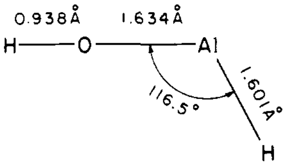
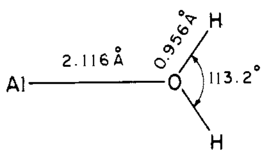
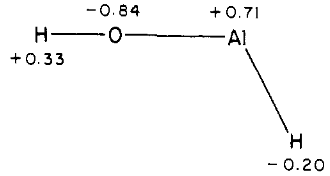
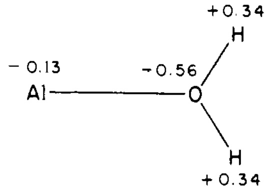
Å and a dissociation energy[9] of 12.3 kcal/mol using the model potential and 8.5 kcal/mol in the all-electron calculation. We also find that the $^2B_1$ state is bound by ~7.0 kcal/mol while the $^2A_1$ state is unbound.

For the HAlOH structure, we have carried out a complete optimization of all bond lengths and angles. The resulting HAlOH species is stable by 54.3 kcal/mol (38.1 kcal/mol in the all-electron calculation) with respect to $H_2O + Al$ and has a HAlO bond angle nearly the same as the HAlH angle of AlH_2 and an Al–H bond distance close to that of Al–H_2.[10] Our minimum energy structures for the HAlOH and C_{2v} $H_2O{\cdot}Al$ species are shown. The charge densities obtained from a Mulliken population analysis reveal that the hydroxyhydride has appreciable ionic character, with the Al atom losing nearly one electron to the H and OH groups. On the other hand, the aluminum atom carries a small negative charge (0.1 e) in the C_{2v} adduct. ESR studies[3] on the $H_2O{\cdot}Li$ and $H_2O{\cdot}Na$ complexes have shown that the metal atom is negatively charged. This has also been found in the theoretical studies of Trenary et al.[6]









The differences between the geometry and energy of the C_{2v} species obtained in the present study and those of Trenary et al. arise primarily from two sourses: (1) the use of the effective core potential for Al and (2) differences in the basis sets employed, mainly the lack of d functions in our work. As noted earlier, all-electron C_{2v} calculations using a 6s4p Al basis reduce the dissociation energy to only 8.5 kcal/mol and give an optimal Al–O distance of 2.25 Å. For HAlOH, these calculations give an Al–O distance of 1.68 Å and an HAlO angle of 118.11°. From these results it seems that removal of the Al core potential does not have a significant effect on the structure of these compounds. At present we are exploring the effect of the basis set by adding d functions to both the O and Al and reoptimizing the HAlOH and $H_2O{\cdot}Al$ structures.

Gransden et al.[1] have found that the Al–H and O–H stretching frequencies of AlOH are 1743 and 818 cm^{-1}, respectively, indicating that the HAlOH complex is strongly bound. This is borne out by the results of the present study. The all-electron calculations, carried out at the geometry optimized using the effective potential, indicate that the HAlOH species is stable (with respect to $Al + H_2O$) by 38 kcal/mol. Reoptimization of the geometry in the all-electron SCF procedure should give rise to a slightly larger value.

While we have not yet mapped out the complete potential energy surface and have not established the minimum energy path for the $Al + H_2O$ insertion, we have found that the approach of Al perpendicular to one of the O–H bonds inserts without encountering a barrier. Furthermore, we believe that the C_{2v} species may be a local minimum on the potential energy surface. However, the barrier for the $H_2O{\cdot}Al \rightarrow HAlOH$ rearrangement may be small.

In addition to the more detailed studies employing d functions, examination of the effects of electron correlation are under was on the HAlOH species. We have also begun to examine the reaction of H_2O with other metals including Be, B, Mg, Sc, and Zn. Preliminary studies of $B + H_2O$ indicate that HBOH is stable by 68 kcal/mol with respect to the reactants. We have found that, in agreement with Trenary et al.,[6] that the ground state of Li (^2S) + H_2O is the C_{2v} $H_2O{\cdot}Li$ adduct. There is the interesting possibility that the ^2P excited state of Li inserts into water to form the hydroxy hydride as do Al and B. The thermal $Sc + H_2O$ reaction has been shown by Liu and Parson to yield $ScO + H_2$. The role of the unpaired d electron in this reaction is especially interesting. Hange, Kauffman, and Margrave[11] have observed spontaneous reactions of Sc, Ti, and V with water to form ScO, TiO, and VO, respectively, in rare gas matrices at 10 K.

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pH-Dependent Constraint Angle Effects on the Order Parameters of Bilayer Systems

Sir:

It has recently been reported that the absolute values of the quadrupole splittings for specifically deuterated cis unsaturated phospholipids in bilayer model membranes yield an unusual order parameter profile.[1] The degree of order of a C—D bond axis, S_{CD}, depends upon the angle θ between the C—D bond axis and the director. Because of the geometric constraint of the cis C=C bond, the degree of order undergoes a dramatic decrease in magnitude near the site of unsaturation and then rises once more to a value close to that of a fully saturated chain before falling off once more as the mobile chain terminus is approached. We have observed that the degree of order profile for bilayer lyotropic liquid crystalline systems depends upon several factors, one of which involves constraints placed upon the orientation of amphiphilic molecules in a bilayer model membrane.[1-11] It is reported here that, in certain cases, these constraints may be pH dependent.

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Table I. Quadrupole Splittings[a] (Hertz) for Adipic Acid-d_8 and Sebacic Acid-d_{16} Incorporated into HDTMABr and SDS Mesophases at 38.5 °C

	adipic acid				sebacic acid		
position	acid	temp dependence[b]	anion	temp dependence[b]	acid	anion	temp dependence[b]
				HDTMABr			
α	34	+	94	+	4853	4783	+
β	1618	+	1193	+	*c*	*c*	
HOD	<10	+	<10	+	<10	<10	
				SDS			
α	615	small −	459	small −	4475	3285	+
β	2100	+	1504	+	*c*	*c*	
HOD	399	small	391	small	443	388	

[a] Error is <1%. [b] A positive temperature dependence is defined as an increase in quadrupole splitting when temperature is lowered. [c] Quadrupole splittings of the β, γ, and δ methylene groups of sebacic acid in the range of 200–1500 Hz are unassigned.

The first of the above-mentioned factors is the chemical identity of the hydrophilic head group. Bilayer components of the same chain length, but with differing head groups, have quite different order parameter profiles because of their characteristic stereochemical anchoring and interaction with water at the interface.[2-5] Secondly, any heterogeneity in the length of the hydrophobic chain also results in quite significant alterations in the profile of the experimentally determined quadrupole splittings.[6-9] Thirdly, in the case of finite bilayer micelles in equilibrium with infinite lamellae, oscillation of the micelle as a whole greatly reduces the experimentally determined order parameters from those obtained for the infinite lamellae.[12]

Counterion substitution may lead to phase changes and also marked changes in the degree of order profile of the amphiphile chain segments, especially when the counterion has a partly hydrophobic nature. These counterion effects on chain motion are extremely small among alkali metals but larger with anions.

As mentioned previously one most important complication of the degree of order profile may be introduced by angular constraints since S_{CD} is the order parameter of the C—D bond axis and θ is the angle between the C—D axis and the mesophase director. Should the C—D axis by some stereochemical constraint be confined to move about an angle ϕ to the director of the mesophase, and α is the angle with reference to this constraint axis, then the alternate form of eq 1 can be used with α and ϕ.

$$S_{\text{CD}} = \tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle = \tfrac{1}{2}\langle 3\cos^2\alpha - 1\rangle \tfrac{1}{2}(3\cos^2\phi - 1) \qquad (1)$$

One possible method of investigating such an effect is to employ an amphiphile which possesses two polar groups such as a dicarboxylic acid. If the diacid chosen is sufficiently short so that it cannot span the bilayer, both carboxyl groups will be present at the same interface. To accomplish this, the chain must be sent back upon itself.[14] The bilayers used in this study are based either on sodium decylsulfate (SDS) or hexadecyltrimethylammonium bromide (HDTMABr) and are composed of finite disk-like micelles[9,15] which spontaneously align in an applied magnetic field such that the director (in this case, the bilayer normal) is perpendicular to the applied magnetic field.

Into these mesophases has been incorporated deuterium-substituted adipic acid or sebacic acid and their corresponding dianions. Mesophases were prepared with the following composition by weight (percent). A: HDTMABr (may contain a small amount of HDTMABr-d_9 deuterated at the *N*-methyl position), 33.61; Na_2SO_4, 3.24; adipic acid (-d_8 or -β,β'-d_4), 2.59; decanol, 5.51; H_2O (0.5% D_2O, pH 2 or 12), 55.05. B: SDS (may contain a small amount of SDS-9,10-d_2), 35.45; Na_2SO_4, 5.59; adipic acid (-d_8 or -β,β'-d_4), 1.95; decanol, 5.78; H_2O (0.5% D_2O, pH 2 or 12), 51.23. Similar mesophases were prepared which contained perdeuteriated or α-deuteriated sebacic acid. Adipic acid was synthesized from cyclohexanol[16] and perdeuterated as described previously.[3] Adipic acid-β,β'-d_4 was prepared by α protonation of adipic acid-d_8.[6] ^{2}H NMR spectra were determined on a Bruker SXP spectrometer operating at 9.2 MHz.

Adipic acid possesses four methylene fragments, two of which are α and two of which are β to a carboxyl group. The ^{2}H NMR spectrum of perdeuterated adipic acid yields two distinct quadrupole splittings. Since the molecule is symmetrical, both α positions and both β positions are equivalent. Assignment of the two resonances, however, is not trivial since there are the same number of deuterons at the α positions as at the β, and because of possible complications due to angular constraints (eq 1). Through the use of the β,β'-d_4 species, it was found that the deuterons at the β position are responsible for the *larger* quadrupole splitting in both mesophases studied, regardless of whether the presence of adipic acid is the dicarboxylic acid or dianion form. Quadrupole splittings and assignments for all systems studied are given in Table I, together with the temperature dependence of the quadrupole splittings. In all cases $\Delta\nu_\alpha \ll \Delta\nu_\beta$. This is particularly pronounced in the case of the HDTMABr system where a value of 34 Hz is determined for the α positions. Such a low value does not imply that the guest molecule is poorly ordered, but rather that, on the average, the α C—D bond vector is constrained with the ϕ of eq 1 near the "magic angle"; i.e., $S_{\text{C-D}}$ as calculated from eq 1 is identically equal to 0° for θ = 54° 44′.

In the SDS mesophase, the quadrupole splittings for both the α and β positions of adipic acid decrease ~25% upon ionization as expected from solubility arguments;[6] i.e., the dianion is more soluble in the aqueous region (where its degree of order is very low) than the dicarboxylic acid. However, in the HDTMABr mesophase, the quadrupole splitting of the β positions of adipic acid decrease from 1618 to 1193 Hz upon ionization, while that of the α position *increases* from 34 to 94 Hz. In other words, a change in the angle of the α C—D bond vector with respect to the bilayer normal, away from 54° 44′, more than compensates for the change in distribution coefficient upon ionization. This result shows that the stereochemistry of the anchoring of the headgroup at the interface is pH dependent.

Lengthening the dicarboxylate chain by four CH_2 units (i.e., sebacic acid) decreases the angular constraint near the interface. Use of the α,α'-sebacic acid-d_4 species showed that the α deuterons once more give rise to the largest of the four quadrupole splittings observed for the eight methylene fragments (see Table I). In light of the dependence of the observed quadrupole splitting on ϕ on eq 1, however, assignment of a complete order profile for sebacic acid must await further specific deuteration experiments. Care must be exercised in the assignment of the quadrupole splittings for perdeuterated amphiphiles since constraints placed upon the orientation of the C—D bond axes by anchoring of the head group at the interface may predominate. In addition, these effects may be pH dependent.

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A Proton Nuclear Magnetic Resonance Study of "H(phen)$_2$$^+$": Self-Stacking of Protonated Phenanthroline

Sir:

Both potentiometric[1,2] and calorimetric[3] studies on 1,10-phenanthroline in acidic solutions have suggested the presence of H(phen)$_2$$^+$. However, as recent ^{1}H NMR studies[4] showed that phenanthroline itself self-associates strongly in aqueous solution, forming a stack, and that even the charged Zn(phen)$^{2+}$ also stacks, albeit much more weakly, it seemed likely that self-stacking of phenanthroline would also occur in the acidic solutions used in the earlier studies.[1-3] Measurements of the concentration dependence of the ^{1}H NMR spectrum of phenanthroline in acidic solution now show that considerable self-stacking occurs, and that this self-stacking accounts better for the earlier results than does the discrete molecular species H(phen)$_2$$^+$ alone.

The ^{1}H NMR spectrum of 1,10-phenanthroline at pD 1.8 [corresponding to H(phen)$^+$][5] and at pD 5.4 [corresponding to the supposed H(phen)$_2$$^+$][6] changes considerably as the concentration is increased from 0.01 to 0.1 M: the resonances of H_α, H_β, H_γ, and H_δ shift 0.263, 0.193, 0.324, and 0.415 ppm upfield at pD 1.8, and 0.424, 0.397, 0.603, and 0.744 ppm upfield at pD 5.4, respectively. A computer-calculated least-squares fit[7] of the variation with concentration of the chemical shifts of all four protons and of the differences between the chemical shifts of the individual protons[9] gave the stability and constants which are listed in Table I. The values for unprotonated phenanthroline are also listed for comparison.

Table I. Equilibrium Constants for Stacking, and Chemical Shifts of Monomeric and Stacked Phenanthroline[a]

	H_α	H_β	H_γ	H_δ	av[b] K, M^{-1}
			pD 8		
K	20.8	20.3	21.8	24.5	23.6 ± 1.8
δ_0, ppm	9.087	7.847	8.547	8.021	
δ_∞, ppm	8.23	6.79	6.72	5.67	
$\delta_0 - \delta_\infty$, ppm	0.86	1.06	1.82	2.35	
			pD 5.4		
K	18.7	17.5	20.7	22.5	19.6 ± 2.1
δ_0, ppm	9.112	7.958	8.671	8.039	
δ_∞, ppm	7.93	6.86	6.98	5.93	
$\delta_0 - \delta_\infty$, ppm	1.18	1.10	1.70	2.11	
			pD 1.8		
K	9.0	8.0	11.3	11.0	12.0 ± 2.0
δ_0, ppm	9.223	8.159	8.950	8.242	
δ_∞, ppm	8.38	7.54	7.92	6.91	
$\delta_0 - \delta_\infty$, ppm	0.85	0.62	1.03	1.33	

[a] Measured on a Bruker WH-90 FT spectrometer (90.025 MHz) at 27 °C, $I = 0.1$ ($NaNO_3$ in D_2O), using $(CH_3)_4N^+NO_3^-$ as internal reference at 3.188 ppm. [b] Weighted mean of the values of K given by the chemical shifts of H_α, H_β, H_γ, and H_δ and by the six relative shifts $\delta_\alpha - \delta_\beta$, $\delta_\alpha - \delta_\gamma$, . . . $\delta_\gamma - \delta_\delta$ (see text and note 9).

The stability constant for self-stacking is lower for H(phen)$^+$ (pD 1.8) than for phenanthroline itself, owing to Coulombic repulsion; this repulsion is however much smaller than in Zn(phen)$^{2+}$ for which the stability constant[4] is only 1.1 M^{-1}. It is noticeable that the stability constant at pD 5.4 is not much lower than that for unprotonated phenanthroline (at pD ~8); at pD 5.4, on an average, alternate molecules in the stack are protonated, and, owing to the increased distance between the charges, the Coulombic repulsion is only small. All of the resonances of monomeric phenanthroline shift downfield on protonation as expected. The same is true for the calculated positions of the resonances of H_β, H_γ, and H_δ in fully stacked phenanthroline; however the calculated position of the resonance of H_α is shifted slightly upfield as the pD is decreased from ~8 to 5.4, presumably due to a slight change in the orientation of the molecules in the stack; on further acidification the expected downfield shift occurs.

Rund and Keller measured[10] the variation of the ^{1}H NMR spectrum of phenanthroline with added acid[11] and concluded that, as the solubility of unprotonated phenanthroline is low (0.015 M at 25 °C), unprotonated phenanthroline could not account for the strong solutions possible,[13] but that H(phen)$_2$$^+$ must be present in solutions with H$^+$:phen ratios of 1:2. However the formation of a stack in which some molecules are protonated completely accounts for the variation of the NMR spectrum with pH[10] and with phenanthroline concentration as observed here and for the variations of the solubility with pH observed earlier.[1,10]

A preliminary X-ray measurement[14] of the unit cell size of the solid "H(phen)$_2$ClO$_4$" isolated from weakly acidic solutions indicated insufficient space for a regular tetrahedral arrangement of nitrogen atoms about the hydrogen ion in the proposed H(phen)$_2$$^+$ cation: the structural measurements have never been completed. Presumably the crystals contain a stack of phenanthroline molecules, for which there is sufficient space in the unit cell.

In the earliest report[1] of potentiometric evidence for the existence of H(phen)$_2$$^+$ and H(phen)$_3$$^+$, 0.015 M solutions of phenanthroline were used. Owing to the similarity between the stability constants for stacking in neutral solution and at pD 5.4, the proportions of the variously sized stacks changes little