2H NMR study of sodium bis(2-ethylhexyl) sulfosuccinate in liquid crystals. Acyl chain packing and effects of molecular chirality on quadrupolar splitting patterns

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polymers may form in the present model without the formation of stable pentacoordinated silicon.

VI. Summary

In summary, a new interatomic potential has been developed for MD simulations of systems containing silicon, hydrogen, and oxygen interactions. The potential has been used to simulate H_4SiO_4–H_4SiO_4, H_2O–H_4SiO_4, H_2O–$H_6Si_2O_7$, and H_2O–H_2O molecular interactions as well as liquid water. Simulations of monomeric silicic acid sols have provided a microscopic description of oligomerization and have found interaction intermediates to include ionized monomers and pentacoordinate silicon. The ground-state structure and binding energy of H_4SiO_4–H_2O complexes compare favorably with ab initio calculations. In addition, the structure of H_2O dimers, H_2O trimers, and simulated water are found to be in fair agreement with quantum chemical calculations and neutron and X-ray diffraction results.

^{2}H NMR Study of Sodium Bis(2-ethylhexyl) Sulfosuccinate in Liquid Crystals. Acyl Chain Packing and Effects of Molecular Chirality on Quadrupolar Splitting Patterns

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The ^{2}H quadrupolar splitting patterns of selectively deuterium labeled sodium $[3,3'-^2H_4]$bis(2-ethylhexyl) sulfosuccinate (AOT) in various anisotropic liquid crystalline phases are examined. The complex ^{2}H spectra are interpreted in terms of the asymmetry of the AOT molecule and the presence of three chiral centers. Due to the former property, the two acyl chains are not equivalent, whereas the latter property produces nonequivalent deuterons within the methylene segments. The effects of the chiral centers are found to be short range. The discussion is extended to include the analogous properties of phospholipids. Finally, the relaxation of a methylene ^{13}C nucleus through fluctuating dipolar couplings to the directly bonded but, as a consequence of molecular chirality, nonequivalent protons is addressed within the framework of the "two-step" formalism.

Introduction

Amphiphiles, i.e., molecules such as surfactants, soaps, and lipids, aggregate in solution to form monolayers of oriented molecules.[1] Depending on the conditions, surfaces may enclose a finite volume as in micelles or be continuous in one, two, or three dimensions.[2] Perpendicular to the normal to the polar–apolar interface, N, describing the preferred orientation of the molecules, the molecular film has liquid properties. This means that local molecular motions are slightly anisotropic due to the preferred orientation, leaving a residual order that can be measured by NMR in terms of one or, sometimes, two order parameters. ^{2}H and ^{13}C NMR spectroscopy have proven to be powerful tools for investigating the hydrocarbon chain order and dynamics of aggregated amphiphilic molecules. Through the orientational-dependent magnetic dipole and electric quadrupole interaction, the residual anisotropy is quantified in terms of order parameters for the C–D and C–H bonds, respectively. In particular, ^{2}H NMR has been extensively applied to the study of phospholipid properties in model and biological membranes,[3-5] as well as to surfactant systems.[6-8]

Alkyl chains in the liquid state have a local plane of symmetry. This symmetry remains when the chain has a preferred orientation as in the case of surfactant monolayers. Consequently, the order parameters for the two C–D bonds within a methylene segment are equivalent. In chiral molecules, however, this symmetry is broken and the two hydrogens (deuteriums) in a methylene group are *in principle* nonequivalent.

Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) is an asymmetric, double-chained anionic surfactant. From the point of view of phase behavior, it exhibits the usual properties of double-chained surfactants. Due to its bulky hydrophobic part, the isotropic water-rich solution phase, L, can solubilize only small amounts

of surfactant, and the phase diagram of the binary system AOT–water is dominated by a large lamellar liquid crystalline phase,[9] D, as is shown in Figure 1. In addition, at high surfactant content, a bicontinuous cubic phase, I_2', and a reversed hexagonal phase, F, are formed. Most likely due to the branched hydrocarbon chains, AOT cannot be obtained in crystalline form. Indeed, "pure" AOT rather comes as an F phase containing also water.

The molecular structure of AOT is shown in Figure 2. The present study deals with the average conformational properties of AOT in the D and F phases formed in the binary system with water and a ternary system with isooctane as the third component. For this purpose, we have introduced deuterium into the methylene segments at the 3- and 3'-positions of the two chains as indicated in Figure 2. The AOT molecule contains three chiral centers, at positions 1, 4, and 4', which are also indicated in Figure 2. In particular, the consequences of chirality on the appearance of the ^{2}H NMR spectrum from anisotropic phases is analyzed. We compare our experimental findings with earlier ^{2}H NMR studies of phospholipids in lipid bilayers and also discuss the analogous effects of chirality in the lipids. Finally, we briefly address the NMR relaxation of a ^{13}C nucleus in a methylene segment when it is relaxed through a fluctuating dipolar coupling to two directly bound protons that are to be considered nonequivalent due to the chirality of the molecule.

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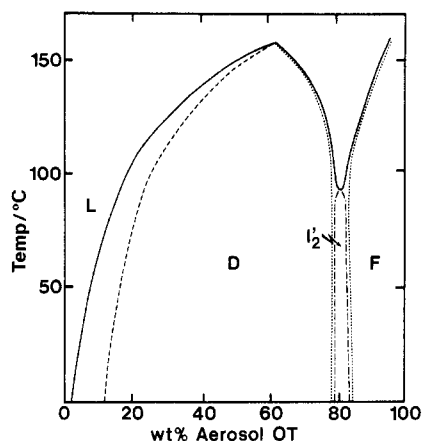(9) Rodgers, J.; Winsor, P. A. *Nature (London)* **1967**, *216*, 477.

Figure 1. Phase diagram of the binary system AOT–water. L denotes a homogeneous isotropic liquid phase. D, I_2', and F are lamellar, cubic, and reversed hexagonal liquid crystalline phases, respectively. The phase diagram was drawn by using data from ref 9.
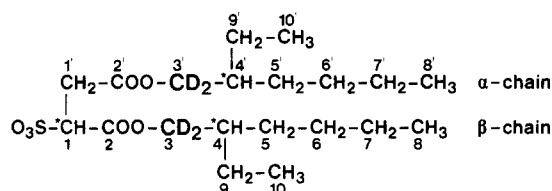

Figure 2. Molecular structure of AOT. The three chiral centers are indicated by asterisks (*). Also indicated are the two chains, α and β, respectively, for both of which the numbering of the carbons starts from the headgroup region. The AOT is deuterated at the 3 (α-chain) and 3' (β-chain) positions, respectively, as indicated in the figure.

Experimental Section

Materials. AOT, deuterium labeled at the methylene positions 3 and 3', was synthesized by Syntestjänst, Chemical Center, University of Lund. The starting material was *rac*-2-ethyl-1-hexanol, and none of the steps in the synthesis is expected to introduce any selectivity with respect to the isomeric composition of the final product. Thus, a racemic product, containing equal amounts of all enantiomers, is expected. From a recorded ¹H NMR spectrum, the deuterium content was estimated to be better than 99%.

Samples were prepared by weighing the components into glass tubes that were then flame sealed. Equilibration of the samples was achieved by repeated centrifuging and gentle heating. After homogenizing, the samples were stored at room temperature for at least 2 months before the first measurements. Deuterium-depleted water (Sigma) was used in all samples.

Methods. ²H NMR spectra were recorded, using the quadrupolar echo sequence[10] on a Bruker MSL-100 NMR spectrometer operating at 15.4 MHz and on a Nicolet 360 NMR spectrometer operating at 55.5 MHz by recording the free induction decay after a $\pi/2$ pulse.

Theoretical Considerations

For an aliphatic deuteron in an anisotropic environment, the quadrupolar interaction is only partially averaged. The residual interaction results in a quadrupolar splitting (the frequency difference between the 90° peaks in the powder spectral pattern), Δ, that in the case of a lamellar phase is given by[3,11]

$$\Delta_{lam} = \tfrac{3}{4}\chi S_0 \qquad (1)$$

Here it is assumed that the asymmetry parameter of the electric field gradient is zero and that the molecular motions that partially average the interaction take place with a 3-fold or higher symmetry

around the normal to the polar–apolar interface, N. χ is the quadrupolar coupling constant, which is usually assigned the value 170 kHz[12] for aliphatic deuterons. S_0 is the zeroth component of the second-order C–D bond order parameter tensor and may vary as $-\frac{1}{2} < S_0 < 1$ (note, however, that the sign of S_0 cannot be determined from the quadrupole splitting); it is given by the time-averaged second-order Legendre polynomial

$$S_0 = \tfrac{1}{2}\langle 3 \cos^2 \Theta_{NM} - 1 \rangle \qquad (2)$$

Θ_{NM} is the angle between the C–D bond vector and the normal to the polar–apolar interface, and the time average includes all molecular motions occurring on time scales shorter than Δ^{-1}. In the hexagonal phase, the surfactant diffusion around the cylinder long axis reduces the interaction further. However, due to the cylindrical interface, the assumption of 3-fold or higher symmetry around the normal to the interface is not strictly true for the local molecular motions. The quadrupolar splitting for such a case is given by[13]

$$\Delta_{hex} = \frac{3}{4}\chi\left(\frac{1}{2}\right)\left[S_0 + \frac{6^{1/2}}{2}S_2 \right] \qquad (3)$$

where the second-order parameter, S_2, is related to the residual order in the plane perpendicular to N.

$$S_2 = \frac{6^{1/2}}{2}\langle \sin^2 \Theta_{NM} \cos 2\Phi_M \rangle \qquad (4)$$

Φ_M describes the orientation of the C–D bond vector in the plane perpendicular to N.

Results

Figure 3a shows a powder spectrum from the F phase in the binary system. In this spectrum, five individual quadrupolar splittings are resolved. Figure 3b is a computer-simulated powder spectrum which demonstrates that the experimental spectrum is consistent with a superposition of five splittings having the relative weights $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{8}$, and $\frac{1}{8}$, starting from the largest splitting. A similar spectrum to the one shown in Figure 3a, again with five resolved splittings, but with about twice the magnitudes, was obtained in the binary D phase. In Figure 4, we show a spectrum from the F phase in the ternary system AOT–water–isooctane. In this case the F phase has been almost completely oriented in the magnetic field (8.5 T) by transforming the sample from an isotropic liquid phase, L_2, at higher temperatures, to F, by slow cooling in the magnetic field. This F phase orients with its symmetry axis parallel to the external magnetic field, which can be deduced from comparing the magnitudes of the splittings from the oriented parts of the sample with those from the small amount of remaining powder (cf. Figure 4). In this spectrum six individual splittings are easily resolved. This increase in number of splittings is simply a consequence of enhanced resolution upon orienting the sample.

An interesting temperature dependence of the five splittings in the D phase was observed and is presented in Figure 5. The two large splittings have a moderate temperature dependence and monotonically decrease with increasing temperature. The three inner splittings, on the other hand, show a more unusual dependence on temperature. The largest of these three inner splittings monotonically increases with increasing temperature, whereas the two smallest splittings show a nonmonotonic temperature dependence. Their magnitudes decrease to zero and then increase again, which should be interpreted as a zero crossing and a change of sign of the order parameter, upon changing the temperature.

Discussion

The presence of three chiral centers give rise to $2^3 = 8$ separate stereoisomers, existing as four enantiomeric pairs. The four deuterons within each of the eight stereoisomers are mutually

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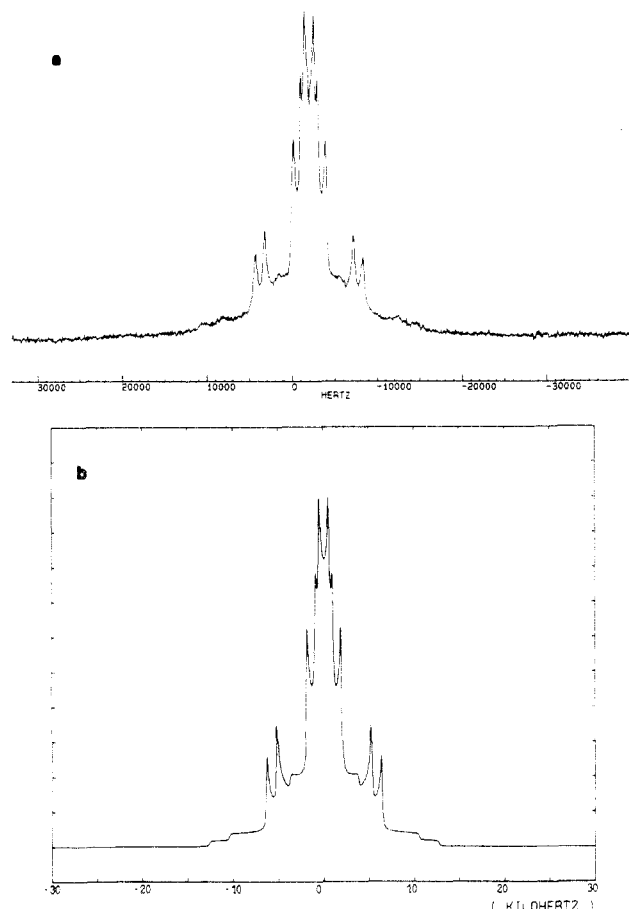(13) Halle, B.; Wennerström, H. *J. Chem. Phys.* **1981**, *75*, 1928.

Figure 3. (a) ^{2}H NMR spectrum of AOT in the F phase of the binary system (88.8 wt % AOT; 11.2 wt % H_2O). The spectrum was recorded at 15.4 MHz using the quadrupolar echo sequence. The $\pi/2$ pulse length was 4 μs, and the separation between the two phase-shifted $\pi/2$ pulses was 100 μs. Changing the pulse separation to 40 μs produced an essentially identical spectrum. (b) Simulated powder spectrum of five superimposed splittings. The magnitudes of the splittings are 12.7, 10.5, 3.8, 1.9, and 1.1 kHz, respectively, with the relative weights of $^1/_4$, $^1/_4$, $^1/_4$, $^1/_8$, and $^1/_8$. An isotropic Lorentzian line broadening of 150 Hz was added equally to all splittings.
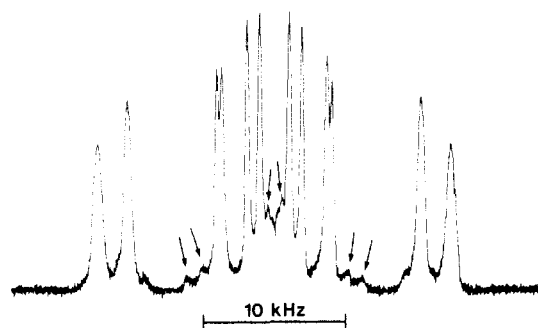

10 kHz

Figure 4. ^{2}H NMR spectrum of AOT in the F phase of the ternary system (57.4 wt % AOT; 30.2 wt % H_2O; 12.4 wt % isooctane) oriented parallel to the magnetic field. The AOT was a 1:1 by weight mixture of the deuterated compound and commercial AOT. The spectrum was recorded at 55.5 MHz by recording the free induction decay after a $\pi/2$ pulse. The oriented F phase was formed by letting a homogeneous liquid phase (L_2) at higher temperature cool down slowly into the F phase in the magnetic field (8.5 T). Small amounts of nonoriented sample regions remain. The resulting residual powder peaks are indicated by arrows in the figure. A consistent factor of 2 difference between the powder peak and oriented peak separations indicates that the phase orients parallel to the external magnetic field.

nonequivalent. An optically active environment, or some other property that breaks the enantiomeric symmetry, will thus result in a total of 32 *in principle* nonequivalent deuterons in the system.
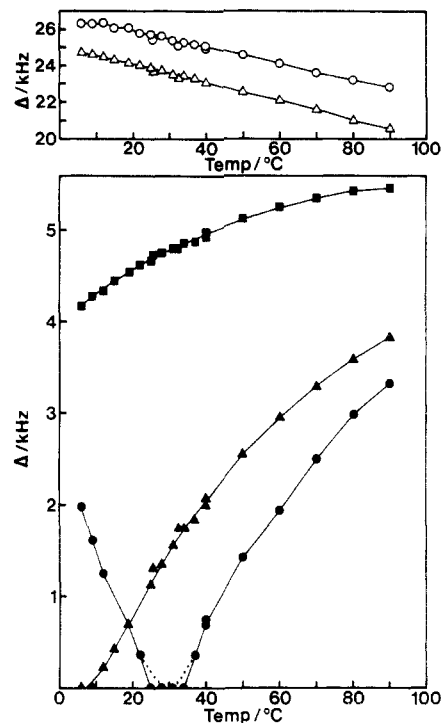

Figure 5. Temperature dependence of the observed quadrupolar splittings of AOT in the D phase of the binary system (47.7 wt % AOT; 52.3 wt % H_2O). The two larger splittings are shown in the upper diagram, whereas the three smaller splittings are shown in the lower diagram. The spectra were recorded at 55.5 MHz by means of single pulse exitation. With the present resolution, quadrupolar splittings smaller than 200 Hz could not be distinguished from a single peak.

TABLE I: Scheme Relating Magnitudes of 16 Quadrupolar Splittings to the Different Deuterons on Different Stereoisomers

configuration			splitting			
4	1	4'	$3'_1$	$3'_2$	3_1	3_2
R	R	R	A	B	I	J
S	S	S	B	A	J	I
R	S	R	C	D	K	L
S	R	S	D	C	L	K
R	R	S	E	F	M	N
S	S	R	F	E	N	M
R	S	S	G	H	O	P
S	R	R	H	G	P	O

[a] 4, 1, and 4' are the positions of the three chiral centers of the AOT molecule (see Figure 1). The three columns on the left-hand side describe the configurations at the three chiral centers. The two deuterons at the 3- and the 3'-carbons are denoted by indexes 1 and 2, respectively. A–P are the 16 *in principle* different magnitudes of quadrupole splittings.

However, in an environment where this symmetry is not broken, each deuteron in the system has an equivalent counterpart in the corresponding enantiomer. Thus, in a racemic mixture of AOT, we expect the system to contain 16 *in principle* nonequivalent deuterons, giving rise to 16 different quadrupolar splittings. The situation can be schematically outlined as shown by the scheme in Table I, where the letters A–P represent the 16 splittings. The three columns on the left-hand side represent the eight different stereoisomers in terms of the configuration[14] at the three chiral centers.

However, depending on the experimental resolution, the number of *practically* resolvable nonequivalent deuterons may be reduced from the maximum value of 16. This means that some inequalities may be too small to be resolved in the particular experiment, which for the liquid crystalline samples are limited to about 100–200

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Hz. Indeed, only five splittings are resolved in the powder spectra. Orienting the samples improves the resolution somewhat, and as is seen in Figure 4, six splittings can be resolved in the oriented F phase. The fact that not all 16 splittings are resolved in the spectra means that some of the magnitudes of A–P in Table I are *practically* equivalent.

Figures 3–5 indicate that the observed splittings in the spectra can be divided into two groups with respect to their relative magnitudes and temperature dependences. On the one hand, there are the two larger splittings—>20 kHz in the D phase and >10 kHz in the F phase—the magnitudes of which decrease monotonically with increasing temperature. On the other hand, there is the group of smaller splittings—three of which are resolved in the powder spectra and four of which can be resolved in the oriented F phase—that have a more unusual temperature dependence. These two groups of splittings carry equal intensity in the spectrum as implied by the good agreement between the simulated and experimental spectra in Figure 3. Taking this into account, and also considering the differences in magnitudes and temperature dependences, it is reasonable to attribute the two groups of splittings to deuterons on different chains. According to the scheme in Table I, the two groups then correspond to splittings A–H and I–P, respectively. This in turn implies that the two deuterons giving rise to the two large splittings sense *in practice* only one chiral center, whereas the two deuterons on the other chain sense *in practice* two chiral centers.

When assigning the two groups of splittings to the deuterons on the two different chains of the AOT molecule, it is suitable to compare with phospholipid molecules in lipid bilayers. The phospholipids have several features in common with AOT. Both are asymmetric double-chained surfactants, and they show a similar phase behavior which is to a great extent governed by the property of having a bulky hydrophobic part. Moreover, the lipids contain (at least) one chiral center, situated at the *sn*-2 position of the glycerol backbone. Due to the asymmetry of the molecules, the two acyl chains are not equivalent. The difference has been shown to be particularly evident when the two C-2 positions adjacent to the ester groups are compared. When the C-2 positions (adjacent to the ester groups) of the two acyl chains are labeled with deuterium, three quadrupolar splittings are usually observed.[15] (Four splittings have, however, been observed on at least one occasion.[16]) From specific labeling of only one of the two chains, it was shown that the largest splitting arose from the C-2 deuterons on the *sn*-1 chain, whereas the two smaller splittings arose from the two C-2 deuterons on the *sn*-2 chain.[17] By selective deuteration of only one of the two C-2 positions on the *sn*-2 chain, it was further shown that the two splittings were a consequence of nonequality of the two deuterons in this position.[18] The difference in magnitude between the splittings from the two chains has been ascribed as due to a specific packing of the lipids in the bilayer. The *sn*-1 chain is pictured as being parallel to the bilayer normal, while the *sn*-2 chain starts out perpendicular to the normal and is then bent parallel to it after the C-2 segment. This difference in chain packing of the two chains is a consequence of the asymmetry of the molecules and is also found in the crystalline state.[19–21]

AOT cannot be obtained in crystalline form, probably due to the branched hydrocarbon tails. However, the analogous nonbranched sodium diheptyl sulfosuccinate crystallizes in an arrangement similar to the phospholipids,[22] with a bend in the chain closest to the sulfonate group (which in our terminology is refered

TABLE II: Reduced Scheme for the Deuterons at the 3'-Position, Affected by the Chiral Center at the 4'-Position

configuration	splitting	
4'	3'₁	3'₂
R	A	B
S	B	A

TABLE III: Reduced Scheme for the Deuterons at the 3-Position, Affected by the Chiral Centers at the 1- and 4-Positions

configuration		splitting	
1	4	3₁	3₂
R	R	I	J
S	S	J	I
R	S	K	L
S	R	L	K

to as the β-chain; cf. Figure 2). It should be noted that the phospholipids and sodium diheptyl sulfosuccinate crystallize, as is normally the case for amphiphilic molecules, in stacks of monolayers arranged face-to-face and tail-to-tail, resembling the arrangement in the liquid crystalline bilayer.

Finding this analogy with phospholipids, it seems reasonable that a similar difference in chain packing between the two chains occurs also for AOT; i.e., that we may picture the α-chain to appear straight and the β-chain to exhibit a bend in the vicinity of the ester group. Thus, we conclude that the large splittings in the present system arise from the deuterons on the α-chain, which *in practice* sense only one chiral center, and that the small splittings arise from the deuterons on the β-chain, which sense *in practice* two chiral centers.

Further support for this assignment is given by the temperature dependencies of the various splittings as shown in Figure 5. The C–D bond for a straight chain makes an average angle of about 90° with N. Thus, an increase in temperature will only increase the motional averaging and thus decrease the splitting. On the other hand, the bent chain apparently makes the C–D bond direction very close to the magic angle with respect to N. Small changes in the average orientation (upon changing the temperature) may cause the splitting to increase, decrease, or change sign.

There are of course several possibilities for the assignment of the effective chiral centers sensed by the 3- and 3'-deuterons, respectively. However, it seems plausible that the deuterons at the 3'-position are affected by the chiral center at the 4'-position, whereas the deuterons at the 3-position are affected by the chiral centers at the 1- and 4-positions. The arguments, or indications, in favor of this assignment are twofold. First, one expects that if the deuterons at the 3-position are affected by the chiral center at the 4-position, then the deuterons at the 3'-position should similarly be affected by the chiral center at the 4'-position. The second argument is that, in analogy with the phospholipids, effects of the chiral center at the 1-position should be resolved at the bent chain but not necessarily at the straight chain. This assignment for the effective chiral centers corresponds in the scheme of Table I to a situation where A = C = E = G and B = D = F = H for the 3'-deuterons. Regarding the deuterons at the 3-position, we have I = P, J = O, K = N, and L = M. Thus, we can write the reduced schemes for the 3- and 3'-deuterons, respectively, as shown in Tables II and III.

In the case of the splittings I–L, the two largest of the four splittings are very close in magnitude. Indeed, they are not resolved in the powder spectra from the binary system. On the other hand, the relative differences of the two smaller splittings appear to be comparably large. However, it should be noted that the order parameter is a rapidly varying function around zero, and thus the difference between the two smallest splittings may be the result of only minor differences in the average orientation of the two C–D bond vectors. Furthermore, as seen in Figure 5, at higher temperatures the two splittings appear to asymptotically approach the same value. Thus, as the temperature is increased, a situation is approached where the two deuterons at the 3-position also may sense only one chiral center. Most likely the most perturbing chiral

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TABLE IV: Scheme Describing the ^{2}H Quadrupolar Splitting Pattern for [α-^{2}H]DPPS in Terms of the Configurations at the Chiral Centers at the Glycerol Backbone (sn-2 Position) and Serine Headgroup, Respectively[a]

configuration		splitting	
sn-2	serine	α_1	α_2
L	L	A	B
L	D	C	D

[a] At the glycerol backbone only the natural L form is considered. The scheme refers to the experimental results obtained in ref 24.

center is the one on the 4-position, which in Table III corresponds to I $\approx$ L and J $\approx$ K. Which pair, I and L or J and K, corresponds to the larger and smaller pairs of splittings can only be deduced from experiments on optically pure stereoisomers. For further assignments, separating I from L and J from K, a selective deuteration at one of the two methylene sites has to be invoked.

Influence of Chirality on the ^{2}H Splittings in Phospholipids. With these results from AOT in mind, we will now proceed to discuss the influence of chirality on the ^{2}H quadrupolar splittings in lipid bilayers. As pointed out above, the phospholipids constitute another class of asymmetric, chiral, double-chained surfactants. They carry at least one chiral center, namely, at the sn-2 position of the glycerol backbone. Most experiments are carried out on lipids extracted from natural sources and thus in the natural optically pure L form (in the case of phospholipids, we follow the nomenclature in previous publications and label the stereoisomers according to the classification, L, D, based on the Fischer projection). As pointed out above, two splittings are usually observed for the C-2 deuterons on the sn-2 chain. This has been found for various headgroups[23-25] and for chains containing unsaturated segments[26] or a cyclopropane ring.[27] It should be noted that in the case of a single chiral center, *a spectrum from an optically pure enantiomer is identical with the spectrum from the racemic mixture.* Two splittings have also been observed from the CD$_2$ segments at the sn-3 position of the glycerol backbone[24] and on the α-methylene (we use the same notations as in the original work to which we refer—α- and β-positions in the phospholipid headgroups should not be mistaken for the α- and β-chains of AOT) segment of the choline headgroup.[28] There also exists a report on two splittings from the C-2 segment on the sn-1 chain.[16] The perturbation from the chiral center appears to be short-ranged. From the C-3 positions and downward in the acyl chains, the two deuterons in the methylenes give almost identical splittings. Also from the β-segments of the choline and ethanolamine headgroups only a single splitting is resolved.

The chiral properties of phospholipids can reach a higher complexity if chiral headgroups like serine[24] or glycerol are considered.[25] The headgroup chirality does not affect the spectrum from the acyl chains (another example of the short-ranged perturbation), but effects are observed in headgroup deuterons. For example, four splittings were resolved from the α-CD$_2$ group of the serine headgroup of dipalmitoylphosphatidylserine (DPPS) containing racemic mixture with respect to the serine headgroup (the glycerol backbone was in the natural L configuration).[24] The nonequivalence of the two deuterons was confirmed by comparing with a spectrum from the optically pure L,L stereoisomer. The four splittings come as two pairs where the difference in magnitude within each pair is very small, indicating that one of the two chiral centers has a relatively minor influence. Table IV shows the simple scheme expected for the α-deuterons of (L-L,D)-DPPS. Since the influence of the sn-2 chirality on the α-CD$_2$ spectrum in dipalmitoylphosphatidylcholine and dipalmitoylphosphatidylethanolamine is very small, it is reasonable that this is also the

case for DPPS. Thus, we expect A $\approx$ D and B $\approx$ C.

For the β-CD in DPPS, only a single splitting is observed even in a racemic mixture with respect to the serine headgroup. This observation means that the influence of the chirality at the sn-2 position is too small to be resolved at the β-position. No effect from the chiral β-position is expected for this deuteron, since *a single deuteron bound to a chiral carbon is equivalent to the corresponding deuteron in the corresponding enantiomer* (if the enantiomeric symmetry is not broken). Equivalently, a single splitting is also observed from a deuteron bound to the chiral sn-2 carbon.

Implication of Nonequivalent Protons on ^{13}C Relaxation in Surfactant Chains in Isotropic Solution. We will extend our discussion of nonequivalent hydrogens in a methylene segment and briefly address the relaxation of a methylene ^{13}C nucleus, in isotropic medium, through the fluctuating dipolar coupling to the directly bonded but nonequivalent protons.[29-31] In particular, we will do so within the framework of the "two-step" formalism[13,32] which has been shown to be able to rationalize relaxation data from aggregated surfactant systems.[8,33] This is of interest, since the segmental order parameters extracted from frequency-dependent ^{13}C relaxation are related to the C-D bond order parameters obtained from ^{2}H quadrupolar splittings.

Within the "two-step" formalism, the dipolar Hamiltonian separates into a rapidly fluctuating part, $H_f(t)$, with a nonzero average and a slowly fluctuating isotropic part, $H_s(t)$.

$$H(t) = H_f(t) + H_s(t) \tag{5}$$

Furthermore, it is assumed that $H_f(t)$ has a 3-fold or higher symmetry around the local symmetry axis, which for the case of micelles is the normal to the aggregate surface. In the treatment of relaxation data, it is further assumed that the fluctuations of $H_f(t)$ are in extreme narrowing. Thus, the fast dynamics is described in terms of an effective correlation time, i.e., an integral over the correlation function. The separation of time scales and the symmetry of the fast motions imply that $H_s(t)$ separates further into a sum of the two interactions[32]

$$H_s(t) = (S' + S'')H_s'(t) \tag{6}$$

Here, S' and S'' are the order parameters for the two C-H bonds, which have the same interpretation as in the deuterium case (eq 2). For "normal" aliphatic chains the local plane of symmetry implies $S' = S'' = S$, and the longitudinal relaxation rate, R_1, of a ^{13}C nucleus is usually written in the form[32,34]

$$R_1 = N[A\tau_c^f + BS^2f_s(\omega)] \tag{7}$$

where A and B are constants, including the interaction constant squared, and $f_s(\omega)$ is a linear combination of reduced spectral densities describing the slow dynamics. N denotes the number of directly bonded protons—for a methylene carbon, $N = 2$—thereby normalizing the relaxation expression so as to allow direct comparisons between methine, methylene, and methyl carbons. Scaling the relaxation rate with N implicitly assumes the absence of cross correlations.

If we instead consider the case where the two protons are not equivalent and consequently $S' \neq S''$, R_1 can be written as

$$R_1 = a + b(S'^2 + S''^2)f_s(\omega) \tag{8}$$

The sum of the squares of the order parameters is a consequence of the separation of time scales and the symmetry of $H_f(t)$, and it applies to the general case of eq 8 as well as to the special case when $S' = S'' = S$.

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Concluding Remarks

We have demonstrated that the quadrupolar splitting patterns from [3,3'-$^2H_4$]AOT, in anisotropic phases, may be understood from considering the asymmetry of the molecule and the presence of three chiral centers. However, for a particular methylene segment, not all chiral centers are effective to produce inequivalence of the two deuterons.

We have found that the molecular packing of AOT in surfactant layers is similar to what is found in phospholipid bilayers—with a preferred bending of one of the chains close to the headgroup region. This particular packing of AOT and phospholipids is due to the asymmetry of the molecules. It is interesting to note that, in the case of AOT, this particular packing is found not only in a bilayer (the lamellar phase) but also in a monolayer where the mean curvature of the polar–apolar interface is toward the polar solvent (the reversed hexagonal phase).

We note, finally, that the system AOT–H_2O, strictly speaking, should be recognized as a nine-component system. Stereoisomers are distinct molecules having their separate spectral, thermal, and phase properties. The effect of chirality on molecular interactions in membranes has received increasing attention in recent years.[35-38]

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Critical Behavior of a Conducting Ionic Solution near Its Consolute Point

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Measurements are reported of the coexistence curve and electrical conductivity of the partially miscible aqueous solution of tetra-*n*-pentylammonium bromide near its consolute point, which was located at $T_c = 404.90 \pm 0.01$ K and approximately 0.03 in mole fraction. The compositions of coexisting phases were measured over three decades of temperature, from 21 to 0.01 K from the consolute point. The conductivity was measured in the supercritical regime, from high dilution to compositions exceeding the critical. The degree of dissociation was estimated to be higher than 20% at the critical composition. In the data analysis, attention was given to the assessment of experimental error and proper weight assignment, and also to asymptotic range and choice of order parameter. No evidence of classical behavior was found. This finding is in contrast to several recent reports of effectively classical critical behavior in ionic solutions similar to ours; but it is in accordance with earlier measurements in very weak electrolytes. We present reasons why our conclusion differs from these recent results; an explanation is given why nonclassical behavior might be expected in systems of this type.

Introduction

Recently, there have been a number of reports of effectively classical critical behavior of coexistence curves of ionic solutions near gas–liquid and liquid–liquid critical points.[1-4] Classical, mean-field, or van der Waals-like behavior implies that the top of the coexistence curve is parabolic, in terms of suitably chosen variables. For one-component fluids, these are the coexisting densities and temperature; for partially miscible binaries, they are composition and temperature; for binaries near a gas–liquid critical point, several choices are possible, one of them being the isothermal coexisting densities versus pressure. Classical behavior is expected to prevail if the molecular interactions are long-ranged.[5] The range of intermolecular potentials can be expressed by the value of the exponent n in the $1/r^n$ dependence of the potential on the distance r. Potentials with n smaller than 4.97 lead to critical behavior that begins to depart from the nonclassical behavior associated with short-ranged forces.[6] Most fluids and fluid mixtures have interactions that are (barely) short-ranged,[6] with an exponent value of $n = 6$; their critical behavior has been demonstrated to be nonclassical, as exemplified in the shape of their coexistence curves, which are nearly cubic.[7-11] Since Coulombic potentials, with $n = 1$, are long-ranged, it has been recently suggested by Pitzer and co-workers[1-3] that ionic systems might display classical critical behavior. The experiments reported here are meant to test this hypothesis.

In this Introduction, we will discuss the experimental evidence in favor of and against the hypothesis that ionic systems have classical critical points. In order to do so, we need to briefly introduce concepts and terminology of the theory of critical phenomena.

The concept of universality of critical behavior implies that "near" a fluid–fluid critical point, be it a vapor–liquid critical point in a one-component system or a liquid–liquid consolute point in a binary mixture, the thermodynamic properties scale with critical exponent values that are the same for the large class of three-dimensional Ising-like systems; this class includes most fluid critical points. The values of the critical exponents are extremely well-known from renormalization group theory.[12] As an example, the

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