO ₃	SDS, DACl, dipalmitoyllecithin, palmitic acid, butanoic acid		29, 40, 44, 63
HDPyr, ^a decanol	Cl ⁻	NaCl	SDS or DACl		29, 63
HDPyr, ^a decanol, HDTMA ^a	Cl ⁻ , Br ⁻	NaCl			63
laurate, decanol	Rb ⁺ , Cs ⁺ K ⁺ , Na ⁺	NaBr, KCl, RbCl, CsCl	benzene, ethylenimine, methanol		17, 42, 64
laurate, DTMA ^a	K ⁺ , Br ⁻	NaBr			42
DA ^a	Cl ⁻ , BF ₄ ⁻	NaCl, NH ₄ Cl, NH ₄ BF ₄	Tl(CH ₃) ₂ NO ₃ , laurate, palmitate, alcohols, alkanes		19, 20, 37, 41, 65
DA, ^a decanol	Cl ⁻ , acetate ((CH ₃) ₂ AsO ₂) ⁻ BF ₄ ⁻ , F ⁻	NH ₄ Cl, NH ₄ BF ₄ , NaOAc	methanol, cholesterol cesium <i>p</i> -nitrobenzoate		33, 38, 46, 65-67
Da, ^a HDTMA, ^a decanol	Br ⁻ , Cl ⁻	NaCl			43
lauroyl sarcosinate, decanol	Na ⁺	Na ₂ SO ₄			68
B. Type I CM Lyomesophases					
decyl sulfate, decanol	Na ⁺ , Cs ⁺ , Rb ⁺ , Li ⁺ , anilinium, NH ₄ ⁺ , C ₂ H ₅ NH ₃ ⁺				14, 52, 53
decyl sulfate	Cs ⁺ , Na ⁺	Na ₂ SO ₄			16, 19, 45
laurate	K ⁺	KCl			16, 19
C. Induced Cholesteric Mesophases					
decyl sulfate, decanol	Cs ⁺		tartaric acid	II	32
decyl sulfate, decanol	NH ₄ ⁺	(NH ₄) ₂ SO ₄	brucine sulfate	II	32
decylammonium	Cl ⁻		cholesterol	II	32
<i>N</i> -lauroyl-DL-alanine	K ⁺	K ₂ SO ₄	brucine	II	68
lauroyl sarcosinate	Na ⁺	Na ₂ SO ₄	brucine	II	68

D. Cholesteric Lyomesophases ^b			
L-alanine decyl ester hydrochloride	Cl ⁻	Na ₂ SO ₄	II 29
D-alanine decyl ester hydrochloride	Cl ⁻	Na ₂ SO ₄	II 29
N-lauroyl-L-alanine, decanol	K ⁺	K ₂ SO ₄	I 31
N-lauroyl-L-serine, decanol	K ⁺	K ₂ SO ₄	II 69

^a Abbreviations used: HDTA, hexadecyltrimethylammonium; HDPy, hexadecylpyridinium; DA, decylammonium; DM, disk micelle; CM, cylindrical micelle; SDS, sodium decyl sulfate. ^b Racemic mixtures of the optically active amphiphiles may be used to prepare noncholesteric Type I CM or type II DM phases.

II DM mesophase, very different order parameters have been observed for the two amphiphilic species, decyl sulfate and decanol, which differ only in the nature of the hydrophilic head group.³⁶ In addition, given the same head group, variation in chain length plays an important role in the observed order profile; i.e., the profile of a guest or probe molecule present in small quantities is influenced by the effective length of the host amphiphile. These two points will be discussed in more detail in succeeding sections.

Motion of Hydrocarbon Chains in Bilayers

Many possible motions are possible for lyotropic nematic mesophases, and each of these contributes to the experimentally determined order parameter. Thus²⁷

$$S_{\text{exp}} = S_{\text{MO}} S_{\text{CO}} S_{\text{k/j}} S_{\text{diff}} \times \frac{1}{2}(3 \cos^2 \Omega - 1) \quad (5)$$

where S_{MO} is due to oscillation of a finite micelle as a whole about the director, S_{CO} is due to rigid body movement of the long axis of the chain in an oscillatory fashion about the perpendicular to the hydrophobic-hydrophilic interface, $S_{\text{k/j}}$ is due to segmental motion of the trans-gauche type which result in the formation of kinks and/or jogs in the chain long axis, and S_{diff} is due to diffusion of amphiphiles around the edges of a finite micelle (edge effects). Kinks and jogs are defined as gauche[±]/trans/gauche[∓] and gauche[±]/multiple trans/gauche[∓] sequences, respectively. Motions of the type which contribute to S_{MO} , S_{CO} , and S_{diff} are common for all segments of a chain, and therefore a relative measure of motions of the gauche-trans type which contribute to $S_{\text{k/j}}$ can be determined by taking ratios of the form

$$\frac{(S_{\text{exp}})_x}{(S_{\text{exp}})_y} = \frac{(S_{\text{k/j}})_x}{(S_{\text{k/j}})_y} \quad (6)$$

where x and y refer to two different segments of the same chain. For example, taking the y th segment to be the terminal methyl group, an amphiphile in the all-trans conformation rotating rapidly about its long axis would yield a ratio of 3.00 for all positions, x .³⁸ In other words a plot of the relative order parameters (or quadrupole splittings to which they are related) vs. chain carbon number would show a plateau at the value of 3.00 which would drop to 1.00 for the terminal methyl group. Therefore deviations from an all-trans chain are manifested in alteration from a value of 3.00 for positions x on the chain. In this way the relative amounts of k/j motion of different chains in the same liquid crystal may be compared. One interesting application of the use of ratios of quadrupole splittings has been the study of trans-gauche type motions, as type II DM mesophases are diluted with water over the range of stability of the aligning liquid crystal.^{33,39} It was found that changes in the absolute degrees of order of the chain varied, but that the ratios of quadrupole splittings remained constant. Such an effect indicates a decrease in micelle size or an increase in intermicellar distance as the water content is increased but that motions of the trans-gauche type are unchanged. In other words, amphiphile-amphiphile packing of the micellar units is not affected by dilution of the liquid crystalline system within the range of the liquid crystal.

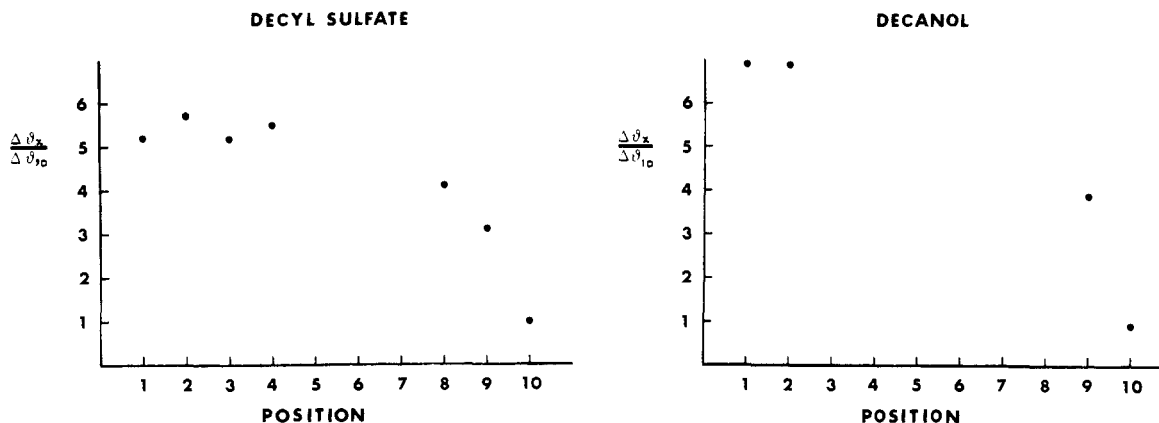


Figure 10. Ratios of deuterium quadrupole splittings for positions x along the chain, relative to that observed for the terminal position in a type II DM liquid crystal. The ratios for decanol are much higher, indicating more motion of the trans/gauche type. (See eq 6.)

As previously noted, many chemical factors may affect the experimentally determined order parameters of lyotropic nematics. These include the chemical identity of the hydrophilic head group, heterogeneity of chain length, oscillation of the micelles as a whole, the nature of the counterions, effects of added electrolyte, and angular effects due to constraints placed upon molecular conformations as well as the effect of guest molecules.

Influence of Head Group

In a lyomesophase based on amphiphiles of the same chain length, differing only in the nature of the head group, quite dissimilar motion profiles may be observed. This effect was first seen in 1975 for decyl sulfate and decanol copresent in the same type II DM liquid crystal.³⁶ This effect is illustrated in Figure 10, where decyl sulfate exhibits a characteristic alternation of order parameter for segments near the head group. Decanol (a neutral amphiphile), on the other hand, exhibits a quite different motional profile. A second example is the case of the differing profiles of palmitic acid and dipalmitoyllecithin, guests present in a type II DM liquid crystal based on hexadecyltrimethylammonium bromide, where these amphiphiles all possess hydrocarbon chains 16 carbons in length.⁴⁰ Only the head groups are different. These facts illustrate that for an amphiphile of given chain length, the chemical nature of the head group and its characteristic anchoring with water at the interface dictate to a large extent the experimentally determined order parameter.

Effect of Chain Length

The effect of heterogeneity of chain length on the experimentally determined order profiles has been examined in a number of studies employing small amounts of a guest carboxylic acid or carboxylate which does not conform to the length of the host detergent.^{37,41,42} It has been found that the degree of order of the α position of each guest species increases with increasing chain length up to that point where the length of the guest chain approximately matches that of the host, at which point no further increase is observed. Such behavior is indicative of either a decrease in the freedom of conformational motions as the chain is lengthened or a decrease in the amplitude of oscil-

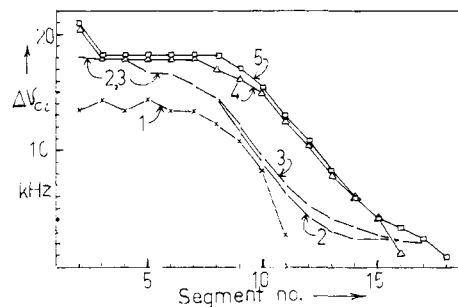


Figure 11. Deuterium NMR quadrupole splittings of palmitic and stearic acids and their corresponding anions in a sodium decyl sulfate type II DM mesophase. (1) Sodium decyl sulfate profile. (2) Stearic- d_{35} acid. (3) Palmitic- d_{31} acid. (4) Palmitate- d_{31} . (5) Stearate- d_{35} .

lations of the average chain axis about the normal to the interface. This work has recently been extended to include complete order parameter profiles which bear upon the aspect of misfit chains.³⁷ In the case of "too long" fatty acid guests intercalated into a type II DM mesophase based on sodium decyl sulfate, the guest head group anchoring determines the form of the order profile to a very large extent within the half-bilayer distance, but the guests are uniformly of higher order than the host in the first methylene segments. The excess chain lengths participate in the disordered region at the center of the bilayer and have low and steadily decreasing order. Ionization of guest head groups produces a dramatic change in the guest profile. This effect is illustrated in Figure 11 which shows a very long plateau of constant order for the carboxylate chains and a higher degree of order for these guests which extends well beyond the half-bilayer distance. Clearly the anchoring of the carboxylate head group is much different than that of the protonated form and may occur by means of hydrogen bond bridges through water structure between head groups.

A different situation arises for the carboxylic acids palmitic and myristic acid incorporated into a decylammonium chloride type II DM mesophase. In this case, the fall in order of the guest chains is extremely rapid, occurring within the plateau region of constant order of the host. The hydration anchoring of adjacent NH_3^+ and COOH groups must be the specific cause of these changes in the average motion of the guest chains.

As mentioned previously, determination of order parameters of C-D bond vectors leads to some esti-

mation of the number of gauche rotamers along the amphiphile chains. However, determination of the average conformation is not in general possible, due to the large number of conformations which must be considered in addition to the importance of the anchoring of the hydrophobic-hydrophilic interface which must be considered. If the amphiphile is chosen to be sufficiently short, the problem is greatly simplified. On the basis of two possible models of anchoring of the polar group at the interface, the conformation of butanoic acid present as a guest in type II DM liquid crystals has been explained in terms of two predominant conformations, one an all-trans arrangement (63%) and the second possessing a single gauche rotation about the α, β C-C bond (37%).⁴⁴

Electrolytes

A logical extension of the effect of differing head groups on chain profiles involves a continuous variation in the net charge at the micelle interface and the study of the binding of ions and water at the interface. A type II potassium laurate DM mesophase which possesses a negatively charged surface may be chemically varied by the replacement of up to 65% of the laurate by the positively charged decyltrimethylammonium ion and up to 100% by a hexadecyltrimethylammonium amphiphile.^{42,43} Thus the charge on the finite disk micelles may be readily and continuously varied. Deuterium magnetic resonance spectra of deuterated water show that there is a water structure built around the carboxylate head groups which ceases to be stable when about 30% of the laurate is replaced by decyltrimethylammonium. The alteration of water structure is characterized by a rapid decrease in quadrupole splitting of the D₂O without an accompanying phase change.

By studies of the change in quadrupole splittings of ²³Na of added electrolyte and the ⁸¹Br co-ion, the binding of ions to the micelle surface has been investigated. The results can be interpreted in terms of a three-site model. In the first site, sodium ions are located within the plane of the interface, shared by two carboxylate residues. With replacement of carboxylate by trimethylammonium, some of these bridging sites are not longer available, and they are replaced by weakly hydrated sites involving a single carboxylate group in which the sodium ions are displaced from the plane of the interface but are still bound to it via the single carboxylates. In the third site sodium ions are remote from the interface in an aqueous environment. Exchange between all sites is rapid on the NMR time scale, and thus the observed sodium quadrupole splitting is given by

$$\Delta\nu_{\text{Na}} = X_I \Delta\nu_I + X_{II} \Delta\nu_{II} + X_{III} \Delta\nu_{III} \quad (7)$$

where X_i are the mole fraction of sodium ions in site i , and $\Delta\nu_i$ are the characteristic quadrupole splittings for each site.

The effect of added electrolyte on the inner structure of the micelles is generally small; however, it has been found that a type I sodium decyl sulfate/decanol/water mesophase is transformed into a type II mesophase by the addition of less than 0.3 wt % sodium sulfate (see Figure 6c). Obviously in this case the presence of an extremely small amount of sodium ions bound at the

interface is a sufficient perturbation to alter the curvature of the interface itself.¹⁹

Counterion Effects

The effect of changing counterions may in general be quite varied, affecting the flexibility of the chain to a greater or lesser degree or even inducing phase changes. From the changes in ratios of quadrupole splittings of type II decyl sulfate mesophase with counterion, the series $(\text{CH}_3)_2\text{NH}_2^+ > (\text{CH}_3)_3\text{NH}^+ \sim \text{CH}_3\text{NH}_3^+ > \text{NH}_4^+ \sim (\text{CH}_3)_4\text{N}^+$ has been shown³⁸ to describe the ability of various counterions to build structure in the electrical double layer interface. In addition, the chain flexibility is a function of counterion even near the chain termini; i.e., the influence of counterion on interface architecture is felt over considerable distances.

More spectacular modifications are witnessed upon the substitution of various other alkali metal cations for Na⁺ of sodium decyl sulfate type I mesophases.¹⁴ For example, substitution of less than 5 mol % CsDS for NaDS induces a phase change from type I to type II. That such a small change in the chemical composition induces a modification of the interface curvature illustrates the importance of the nature of the counterion in the dictation of the properties of the mesophase.

Association of monoatomic ions with the interface of the micelles results in a distortion of their average spherical symmetry. This distortion should result in an anisotropy in the chemical shift, and indeed such an effect has been reported.⁴⁵ Similar distortions have been observed for tetrahedral counterions where dipole-dipole or nuclear quadrupole couplings are averaged to zero in true tetrahedral symmetry, but become nonzero for slightly distorted tetrahedra. One example of such a phenomenon is the case of the BF₄⁻ ion in a lyotropic nematic phase based on decylammonium tetrafluoroborate.⁴⁶ In this case the ¹⁹F NMR spectra (a quartet of quartets) is composed of a main 1:1:1:1 quartet caused by a combination of scalar and dipolar ¹¹B-¹⁹F coupling which are in turn split into 1:3:3:1 quartets due to smaller F-F dipolar coupling in the distorted tetrahedron. Similar distortions have been observed for NH₄⁺ and DH₄⁺ associated with lyotropic liquid crystalline phases.⁴⁷

Angular Effects of Local Constraints on Motion

Another very important contribution to experimentally determined motion profiles is the effect of angular constraint. For example, the absolute values of the ²H NMR quadrupole splittings for specifically deuterated cis-unsaturated phospholipids in bilayer model membranes yield an unusual order parameter profile.⁴⁸ Since the degree of order of a C-D bond axis depends on the angle θ between the C-D bond axis and the director (see eq 4) and because of the geometric constraint of the cis-C=C bond, the degree of order profile undergoes a dramatic dip since $S_{\text{CD}} = 0$ at $\theta = 54^\circ 44'$. Another such case illustrating the importance of angular constraints involves the dicarboxylic acid adipic acid, incorporated as a guest into type II DM lyomesophases.⁴⁹ In this system both carboxyl groups of the dicarboxylic acid are present at the same interface; i.e., the chain is bent back upon itself, producing a very unusual order profile. In addition, this stereochemical constraint has

been shown to be pH dependent, and, as expected, lengthening the chain reduces the imposed constraint for methylene fragments near the head groups.

Order Profiles for Chains with α, ω Head Groups

As mentioned in the previous section, α, ω -dicarboxylic acids incorporated as guests in bilayer systems may give rise to unusual order parameter profiles if the acid is bent back on itself. If, however, the dicarboxylic acid is chosen such that it is just long enough to span the bilayer (the two head groups are present at different interfaces), the chain will be forced into an extended all-trans conformation, and a flat order profile will be obtained. Such an effect has been observed when perdeuterated docosanedioic acid is incorporated into a type II DM mesophase based on potassium decanoate.⁵⁰ The use of α, ω -dicarboxylates of varying chain length may then be used to measure directly the bilayer thickness of DM mesophases based on amphiphiles of all chain lengths. The ^2H NMR spectra of a dicarboxylic acid which illustrates this point is shown in Figure 12.

Micelle Motion

Up to this point, the discussion of contributions to the experimentally determined order parameter profiles have been equally applicable to infinite mesophases which possess positional order as well as to lyotropic nematics. However, there exists for the finite micelles of the lyotropic nematic systems additional freedoms of motion which lower the experimentally determined ^2H NMR quadrupole splittings. These include motion of the micelle units as a whole as well as diffusion of amphiphiles around the ends of the finite micelles (edge effects). Simple geometrical considerations reveal that edge effects are expected to be quite small, but it has been shown that oscillations of the micelle units of type I CM and type II DM lyomesophases lower the experimentally determined order profile compared with H_α and L_α phases, respectively, with which they may be prepared in equilibrium. The related coexistent phases have degrees of order profile in the chains which differ by a constant factor in both the type I CM/hexagonal and type II DM/lamellar cases. This finding not only illustrates the similarity in structure and molecular packing of the lyotropic nematics with hexagonal and lamellar phases but also allows the estimation of an upper limit of oscillation of the micelle symmetry axes about the directors of the mesophases of 23° in the case of cylindrical micelles in equilibrium with a hexagonal phase and 27° in the case of disk micelles in equilibrium with a lamellar phase.²⁷

Using the experimentally determined lowering of the ^2H NMR order parameters of the lyotropic nematics, it is possible to calculate a minimum size for both the length of the type I cylinders and the diameter of the type II disks.⁵¹ The calculated length of cylinders of a type I potassium laurate phase in equilibrium with a hexagonal laurate phase is 810 Å. This length is in good agreement with that found for a pre-type I system (very much diluted) based on sodium dodecyl sulfate which yielded a rod length of approximately 600 Å.²²

It has also been found that the length of the cylinders of a sodium decyl sulfate CM phase decreases with

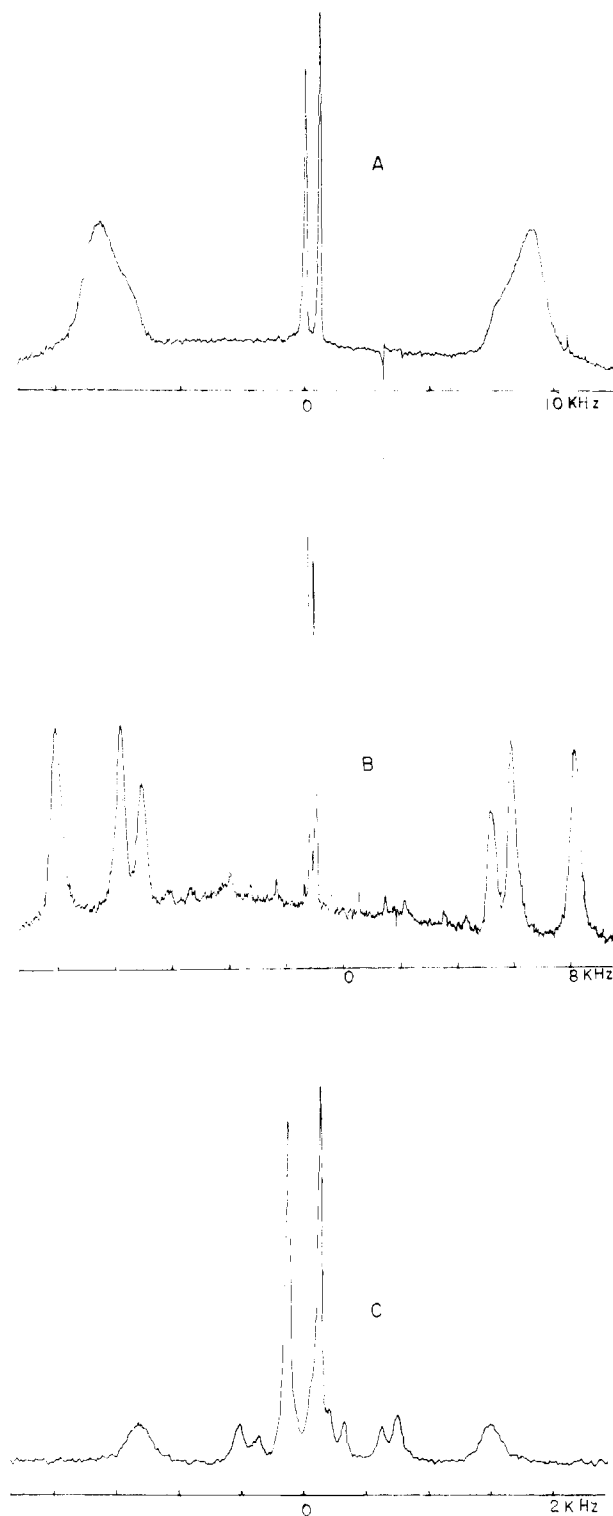


Figure 12. (A) Deuterium NMR spectrum of docosanedioic- d_{40} acid in a type II DM mesophase based on potassium decanoate. The center doublet is due to HOD bound to the disk surface. The diacid spans the bilayer, and therefore the quadrupole splittings for all segments of the chain are nearly coincident. (B) Octadecanedioic- d_{32} acid present in a type II mesophase based on decylammonium chloride which shows an equilibrium between extended and folded conformations. (C) Octadecanedioate- d_{32} in a DM mesophase of sodium lauroyl sarcosinate. The dianion is present in the folded conformation only.

increasing electrolyte concentration until a phase transition to a type II DM phase occurs. Subsequently the diameter of the disk thus formed increases with increasing electrolyte concentration. As well, the size of the micelles depends on the chemical composition

of the aggregates. Cylinders of type II CM potassium laurate decrease in length with addition of the neutral amphiphile, 1-decanol, until a phase transition to the type II DM phase occurs. Additional decanol again increases the mean disk diameter throughout the range of the type II phase.

The diameter of the disk micelles has also been shown to be a sensitive function of water content throughout the range of the DM region of the decylammonium chloride/ammonium chloride/water system. Upon dilution of the precursor lamellar phase, at a certain point the DM phase separates, being initially composed of very large disks. Further dilution results in a decrease in the disk diameter, and at a point where the DM phase exists in equilibrium with an isotropic phase, the disks are calculated to be ~ 530 Å across whereas in the middle of the region the diameter is approximately 900 Å. The small size at the water-rich end of the ternary system is very similar to the short region of equilibrium of the L_α and DM phases in the binary mixtures. It is evident that in the binary system, small micelles separate out from the lamellar phase. Very little water addition is required to provoke an isotropic phase. Thus it has been suggested that, in general, type II DM mesophases consist of disks of diameter ~ 500 – 2000 Å. The actual size of course may vary with micelle composition and electrolyte and water content.

Conclusion

Lyotropic liquid crystals may be prepared with the property that they slowly align in magnetic fields at room temperature. The alignment process can be followed by studying the nuclear magnetic resonance signals of nuclei with spin $>1/2$. Two types have been distinguished, those with positive and others with negative bulk diamagnetic anisotropy. The possible chemical variations of these novel liquid crystals include choice of amphiphiles, added electrolytes, and counterions. Systematic chemical studies have been important in preparing systems where a change in the sign of the diamagnetic anisotropy occurs at a phase transition.

The structural aspects of these mesophases has been elucidated by low-angle X-ray diffraction, NMR, microscopy, and their relationship to the parent "lamellar" and "hexagonal" lyotropic liquid crystals. The type II DM ($\Delta\chi < 0$) mesophase has large finite bilayer disk micelles (DM) disposed with little positional order but with long-range orientational order. The type I CM ($\Delta\chi > 0$) lyotropic liquid crystal is related to the "hexagonal" mesophase but consists of finite cylindrical micelles (CM) which retain orientational order but little positional repetition of their centers. The dimensions of constituent micelles have been estimated both from X-ray diffraction and from degrees of order studies in the finite micelle mesophases compared with the parent systems in equilibrium.

A cholesteric analogue of thermotropic systems can be prepared in two types by using optically active amphiphiles only. The racemic mixture phase of type II cholesteric systems becomes type II DM while the racemic phase of type I cholesterics becomes type I CM.

Type II DM mesophases are excellent models for studying membranes, bilayers, interface science, and colloid chemistry. The motion of hydrocarbon chains

in these bilayers shows the influence of head groups, counterion changes, neighbor interactions, and heterogeneity of chain lengths in the micelle. The study of adsorbed ions such as sodium on the micelle interface may be achieved by sodium-23 magnetic resonance. Three distinct adsorption sites on a mixed bilayer interface have been quantitatively estimated from NMR studies. The angular constraints on motion for amphiphiles with two terminal ionic head groups have been discussed, including the situation where the intervening hydrocarbon chain of the α,ω amphiphile exactly spans the micelle bilayer.

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