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Type I CM–Type II DM Transitions of Lyotropic Liquid Crystals

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Abstract: Type I CM lyotropic liquid crystals composed of cylindrical micelles of finite length and based on the amphiphiles sodium decylsulfate or potassium laurate have been transformed into type II DM mesophases composed of finite disk-shaped micelles by the addition of electrolyte or the neutral amphiphile, decanol, respectively. The nature of these phase transitions has been studied by deuterium nuclear magnetic resonance. It is demonstrated that the pretransition region is associated with a decrease in the length of the cylindrical micelles, while in the posttransition region the disk-shaped micelles, once formed, grow in size. The nature of the amphiphile–amphiphile packing and its relationship to the interface curvature and micelle composition is discussed. In addition, lower limits of the size of the micelles of the type II DM systems are calculated.

Lyotropic liquid crystals which spontaneously align in applied magnetic fields have been divided into two main classes: type I CM which has positive diamagnetic anisotropy ($\Delta\chi > 0$) and type II DM which has negative diamagnetic anisotropy ($\Delta\chi < 0$).[1-3] Low-angle X-ray diffraction experiments have been helpful in the elucidation of the structure of these liquid crystals. It has been shown that the type II mesophase, originally prepared by Lawson and Flautt,[4] composed of sodium decylsulfate/decanol/sodium sulfate/water is made up of disk-like micelles (DM) of bilayer thickness, greater than 1000 Å in diameter, separated by an average intermicellar distance of 90–130 Å.[5] This liquid crystal which is related to the lamellar phase aligns in an applied magnetic field such that the director or uniaxis of the liquid crystal (in this case, the bilayer normal) is perpendicular to the field. Omission of electrolyte in the above system, i.e., sodium decylsulfate/decanol/water, results in a mesophase with type I properties; i.e., the director aligns parallel to the field.[3] It has been shown that type I mesophases are related to hexagonal phases,[6,7] and recent low-angle X-ray diffraction experiments have determined that the type I system composed of SDS/decanol/water is made up of cylindrical micelles of finite but undertermined length.[8] Thus type I CM (cylindrical micelle) mesophases and type II DM mesophases are respectively similar to hexagonal and lamellar phases on the basis of the shape of the constituent micelles. They differ, however, in that the micelles are of finite size, and while they align in an applied field, they possess no long range positional order. (The appearance of some positional order, which depends on the container, has been reported by Amaral and co-workers.[8c]) As a result of the finite size of the unit aggregates of these lyotropic mesophases, they possess an additional degree of freedom of motion; i.e., oscillation of the micelles in the aqueous matrix. This motion has been the subject of a recent study in which type I CM and type II DM phases were prepared in thermodynamic equilibrium with hexagonal and lamellar phases, respectively.[6] The lower experimentally determined ^{2}H NMR order parameters in chain segments of lyotropic type II DM and type I CM as compared with those of lamellar and hexagonal phases are associated with oscillation of the symmetry axes of the disks or cylinders about the director of the mesophase. It has been previously shown that a type I CM lyomesophase composed of SDS/decanol/water is transformed to a type II DM by the addition of less than 1 wt % Na_2SO_4.[3] This phase change was studied by ^{23}Na NMR and ^{2}H NMR of deuteriated water; however no detailed examination of the degrees of order of the hydrocarbon chains was undertaken at that time.[3,9] It is such an investigation which is the subject of this paper. In addition to the SDS system which undergoes a phase transition with added electrolyte (i.e., the chemical composition of the micelle interior remains constant), it is reported here that a second system based on potassium laurate/potasium chloride/water which forms a type I CM liquid crystal may be transformed to a type II DM system by the addition of the weak amphiphile, the long-chain alcohol *n*-decanol. In this case, the chemical composition of the micellar aggregate may be gradually altered while the concentration of water and electrolyte are kept constant. In this way using ^{2}H NMR signals of water bound to the micelle surface and of the hydrocarbon chains themselves allows the nature of the phase transition between micelles with a curved interface (type I CM) and those with a planar interface (type II DM) to be studied. The relationships between the degree of order of the hydrocarbon chains of the amphiphiles and the curvature of the interface at which they are bound may also be investigated.

Experimental Section

Specifically and perdeuteriated decylsulfates, decanols, and potasium laurates were synthesized as described previously.[10,11] Mesophases were prepared with the following composition (wt %). (A) Sodium decylsulfate-d_{21} (90% deuterium enriched), 39.30; decanol, 7.00; H_2O (5% D_2O), 53.70. Similar mesophases were prepared with decanol-d_{21}, sodium decylsulfate-*1,1*-d_2, sodium decylsulfate-*2,2*-d_2, *2,2,3,3*-d_4, or sodium decylsulfate-*3,3,4,4*-d_4 as the deuteriated species by substituting equimolar amounts in the above system. Aliquots of Na_2SO_4 were added and spectra determined. (B) Potassium laurate-d_{23}, 38.27; KCl, 2.19; H_2O (5% D_2O), 59.54. Aliquots of decanol were added and spectra determined. A similar experiment was carried out with use of potassium laurate in its protonated form and addition of decanol-d_{21}.

^{2}H NMR spectra were recorded on a Bruker SXP spectrometer operating at 9.2 MHz. Temperature of the observations was 24 °C. Approximately 2000–4000 transients were required.

Results and Discussion

1. Sodium Decylsulfate System. Assignment of the ^{2}H NMR spectrum of sodium decylsulfate-d_{21} present in a type I CM liquid crystalline phase were made with the use of *1,1*-sodium decylsulfate-d_2, *2,2*-sodium decylsulfate-d_2, *2,2,3,3*-sodium decylsulfate-d_4, and *3,3,4,4*-sodium decylsulfate-d_4. Although the

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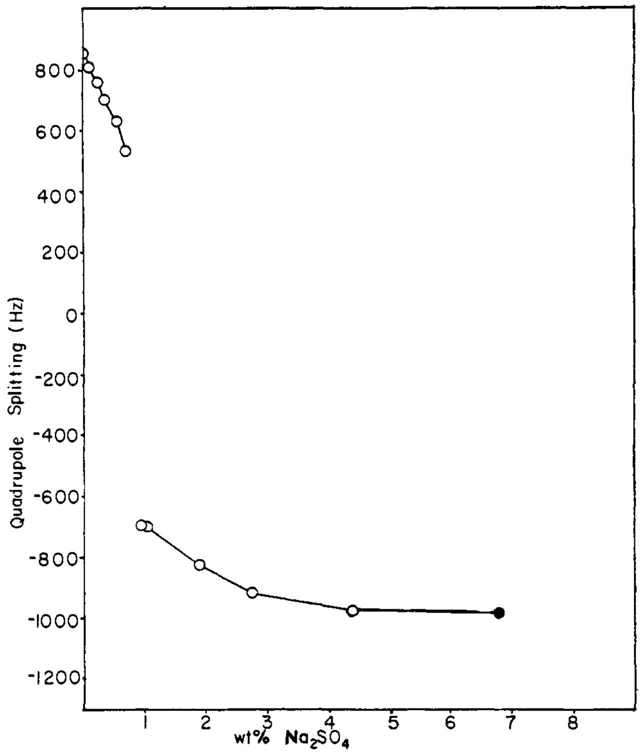

Figure 1. Quadrupole splittings of HOD vs. weight percent of added Na_2SO_4 for cylindrical micelle and disk micelle phases based on sodium decylsufate-d_{21}. Values for the DM phase have been multiplied by −2 to compensate for the change in angle of the director with respect to the magnetic field. The solid point indicates the onset of a lamellar phase.

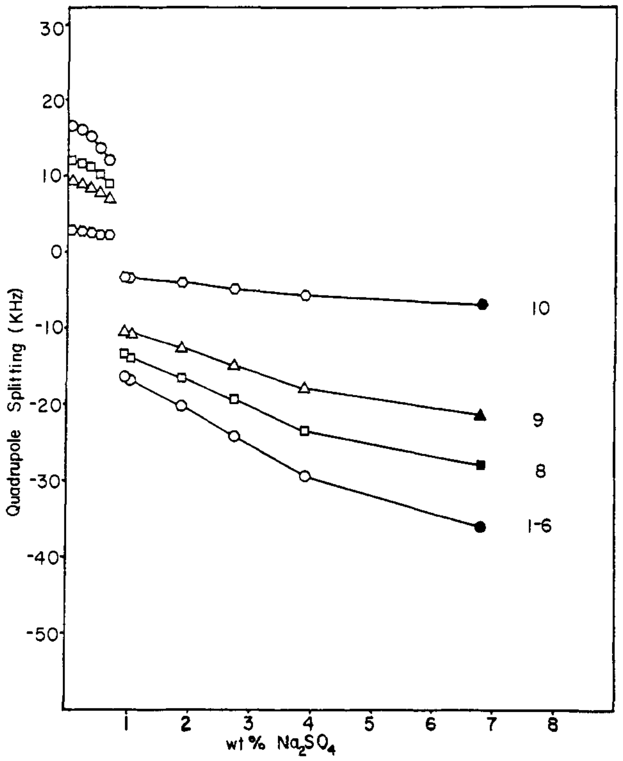

Figure 2. Quadrupole splittings of sodium decylsulfate-d_{21} vs. weight percent of added Na_2SO_4 for cylindrical micelle and disk micelle lyotropic nematics. Values for the DM phase have been multiplied by −2 to compensate for the change in the angle of the director with respect to the magnetic field. The solid points indicate the onset of a lamellar phase.

quadrupole splittings increase as the headgroup is approached (positions 7–10), positions 1–6 are split into two main peaks; i.e., the "plateau" region is not flat. Positions 1 and 3 give rise to lower splittings than positions 2 and 4. Thus sodium decylsulfate exhibits the same characteristic alternation of order parameter in the type I CM system as it does in the type II DM system.[10] Such behavior indicates the preferential formation of "kinks" ($g^{\pm}$ $tg^{\mp}$ conformations) at certain points near the head group.[10–12]

The experimentally determined quadrupole splittings of the chain methylene fragments or of HOD bound at the interface is dependent upon the angle, Ω, between the mesophase director and the applied magnetic field as

$$S_{exp} \propto \tfrac{1}{2}\langle 3\cos^2\Omega - 1\rangle \qquad (1)$$

In the case of type I CM systems, $\Omega = 0°$, leading to a value for this term of unity, while in the case of type II DM systems, $\Omega = 90°$, leading to a value of $-^1/_2$. Thus, in addition to a change in the sign of the order parameter, the magnitude in type I mesophases is twice that of the type II systems. Therefore, so that the the degree of order in the two systems could be directly compared, the experimentally determined quadrupole splittings for the type II liquid crystals have been multiplied by the constant factor of −2.

As electrolyte (Na_2SO_4) is added, the quadrupole splittings for both HOD bound at the hydrophobic–hydrophilic interface (Figure 1) and those of the hydrocarbon chains decrease (Figure 2). Then, at a point of less than 1 wt % added electrolyte, a phase change occurs to a type II mesophase. This is a true phase transition rather than just a change in sign of $\Delta\chi$ because the quadrupole splittings do not change by a factor (−2) exactly. As the phase transition is approached, broadening of the methylene resonances is observed, and at the point immediately following the phase transition, a single resonance is observed for positions 1–6 of the sodium decylsulfate chain; i.e., the difference between the quadrupole splittings is less than the line widths. Subsequent electrolyte addition results in increases in the absolute value of the quadrupole splittings both for the detergent chain and for bound water. As well, two peaks are again resolved for the methylene "plateau" region, verifying the alternating degree of order for positions 1–6 which has been reported previously for the DM species.[10] At high electrolyte concentration (~6.5 wt %), a second transition occurs to a mesohase which no longer spontaneously aligns in the applied magnetic field and is presumed to be lamellar.

The experimentally determined ^2H NMR order parameter is given by eq 2 where S_{exp} is the experimentally determined order

$$S_{exp} = S_{MO}S_{CO}S_{k/j}S_{diff}\tfrac{1}{2}\langle 3\cos^2\Omega - 1\rangle \qquad (2)$$

parameter, S_{MO} is the order parameter associated with micelle oscillation about the director or uniaxis of the liquid crystal, S_{CO} is due to rigid body movement of the long axis of the chain in an oscillatory fashion about the perpendicular to the interface, $S_{k/j}$ 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, S_{diff} is due to diffusion of amphiphiles around the edges of a finite micelle (edge effects), and Ω is the angle between the director of the lyomesophase and the applied magnetic field.

Equation 2 implies that a separation of the degrees of order can be made in the same manner as Phillips and co-workers.[13] The situation of the pseudoextended hydrocarbon chains[14] in bilayer structures,[15] where uniform rotation about the extended chain axis occurs, allows description in terms of only one independent order parameter along this axis. The product ($S_{MO}S_{CO}$) along this axis is not separable, but lateral diffusion does not change the alignment of the chains with respect to the magnetic field, for either CM or DM systems, except at micelle edge or cylinder terminus. We assume large micelles. "$S_{k/j}$" at the local segment has contribution equal to 0 or $-^1/_2$ depending on the

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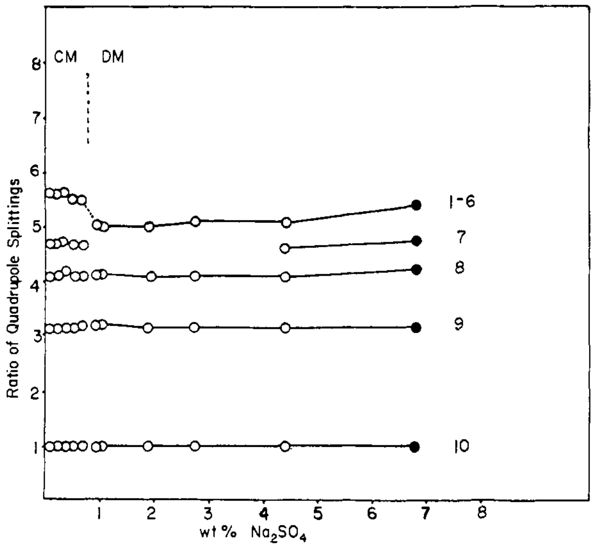

Figure 3. Ratios of quadrupole splittings relative to that of the terminal methyl group for sodium decylsulfate-d_{21} vs. weight percent of added Na_2SO_4 for cylindrical micelle and disk micelle phases. The solid points indicate the onset of a lamellar phase.

position and population of defects in the chain.[15] The degree of order is therefore not uniform along the chain because of these defects in the all trans arrangements.

The changes occurring in trans/gauche motions of the hydrocarbon chains may be separated by taking ratios of quadrupole splittings relative to some standard fragment. Rigid body motions of the type associated with S_{MO}, S_{CO}, and S_{diff} are equal in magnitude in the same mesophase for each position along the chain, and thus by taking the ratio of the experimentally determined quadrupole splittings of any segment "x" to that of a standard segment "i" (usually the terminal methyl group), one obtains

$$S_{\exp(x)}/S_{\exp(i)} = S_{k/j(x)}/S_{k/j(i)} \tag{3}$$

Taking the ith fragment to be the terminal methyl group, an amphiphile in its all trans conformation, rotating rapidly about its long axis, would yield a ratio of 3.00 for all positions "x". In other words, a plot of the relative experimental order parameters (or quadrupole splittings to which they are proportional) vs. carbon number would show a plateau at the value of 3.00 for all methylenes, which would drop to 1.00 for the terminal methyl group.[11] Therefore, deviations from an all trans chain are manifested in alterations from a value of 3.00 for positions "x" along the chain. In this way, changes in the relative amounts of k/j motion as the liquid crystal changes from type I CM to type II DM may be studied. The effect of electrolyte addition upon the ratios of the quadrupole splittings is shown in Figure 3. Note that by use of this method the effect of the term $^1/_2\langle 3\cos^2\Omega - 1\rangle$ of eq 2 need not be considered since it cancels in the ratio. It is interesting that in spite of the different architecture of the interface of the type I CM and type II DM liquid crystals (i.e., a curved interface vs. a planar one), the anchoring of the anionic headgroup, which to a large extent determines the kink/jog motion of the hydrocarbon chains, appears to be quite similar. Note also that in this case the composition of the micelle remains unchanged, with only electrolyte being added to the system. For positions 7–10 in Figure 3, the ratios of quadrupole splittings are relatively constant, indicating little change in the packing of the hydrocarbon chains near the center of both the cylindrical micelle and the disk micelles. There is, however, a small but significant drop in the ratios for positions 1–6, at the point of the phase change. This drop to a value closer to that expected for a rigid all trans chain indicates a small decrease in the number of gauche rotamers near the headgroup caused by the change in interface curvature. The additional amount of electrolyte required to provoke the phase change is extremely small, so that for points immediately preceding and immediately following the phase change the concentration of electrolyte may be taken to be essentially constant. Thus, there occurs only small changes in the trans/gauche motion of the hydrocarbon chain upon alteration of interface curvature for constant amphiphile concentrations, these changes being manifested at positions near the electrical double layer while those positions remote from the surface remain unaffected. What then produces such large changes in the absolute values of the quadrupole splittings in the pre- and posttransition regions, as shown in Figure 2? A reexamination of eq 2 reveals that the large decrease in the absolute value of quadrupole splittings of type I CM, and subsequent increase in magnitude for Type II DM, which affects all positions of the chain in approximately the same manner, is most probably caused by changes in S_{MO}, associated with the oscillation of the micelle as a whole. This assumption is substantiated by the fact that changes in the order parameters for HOD and Na^+ ions have the same general shape as found for the hydrocarbon chains.[3,9] Sodium ions and water in the intermicellar region are free to tumble almost isotropically but do possess order on the time average since they bind to the micelle surface and gain anisotropy of motion by oscillating with it.

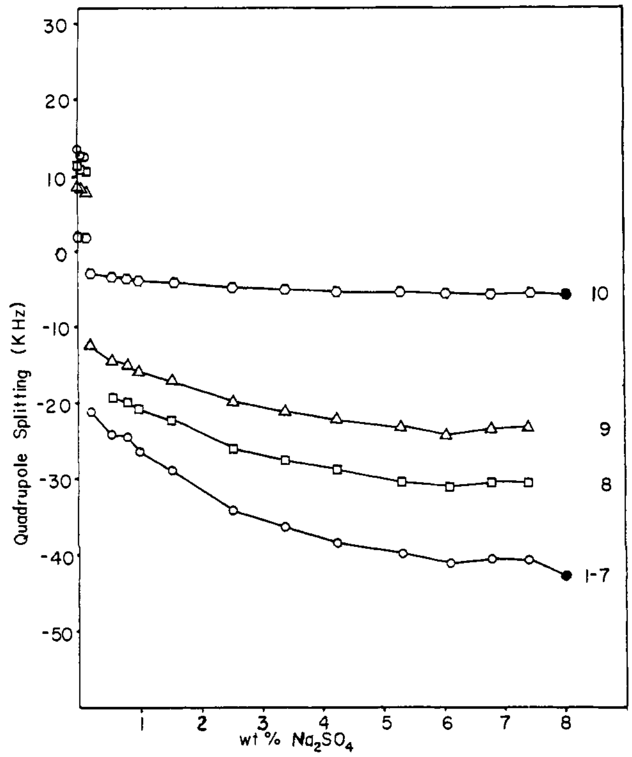

Figure 4. Quadrupole splittings vs. weight percent of added Na_2SO_4 for decanol-d_{21} present in sodium decylsulfate cylindrical micelle and disk micelle phases. Values for the DM phase have been multiplied by −2 to compensate for the change in the angle of the director with respect to the magnetic field. The solid points refer to the onset of a lamellar phase.

A test of the possibility of oscillation of the micelles as a whole being responsible for the dramatic changes in the magnitude of the quadrupole splittings of sodium decylsulfate shown in Figure 2 involves an examination of the chain profiles of the other amphiphile present, namely, decanol. The changes in quadrupole splitting as electrolyte is added is shown in Figure 4. Immediately apparent is the fact that less added electrolyte is needed to provoke the phase change from the cylindrical micelle to the disk micelle system when the major amphiphilic component, sodium decylsulfate, is in the protonated rather than perdeuteriated form. As well, more electrolyte must be added before the disks no longer align in the magnetic field; i.e., the range of this DM lyotropic nematic is shortened when the major component of the micelle is present as a perdeuteriated species. Secondly, although the mgnitude of the quadrupole splittings for the same position may differ since this is, to a large extent, determined by the anchoring of the chemically distinct headgroups at the interface, the shape of the plots are very similar for both decanol and sodium de-

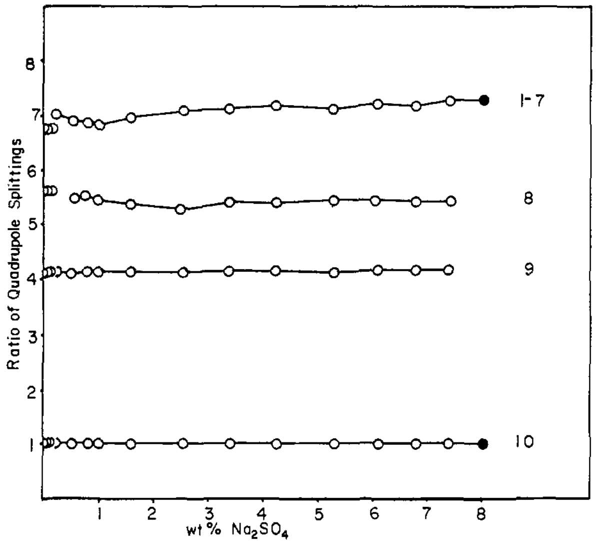

Figure 5. Ratios of quadrupole splittings relative to that of the terminal methyl group for decanol-d_{21} present in sodium decylsufate cylindrical micelle and disk micelle phases vs. weight percent of added Na_2SO_4. The solid points refer to the onset of a lamellar phase.

cylsulfate chains. Compare Figures 2 and 4. For example, the curve for positions 1–7 of decanol is very similar to that for positions 1–6 of sodium decylsulfate, indicating a common underlying cause for the variation in quadrupole splitting with electrolyte addition. Thirdly, an examinatin of the ratios of the quadrupole splittings for the minor component, decanol (Figure 5), once again shows relatively little effect of added electrolyte, as was the case for the major amphiphilic component sodium decylsulfate (compare Figures 3 and 5). Thus, the internal motions of the chains of the trans/gauche type of both sodium decylsulfate and decanol are affected little by the change in interface curvature upon going from a type I CM system to a type II DM system since the composition of the micelle remains constant. It should be noted, however, that the ratios for decanol are higher than those of sodium decylsulfate, as has been noted previously,[10] since these species are chemically unique.

Since the internal motions of two individual chains undergo little change throughout the whole range of electrolyte content and since changes in the absolute values of the quadrupole splittings are very similar, it is revealed that the large changes in quadrupole splittings evidenced in Figures 2 and 4 must be due to variations in a motional process which not only affects each segment of a chain in the same manner but also affects chains of different chemical species in the same manner. Such a motion is the oscillation of the micelles as a whole.

An increase in micelle motion may be caused by a decrease in micelle size or an increase in the average intermicellar distance. Since the amount of water present in the sample remains constant, any change in micelle motion must be caused by variations in micelle size. Thus the initial decrease in the quadrupole splittings of the type I CM phase is caused by an increase in the motion of the micelle as a whole brought about by a decrease in micelle size. In the case of the type I CM mesophase, this size decrease is associated with a decrease in the mean length of the finite cylinders, which corresponds to a decrease in aggregation number. Coupled to a decrease in micelle size is the increased contribution of edge effects, i.e., diffusion of amphiphiles and bound ions or HOD around the "caps" of the cylindrical micelles. These edge effects will not be appreciable until the micelle itself is quite small. However, the spectral broadening near the transition point may be associated with an increase in the size distribution, so in this region the magnitude of edge effects is uncertain. The resolution of sharp quadrupole doublets away from the transition is indicative of a monodisperse system of nearly equal sized micelles. We assume that amphiphiles exchange between micelles at a slow rate on the NMR time scale. However, the dramatic decrease in the quadrupole splittings in the pretransition region is attributed to the rapid shortening of the cylindrical micelles which, at a still low electrolyte concentration (<1 wt %) transform into disk-like structures which grow in size with increasing electrolyte concentration. Eventually, the disks become very large at a high salt concentration, no longer align in the applied magnetic field, and probably nucleate out a positionally ordered lamellar phase.

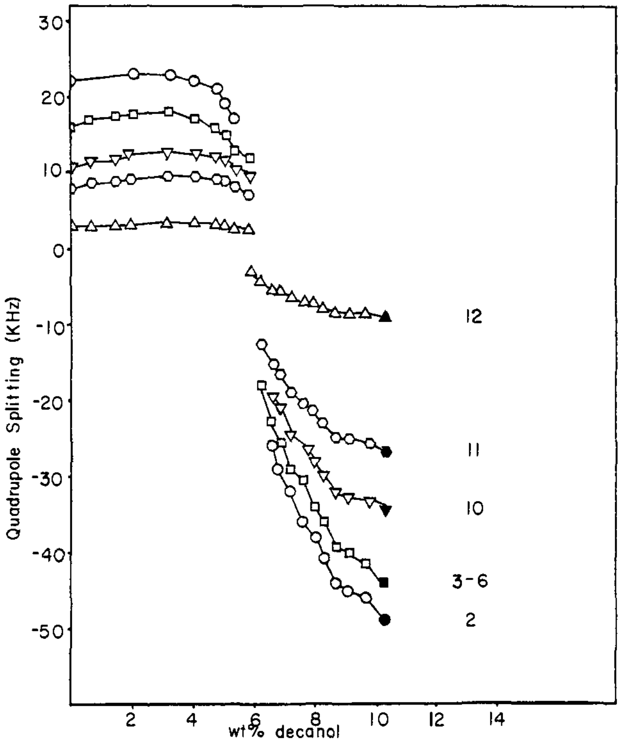

Figure 6. Quadrupole splittings of potassium laurate-d_{23} vs. weight percent of added decanol for cylindrical micelle and disk micelle lyotropic nematic phases. The quadrupole splittings for the DM phase have been multiplied by −2 to compensate for the change in the angle of the director with respect to the magnetic field. The solid points refer to the onset of a lamellar phase.

2. Potassium Laurate System. A type I CM liquid based on the amphiphile potassium laurate may be transformed into a type II DM lyomesophase by the addition of a second amphiphile, the long-chain alcohol, decanol. Unlike the sodium decylsulfate case, this transformation is caused by an alteration of the chemical composition of the micelle itself. The ^2H NMR quadrupole splittings of the laurate chian are plotted against decanol concentration in Figure 6, while those of HOD are shown in Figure 7. Unlike the sodium decylsulfate case in which the quadrupole splittings decreased with increasing electrolyte concentration until a phase change is provoked, the quadrupole splittings in this case increase to a maximum value at ~3 wt % decanol before the onset of a steep decline. However, once the phase change to type II DM has taken place, the absolute values of the quadrupole splittings increase rapidly before leveling off at a value of approximately double the initial magnitude. Further decanol addition results in a mesophase which no longer aligns in the applied magnetic field, presumably lamellar in nature, formed from a nucleation of very large disk-shaped micellar structures. In order to elucidate the cause of these phenomena, it is instructive to consider the trans/gauche type motions of the laurate chains. The ratios of the quadrupole splittings to those of the terminal methyl group vs. decanol concentration are shown in Figure 8. As the transition point is approached, the ratios for positions 9–12 in the center of the cylindrical micelles do not change appreciably, while those for positions 2–6 show significant decreases. Such decreases are associated with less relative motion of the trans/gauche type near the interface, as the second amphiphile decanol is added. Geometric constraints necessitate close lipid–lipid packing in the interior of a cylindrical micelle due to the wedge-shaped volume occupied by the hydrocarbon tails of the laurate chains. So that the larger free volume near the interface could be occupied, a

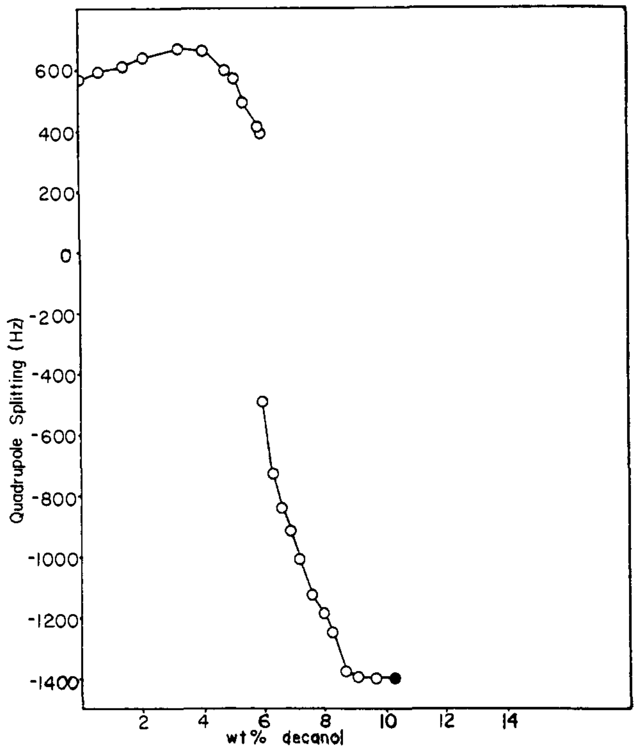

Figure 7. Quadrupole splittings of HOD vs. weight percent of added decanol for cylindrical micelle and disk micelle phases based on potassium laurte-d_{23}. Values for the DM phase have been multiplied by −2 to compensate for the change in the angle between the director and the applied magnetic field. The solid point indicates the onset of a lamellar phase.

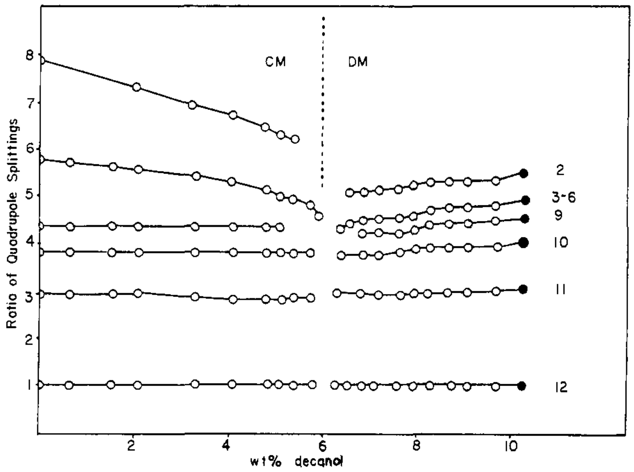

Figure 8. Ratios of quadrupole splittings relative to that of the terminal methyl group for potassium laurate-d_{23} vs. weight percent of added decanol for cylindrical micelle and disk micelle phases. The solid points refer to the onset of a lamellar phase.

relatively large number of gauche rotations, i.e., a crumpling of the chains near the interface, may be necessitated.

As previously elaborated,[16-20] an important property of an amphiphilic molecule is the relationship of the cross sectional area of the polar headgroup, a_0, the length, l_0, and the volume, V_0, of the hydrocarbon chain. For a given chain length, a large value of a_0 and a small V_0 favor rod-shaped aggregates while a small ratio of a_0/V_0 favors a lamellar structure. Addition of a weak amphiphile, as is the case here, decreases the effective ratio, and eventually a planar structure will be formed.[20] The intercalation of the weak amphiphile decanol not only tends to reduce the repulsion of adjacent anionic amphiphiles but also intercalates into the micelle in such a way as to reduce the number of gauche rotamers of the hydrocarbon chain near the interface. Amphiphile packing in the center of the micelle is not expected to be perturbed since the decanol chain is shorter than that of a laurate chain. Thus, the effect of decanol addition is to continuously lower the ratios of quadrupole splittings near the interface while perturbing little the micelle center.

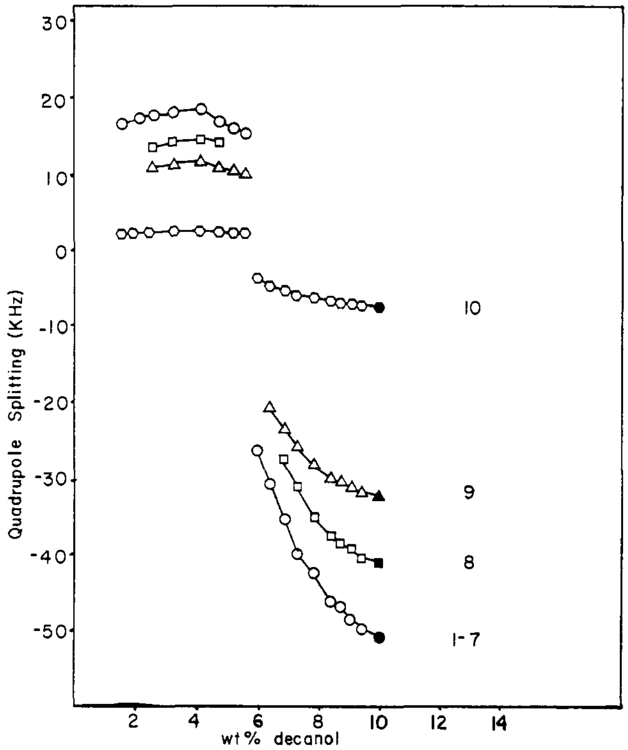

Figure 9. Quadrupole splittings vs. weight percent of added decanol for decanol-d_{21} present in potassium laurate cylindrical micelle, and disk micelle phases. Values for the DM phase have been multiplied by −2 to compensate for the change in the angle of the director with respect to the magnetic field. The solid points refer to the onset of a lamellar phase.

This argument however does not fully explain the pretransition chain behavior. For instance, although the trans/gauche motion of positions 9–12 is unaffected, the absolute values of the quadrupole splittings follow the same general shape as shown by positions 2–6 as well as HOD bound to the micelle surface. The initial increase in absolute values of the quadrupole splittings must be associated with a change in anchoring of the carboxylate headgroups as decanol is added. The weak amphiphile is also expected to perturb the structure, and perhaps the amount of water bound to the interface as well. After the addition of approximately 3 wt % decanol, the absolute values of the quadrupole splittings decrease rapidly, even for positions 9–12 whose relative trans/gauche motion is unaffected. Again this in interpreted in terms of an increase in micelle motion due to decreased micelle size. This effect more than compensates for alterations in head-group anchoring caused by the alcohol intercalation. The onset of the phase transition is accompanied by broadening of the resonances; however, at ~5.9 wt % decanol, two phases are observed in equilibrium. Further decanol addition results in a single type II DM lyomesophase whose quadrupole splittings increase sharply in absolute value until ~10.5 wt % decanol has been added. Subsequent decanol addition once again result in a phase change to a presumably lamellar system which does not align in the applied magnetic field. However, the ratios of the quadrupole splittings for the laurate methylene groups increase only slightly in the post CM → DM transition region, indicating little further effect of neighboring decanol on the packing of the laurate chains.

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Scheme I

no order		orientational order		positional and orientational order
isotropically tumbling cylindrical micelles	→	type I CM, cylindrical micellar phase	→	H_α infinite cylinders, two-dimensional positional order
isotropically tumbling disklike micelles	→	type II DM, disk micellar phase	→	L_α lamellar phase, one-dimensional positional order

It is elucidating at this point to examine the behavior of the second amphiphile chain, decanol, as it is incorporated into the micelles. The 0° quadrupole splittings are plotted in Figure 9 vs. weight percent of added decanol. Although 1–2 wt % decanol-d_{21} must be added before reasonable signal noise is achieved, it is once again apparent that the changes in quadrupole splitting of the decanol chain mimics that of the major amphiphile component, in this case, laurate. The quadrupole splittings rise slightly to a maximum at ~4% decanol and then fall in value until the phase transition from the CM type I mesophase to the DM type II mesophase occurs. In this case no coexistence of the two phases was observed, and it must be emphasized that the range of possible coexistence must be very narrow indeed. Following the phase change, the 0° quadrupole splittings for all positions along the chain which have increased in magnitude from those immediately preceding the transition once again rapidly increase in magnitude before leveling off somewhat as the nonaligning lamellar phase is approached.

It should be noted that in the type I CM region decanol has larger quadrupole splittings when incorporated into the laurate system than when copresent with sodium decylsulfate (compare Figures 4 and 9). In addition, the absolute values of quadrupole splittings for decanol positions are also greater in the type II DM region of the laurate system than in the type II sodium decylsulfate system. Such behavior may be explained by examining the relative lengths of the hydrocarbon chains involved.[21,22] The hydrophobic portion of the laurate chain is longer than that of decylsulfate or decanol, which are of the same length. Therefore decanol intercalated into micelle predominantly composed of potassium laurate will not extend completely to the region of relatively free motion at the center of the micelle but will be anchored such that the decanol chain will experience a slightly more rigid environment of higher order.

The ratios of the quadrupole splittings relative to the terminal methyl group of the decanol chain, which elucidate changes in nonrigid body motions of the trans/gauche type, are plotted in Figure 10 vs. decanol concentration. Again, the shape of the curves for equivalent positions are very similar to those of the host laurate species, dropping in value until the phase transition (compare Figures 8 and 10). This drop in the ratios toward a value of 3.00 may again be explained in terms of a straightening of the chains toward a more all trans conformation as the concentration of the shorter amphiphile is increased. The very dramatic changes in the absolute values of the quadrupole splittings and the similarity of these changes for equivalent positions on two chemically distinct amphiphiles suggest a common cause, the most reasonable of which is changes in micelle size which affect the magnitude of the oscillation of the micelles as rigid bodies about the mesophase directors. The cylindrical micelles decrease in size as decanol is added until the transformation to disk-shaped micelles occurs. Subsequent decanol addition once again increases the micelle size until they become so large that alignment in the magnetic field becomes extremely slow, and finally a positionally ordered lamellar mesophase nucleates.

3. Estimation of Micelle Sizes. Measurements have been made previously[6] of the oscillation of the symmetry axes of both disk micelles and cylindrical micelles about the director of the lyomesophases. It was found that the axes of cylinders are free to oscillate through a maximum angle of 23°, while the disks possess freedom of movement through a maximum of 27° when the CM and DM phases are in thermodynamic equilibrium with a hexagonal and a lamellar phase, respectively. In general, it has been found that the relationship of type I CM and type II DM lyotropic liquid bear the relationship to lamellar and hexagonal phases shown in Scheme I.[6-8] Water content increases to the left.

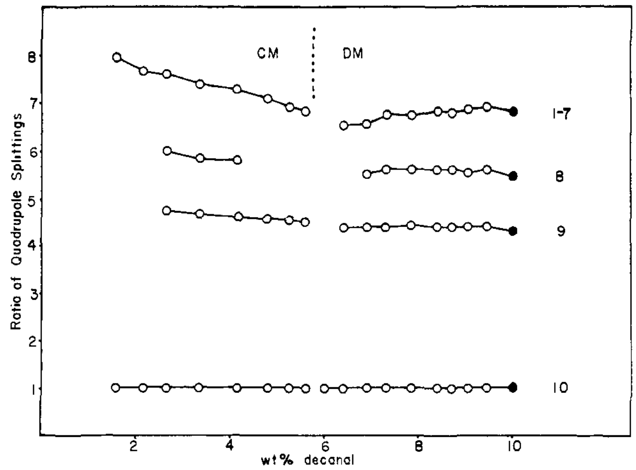

Figure 10. Ratios of quadrupole splittings relative to that of the terminal methyl group for decanol-d_{21} present in potassium laurate cylindrical micelle and disk micelle phases vs. weight percent of added decanol. The solid points refer to the onset of a lamellar phase.

X-ray diffraction results now permit the use of the degree of oscillation of the micellar units in an estimation of the lower limits of the diameter or length of the amphiphilic aggregates. The X-ray experiments have previously estimated the diameter of the micelles of one composition of a quaternary system of sodium decylsulfate/sodium sulfate/decanol/water to be in excess of 500 Å.[5] More recently, it has been proposed that micelle size of a type II DM mesophase based on the laurate chain is dependent on the nature of the counterion[23] and that the size of those in a ternary mixture of decylammonium chloride/ammonium chloride/water are a very sensitive function of water content.[24] In the latter case, it has been possible to show that the disks are reduced from a diameter approximately 2200 Å, shortly after separation from the lamellar phase, to approximately 570 Å near the point of equilibrium of the DM phase with an isotropic phase. The binary decylammonium chloride/water system has an extremely short range of water content (<1 wt%) over which a lamellar system is in equilibrium with the DM phase. Micelle diameter in this region has been placed at ~550 Å, which corresponds to the low end of the size range, and indeed, after the equilibrium with the lamellar phase, there exists a short region of equilibrium with an isotropic phase.[3,24]

A ternary hexagonal potassium laurate/potassium choride/water phase may also exist in thermodynamic equilibrium with a CM phase, again over a small range of water content.[6,7] X-ray diffraction studies have shown the diameter of the cylinders to be approximately 43 Å (this includes a area of ordered water and ions at the interface), while the intercylinder distance lies between 90 and 190 Å.[8] Using an average value of 140 Å for the thickness of the aqueous matrix yields a cylinder length of approximately 800 Å. The decylammonium chloride and laurate systems in these studies have the advantage that the chemical composition of the aggregates remains constant, while only small amounts of water

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are introduced. In the present case, the potassium laurate micelles are being systematically contaminated with the second amphiphile *n*-decanol so the requirements of constant intrachain motion and bilayer thickness may not be so exact. Therefore estimates of micelle size at the present time will be limited to the sodium decylsulfate system where the amphiphile composition is constant, with only electrolyte being introduced. In addition, this system has the advantage that independent estimates of micelle motion and micelle size may be made by using experimental results for either decylsulfate or decanol chains. Obviously, calculations using the two amphiphiles should yield similar results for the rigid body motion of the micelle since both are present in the same micelle and experience this motion equally.

As can be seen from Figures 2 and 4, the quadrupole splittings of all positions of the two amphiphiles increase in magnitude with added electrolyte before leveling off as the liquid crystal approaches the lamellar phase. Also, the ratios of the quadrupole splittings for both types of chains as shown in Figure 3 and 5 change little as the nonaligning phase is approached, indicating a similarity of internal motions of the amphiphiles in the DM and lamellar phases. Therefore the lower values of quadrupole splittings in the type II DM phase are caused by rigid-body motion of the micelles, as discussed previously. Immediately after the phase transition from type I CM to type II DM, the quadrupole splittings for all positions on the decylsulfate chain are 48 ± 2% of those of the lamellar phase, while those of the decanol chain are 50 ± 1% of their value in the nonaligning phase. This similarity indicates a common cause for the chemically distinct chains, that of oscillation of the finite disks. Therefore using 2, we may write

$$S_{\text{exp}}^{\text{type II DM}}/S_{\text{exp}}^{\text{lamellar}} = S_{\text{MO}}^{\text{type II DM}}/S_{\text{MO}}^{\text{lamellar}} \tag{4}$$

Using a constant angle of 90° between the director of the lamellar mesophase and the applied magnetic field yields

$$\frac{\Delta\nu^{\text{type II DM}}}{\Delta\nu^{\text{lamellar}}} = \frac{\frac{1}{2}\langle 3\cos^2\theta - 1\rangle}{\frac{1}{2}\langle 3\cos^2 90° - 1\rangle} \tag{5}$$

For the decylsulfate chains, this ratio is 0.48, yielding an angle, θ, of 65.4° as opposed to 90° in the lamellar case. Thus the symmetry axis of the disk micelles are free to move throughout an angle of 24.6° from the director. A similar calculation based on the quadrupole splittings of the decanol chain results in a value for θ of 65.9° and therefore 24.1° for the micelle motion. Therefore, two different amphiphiles reflect extremely similar values, as indeed they should, if the effect is as proposed, one of motion of the micelle as a whole, since this movement will affect not only all positions on an individual chain in the same manner, but also equally affect chemically different chains in the same bilayer.

Since the contribution of the rigid body motion of the micellar aggregate is known, it is possible to estimate a lower size limit for the particles with use of bilayer thicknesses and average values for the intermicellar distances, as determined by X-ray diffraction. However, it is necessary to invoke the constraint of positional order of the micelles which leads to a minimum value of disk diameter being calculated. Some periodicity has been reported for DM decylsulfate samples in quartz capillaries; however this effect is container dependent.[25]

Nevertheless, with the assumptions of a regular stacking of the disk micelles and no cooperativity in their movement, a bilayer thickness of 38 Å, an average intermicellar distance of 110 Å, 24.6° found for the micelle oscillation by using the quadrupole splitting of the major decylsulfate component, and simple geometrical considerations yield a disk diameter of approximately 605 Å, while use of the quadrupole splittings of *n*-decanol gives rise to a disk diameter of approximately 618 Å. Thus essentially identical disk diameters are found from the independent measurement of degrees of order of the two amphiphiles.

Similarly, calculations may be made at other compositions in the DM region. For example, with 1.82 wt % added Na_2SO_4 in excess of that required to provoke the CM → DM phase transitions, $S_{\text{exp}}^{\text{type II DM}}/S_{\text{exp}}^{\text{lamellar}}$ is 0.68 for the host decylsulfate chains and 0.73 for the guest decanol chains, giving rise to the similar values of 19.1 and 17.5° for micelle oscillation and, subsequently, approximately 780 and ,850 Å for the diameter of the disks.

The preceding calculations clearly demonstrate an increase in the mean micelle size as electrolyte is added throughout the range of existence of the type II DM phase. In addition, it is felt that the necessary assumptions introduce a constant error which would result in an underestimation of micelle diameter by no more than a factor of 2. Therefore, it is estimated that the aggregates of the type II DM sodium decylsulfate liquid crystal range between approximately 500 and 2000 Å in diameter, consistent with the results of X-ray diffraction.[5]

Conclusion

Type I cylindrical micelle nematic liquid crystals based on sodium decylsulfate or potassium laurate may be converted to type II disk micelle phases by the addition of electrolyte or decanol, respectively. In the former case, the chemical composition of the micelle is kept constant, while in the latter it is systematically altered. Examination of the ^{2}H NMR quadrupole splittings reveals that motion of the trans/gauche type for both major and minor component amphiphiles is essentially independent of interface curvature if the chemical composition of the micelle interior is maintained. It has been previously determined that such motion is also independent of water concentration within the range of stability of a type II DM liquid crystal.[26] The invariance of internal motions of the amphiphile chains and the similarity of the effect of added electrolyte on the absolute values of the quadrupole splittings for equivalent positions on the two chains which are anchored at the interface by chemically different head groups indicate that oscillation of the cylindrical micelle as a whole increases with increasing electrolyte concentration in the region of stability of the cylindrical structure, while the effect is opposite for micelles of disk shape. Since the water and amphiphile concentration are held constant, it is concluded that addition of electrolyte to the sodium decylsulfate/decanol type I CM nematic causes a shortening of the mean cylinder length, enabling increased oscillatory motion of the micelle as a whole. Increasing electrolyte concentration in the disk micelle region results in an increase in the mean micelle diameter and consequent decrease in the angle of rigid body micelle motion. Eventually, the disks become so large with respect to intermicelle distances that they no longer align in the applied magnetic field.

In the second case, that of the potassium laurate system, changes in relative concentrations of the two different amphiphiles which make up the micelles result in comparable changes in the trans/gauche motions of both chains. However, the similar gross variation of the absolute values of the quadrupole splittings for both chains again indicates a shortening of the cylinder long axes as the cylindrical micelle–disk micelle phase transition is approached, while continued decanol addition results in an increase in the mean diameter of the disk micelles until a nonaligning lamellar phase nucleates from the lyotropic nematic.

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