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## Studies of Membrane Processes. VII. Hydrocarbon Chain Motions and the Effect of Changing Counterions

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**Abstract:** A number of specifically deuterated decylsulfates and decanols have been prepared and used as components of lyotropic nematic phases. The deuterium magnetic resonance spectra of these phases are a series of doublets arising from partially averaged nuclear quadrupole couplings. By preparing similar phases, but with enrichment in decylsulfate or decanol or both, the doublets can be assigned to specific methylene groups in the chains. While the results are similar to recent results in other detergent and phospholipid bilayer systems, indicating the same general behavior of these membranoid systems, there are significant and interesting differences. A pronounced alternating orientation effect near the ionic head group is assigned to structural effects of the electrical double layer interface which causes preferential formation of kinks at certain carbons more than others near the head group. The region of approximately constant degree of orientation from positions 1 to 8 is less extensive than in longer chain phospholipid systems but is still present and represents a region of kink equilibrium affecting all carbons equally. The fall off in degree of order at the chain ends is analyzed in terms of rotations about the 8,9 or 9,10 carbon-carbon bonds. The decanol chains are considerably more highly ordered than the decylsulfate chains except at the last carbon. This shows that the flexibility of hydrocarbon chains is a function of the head group and that the chains of the bilayer, although ordered much more than in a hydrocarbon solution, do still act as a heterogeneous two-dimensional ordered solution in these phases, rather than a one-component homogeneously ordered system. The chain flexibility is a function of the counterion even down to the free end of the chain. From the changes in ratios of quadrupole splittings with the counterion it is shown that in the series  $\text{NH}_4^+$ ,  $\text{CH}_3\text{NH}_3^+$ ,  $(\text{CH}_3)_2\text{NH}_2^+$ ,  $(\text{CH}_3)_3\text{NH}^+$ , and  $(\text{CH}_3)_4\text{N}^+$ , it is the dimethylammonium ion which has more ability to penetrate and build structure in the electrical double layer interface. Increase in interface order with counterion can be expressed in the following way:  $(\text{CH}_3)_2\text{NH}_2^+ > (\text{CH}_3)_3\text{NH}^+ \sim \text{CH}_3\text{NH}_3^+ > \text{NH}_4^+ \sim (\text{CH}_3)_4\text{N}^+$ .

Several recent papers and communications<sup>1-12</sup> have described the application of the nuclear magnetic resonance (NMR) tool to lyotropic liquid crystal systems which are homogeneously oriented in the magnetic field. There is a lack of low-angle X-ray diffraction data for the particular systems we have studied and none at all for nematic samples oriented by magnetic fields.<sup>13-16</sup> In these recent papers a superstructure array of infinitely long cylinders of the middle step nematic type have been implicitly assumed, but some results obtained are difficult to explain in this model.<sup>10</sup> Ultimately this lack of knowledge of the exact superstructure array is not a serious handicap in probing the nature of the electrical double layer and hydrophobic regions of the phases at the molecular and ionic level.<sup>8</sup> The lipid bilayer matrix associated with most models of the biological membrane is a close relative of the detergent bilayer and other superstructure arrays of lyotropic liquid crystals.<sup>17</sup> The detergent bilayer system is simpler than the branched chain lipid systems,<sup>18</sup> but the NMR results reported for both types of bilayer are remarkably similar.<sup>8,19-22</sup> The same basic processes can be studied in both models<sup>23</sup> and these processes are common to all bilayer membranes. It is this feature which attracts our attention, while separately we have also been successful in orienting complex ions and have determined some ion structures.<sup>2,5,6,8,11,12,24</sup>

The thermotropic liquid crystal is such that each molecule of a one-component phase is aligned in a statistically equivalent manner.<sup>25</sup> The heterogeneity of statistical or-

dering of the microcomponents that make up lyotropic nematic phases is an interesting problem and some work in this field has appeared.<sup>1,7,8,10,16</sup> The division of these lyotropic nematic phases into the hydrophobic, electrical double layer, and hydrophilic regions provides us with a crude membrane model to study typical microprocesses at the level of ions, water, ionic head, or chain segment. In this particular study the preparation of specifically deuterated detergents is described and the lyotropic nematic phases made with these detergents are varied by changing the nature of the counterion. The changes in degree of microorder of various components of the phases are studied with a view to interpretation in terms of ion penetration. Deuterium magnetic resonance is the principal tool used to describe the degrees of order.

### Experimental Section

Deuterium magnetic resonance spectra were obtained at  $\sim 27^\circ$  from a Varian XL-100 spectrometer or a Bruker Hx-90 spectrometer both equipped with Fast Fourier Transform capability. (We are greatly indebted to Professor J. B. Stothers for obtaining the XL-100 spectra for us.) Spectral widths were between 10 and 20 kHz and pulse widths were 25  $\mu\text{sec}$ . About 1000 transients of 8K data points were collected, processed to the frequency mode, then displayed on paper. Time between pulses was 0.3 sec. Noise decoupling of 1.5 kHz bandwidth at 100 MHz was employed to decouple the protons from the deuterium. This resulted in a considerable sharpening of the deuterium transitions but this gain was partially offset by the fact that the data were collected before the system obtained a high degree of homogeneity. Data collection was begun

Table I. The Compositions of the Deuterium Labeled Nematic Phases Prepared and Studied in This Paper<sup>a</sup>

| Phase           | Sodium decylsulfate | Label positions <sup>c</sup> | Decanol | Label positions <sup>c</sup> | H <sub>2</sub> O (0.5% D <sub>2</sub> O) | Ion |  |
|-----------------|---------------------|------------------------------|---------|------------------------------|--|-----|--|
| 1               | 36.4                | 1,2;8,9,10                   | 6.2     |                              | 54.4                                     | 3.0 | (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>    |
| 2               | 40.2                | 1,2;8,9,10                   | 4.3     |                              | 52.3                                     | 3.2 | NH <sub>4</sub> Cl                                 |
| 3               | 33.4                | 1,2;8,9,10                   | 5.1     |                              | 57.0                                     | 4.5 | CH <sub>3</sub> NH <sub>3</sub> Cl                 |
| 4               | 33.7                | 1,2;8,9,10                   | 6.4     |                              | 55.1                                     | 4.8 | (CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> Cl |
| 5               | 33.5                | 2;2,3;8,9,10                 | 6.7     | 2,3;9,10                     | 54.9                                     | 5.0 | (CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> Cl |
| 6               | 33.5                | 3,4;8,9,10                   | 6.7     | 1;3,4                        | 54.8                                     | 5.0 | (CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> Cl |
| 7               | 37.4                | 1,2;8,9,10                   | 6.2     |                              | 50.3                                     | 6.1 | (CH <sub>3</sub> ) <sub>3</sub> NHCl               |
| 8               | 37.4                | 2,3;8,9,10                   | 6.2     | 9,10                         | 50.2                                     | 6.2 | (CH <sub>3</sub> ) <sub>3</sub> NHCl               |
| 9               | 37.5                | 8,9,10                       | 6.2     | 1,2                          | 50.1                                     | 6.2 | (CH <sub>3</sub> ) <sub>3</sub> NHCl               |
| 10              | 39.9                | 1,2;8,9,10                   | 6.8     |                              | 47.7                                     | 5.6 | (CH <sub>3</sub> ) <sub>4</sub> NCl                |
| 11 <sup>b</sup> | 39.4                | 1,2;8,9,10                   | 6.7     |                              | 47.0                                     | 5.5 | (CH <sub>3</sub> ) <sub>4</sub> NCl                |
| 12              | 36.2                | 1;3,4                        | 6.7     | 9,10                         | 54.3                                     | 2.8 | (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>    |
| 13              | 40.3                | 1;3,4                        | 4.2     | 9,10                         | 52.3                                     | 3.2 | NH <sub>4</sub> Cl                                 |
| 14              | 33.4                | 1;3,4                        | 5.0     | 9,10                         | 57.2                                     | 4.4 | CH <sub>3</sub> NH <sub>3</sub> Cl                 |
| 15              | 35.0                | 1;3,4                        | 6.6     | 9,10                         | 53.4                                     | 5.0 | (CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> Cl |
| 16              | 34.8                | 3,4                          | 6.6     | 3,4;9,10                     | 53.6                                     | 5.0 | (CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> Cl |
| 17              | 33.6                |                              | 6.4     | 2,3;8,9,10                   | 55.0                                     | 5.0 | (CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> Cl |
| 18              | 37.4                | 1;3,4                        | 6.6     | 9,10                         | 50.4                                     | 6.1 | (CH <sub>3</sub> ) <sub>3</sub> NHCl               |
| 19              | 40.1                | 1;3,4                        | 6.7     | 9,10                         | 47.6                                     | 5.6 | (CH <sub>3</sub> ) <sub>4</sub> NCl                |

<sup>a</sup>The compositions are given in weight percentages. <sup>b</sup>This phase contains 1.4 wt % methanol. <sup>c</sup>A semicolon indicates the presence of separately prepared compounds.

after the sample was only 15 min in the probe whereas generally several hours are required before high homogeneity is obtained.

**Preparation of the Specifically Deuterated Decanols.** The deuterated alcohols were prepared by standard techniques<sup>26</sup> and only a brief outline of the preparations is given below.

**1,1-Dideuteriodecanol.** Decanoic acid was reduced with LiAlD<sub>4</sub>.

**1,1,2,2-Tetradeteriodecanol.** Decanol (50 gm) was refluxed in D<sub>2</sub>O/pyridine (1:2, 150 ml) for 13 hr after which time the D<sub>2</sub>O/pyridine was removed on a rotary evaporator. The product was treated with a second 150 ml portion of D<sub>2</sub>O/pyridine also for 13 hr, then the solvent was removed and the product was distilled under vacuum (110° (15 mm)). The aldehyde was oxidized to the acid and then reduced with LiAlD<sub>4</sub> to the alcohol.

**2,2,3,3-Tetradeteriodecanol.** 2-Decyn-1-ol was reduced over platinum with D<sub>2</sub> at atmospheric pressure.

**3,3,4,4-Tetradeteriodecanol.** 3-Decyn-1-ol was reduced over platinum with D<sub>2</sub> at atmospheric pressure.

**9,9,10,10,10-Pentadeteriodecanol.** 9-Decen-1-ol was dibrominated with Br<sub>2</sub>; then HBr was eliminated under basic conditions. Base exchange of the acetylenic proton provided the deuterated 9-decyn-1-ol which was reduced with D<sub>2</sub> over Pt. A small amount of isomerization of the triple bond to the 8 position occurred so that some deuterium was obtained at this position.

**Sodium Decylsulfate.** The procedure described by Radley<sup>27</sup> was slightly modified and is described below for a typical preparation. 3,3,4,4-Tetradeteriodecanol (8.0 g) in an Erlenmeyer flask was cooled to -15° then powdered with a spatula. Sulfuric acid (13.9 g; 1 decanol to 3 acid molar ratio) also at -15° was added to the decanol and the mixture was stirred until the decanol went into solution. During this step the solution was allowed to warm to about 0°. Care must be taken that the solution does not become too warm, to prevent decomposition. The solution was let stand overnight at -15° during which time a solid material was formed.

Sodium hydroxide (15 g), in an Erlenmeyer flask, was dissolved in water (15 ml); then cracked ice (~60 g) was added. Some of the NaOH solution (~10 ml) was removed from the Erlenmeyer flask and the remainder was surrounded by ice. The product was allowed to warm until it began to melt. The melt was added to the stirred NaOH solution. Neutralization of the decylsulfuric acid was monitored by pH paper and additional NaOH solution was added as required. It was ensured that the final solution was neutral by adjustment with sulfuric acid when necessary.

Sodium sulfate was precipitated from solution by the addition of ethanol (~200 ml). The mixture was filtered under vacuum then the final solution evaporated under reduced pressure on a rotary evaporator until approximately 50 ml of solution was left. Addition of ethanol (~200 ml) provided more sodium sulfate which was removed by filtration. The resultant solution was evaporated to dryness, taken up in hot absolute ethanol (~150 ml), filtered under vacuum, then allowed to cool finally to -15°. Colorless flakes of

the product were obtained. The product was obtained by filtration then recrystallized from anhydrous ethanol. The product was recovered by filtration then air dried to yield the pure sodium 3,3,4,4-tetradeteriodecylsulfate (9.3 g, 71%).

**Preparation of the Nematic Phases.** The compositions of the nematic phases are given in Table I. Percentages refer to the weight percent of the compounds in the mixture. The dry components were weighed onto weighing paper then added to a small test tube to which the liquid components were then added. Mixing was accomplished with the aid of a small stirring rod. The formation of the phases was aided by warming in a water bath, stirring, then centrifuging the solution. Excessive evaporation was prevented by sealing the test tube with a stopper whenever the solution was not being stirred. No problems concerning reproduction of phases were encountered when this procedure was used.

## Results

**Characteristics of the Spectra.** The spectra obtained from samples containing the same isotopic substitution did not vary greatly from sample to sample. Figure 1 shows spectra obtained for nematic solutions containing the trimethylammonium ion. Discussion of this figure applies equally to spectra obtained from other samples.

Figure 1A shows the spectra obtained from sample 7; this spectrum in conjunction with those obtained from samples 8 (Figure 1B) and 18 (Figure 1C) allows unambiguous assignment of the resonances.

The resonances from positions 8 and 10 are assigned readily on the basis of intensity. Position 10 has three deuteriums compared to two on carbon 9. The resonance from position 8 is no problem since it is of very low intensity because deuterium substitution is only partially complete here. Figure 1A shows the spectrum arising from deuterium substitution at positions 9 and 10 of the decylsulfate. Figure 1B is similar except this spectrum has superimposed on it resonances from decanol also substituted in the 9 and 10 positions. Figure 1C shows the doublets arising from decanol with no 9,10-deuterated decylsulfate.

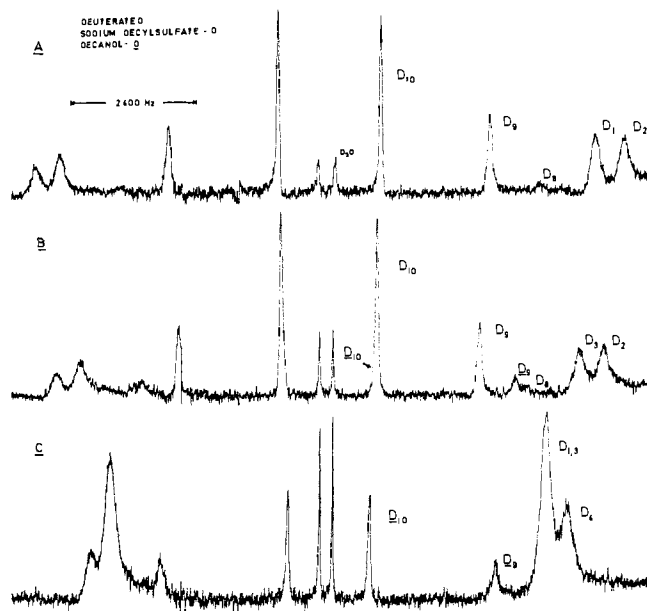
The outer two doublets of Figure 1A arise from labeling at 1 and 2 positions. Clearly there is a chemical shift separation between the two pairs of doublets with the inner doublet being to lower field than the outer. This shows that the inner doublet corresponds to the deuteriums of carbon 1. The outer doublets displayed in Figure 1B correspond to deuteriums at positions 2 and 3. Here there is no observable chemical shift separation. The problem of assigning reso-

nances here is most readily resolved by taking the ratios of splittings at position 2 to that at 10 from 1A then noticing a similar ratio for the 2 and 3 splittings to the splitting at position 10 from Figure 1B. Ratios of splittings were found to be insensitive to changes in the phase although the absolute numbers may vary considerably. From Figure 1A  $\Delta\nu_2/\Delta\nu_{10} = 5.71$ , from Figure 1B the outer doublet has a ratio 5.68, the inner 5.18. Clearly the outer doublet corresponds to the deuteriums of position 2.

Figure 1C shows the spectra obtained from a sample containing 1,1-dideuterio- and 3,3,4,4-tetra-deuteriododecylsulfate as well as 9,9,10,10,10-pentadeuteriododecanol. From the results of Figures 1A and 1B we would expect that the signals arising from positions 1 and 3 would overlap and we would observe a doubly intense inner doublet as is indeed found. This means that the outer doublet corresponds to the resonance arising from position 4. It should be noted that if the assignment of the transitions of Figure 1A were reversed we could make no assignments concerning Figure 1C because of ratio anomalies which are unreasonable in view of other results from this laboratory.<sup>8,28</sup> Indeed even changing the ion could scarcely account for the changes in ratio that would be required, as indicated by comparing the appropriate values in Tables IV and V. Tables II-V give the experimental values of quadrupole splittings and various ratios of splittings of interest.

## Discussion

(a) **Deuterium Quadrupole Coupling in the Chain Segments.** The deuterium NMR spectra of specifically deuterated detergents in nematic phases are all very similar and the effect of counterion substitution on the experimental parameters is somewhat subtle. In Tables II and III the split-



**Figure 1.** Deuterium magnetic resonance spectra of lyotropic nematic phases. 1A from sample 7, 1B from sample 8, and 1C from sample 18. The spectra coincide on the vertical axis with the center of the  $D_2O$  doublet. The peaks are assigned as  $D_i$  for the  $i$ th carbon in the decylsulfate chain and  $D_j$  for the  $j$ th carbon in the decanol chain. The spectra also show how small variations in composition and other factors can affect the quadrupole splittings.

ting of the quadrupole doublet for deuterium is listed for all the nematic phases prepared and all specific positions labeled. These show a quantity proportional to the degree of orientation of the C-D bond axes if we assume negligible asymmetry parameter and a quadrupole coupling constant

**Table II.** Nuclear Quadrupole Splittings Measured for Deuterium in Specifically Deuterated Detergents Used to Make the Phases from Table I<sup>a</sup>

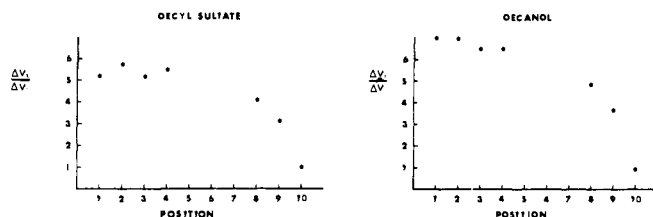
| Phase           | $\Delta\nu_1$ | $\Delta\nu_2$       | $\Delta\nu_3$ | $\Delta\nu_8$      | $\Delta\nu_9$ | $\Delta\nu_{10}$ | $\Delta\nu_{D_2O}$ | Ion              |
|-----------------|---------------|---------------------|---------------|--------------------|---------------|------------------|--------------------|------------------|
| 1               | 7,290         | 7,780               |               | 6,020 <sup>b</sup> | 4,630         | 1,463            | 247                | $(NH_4)_2SO_4$   |
| 2               | 10,150        | 10,750 <sup>b</sup> |               | 8,380              | 6,438         | 2,034            | 359                | $NH_4Cl$         |
| 3               | 10,560        | 11,610              |               | 8,400              | 6,386         | 2,052            | 287                | $CH_3NH_3Cl$     |
| 4               | 12,160        | 13,490              |               | 9,490              | 7,189         | 2,311            | 310                | $(CH_3)_2NH_2Cl$ |
| 5               |               | 13,820              | 12,580        |                    | 7,260         | 2,313            | 307                | $(CH_3)_2NH_2Cl$ |
| 6               |               |                     | 13,090        | 10,090             | 7,623         | 2,440            | 363                | $(CH_3)_2NH_2Cl$ |
| 7               | 10,280        | 11,290              |               | 8,090              | 6,173         | 1,976            | 329                | $(CH_3)_3NHCl$   |
| 8               |               | 10,500              | 9,580         | 7,550              | 5,779         | 1,848            | 260                | $(CH_3)_3NHCl$   |
| 9               |               |                     |               | 6,620              | 5,024         | 1,612            | 291                | $(CH_3)_3NHCl$   |
| 10              | 9,150         | 9,910               |               | 5,860              | 5,658         | 1,795            | 271                | $(CH_3)_4NCl$    |
| 11 <sup>c</sup> | 7,410         | 8,020               |               | 5,860              | 4,440         | 1,414            | 219                | $(CH_3)_4NCl$    |
| Error           | ~40           | ~40                 | ~40           | ~60                | ~15           | ~5               | ~2                 |                  |

<sup>a</sup> Splittings reported are for the deuterated decylsulfate. <sup>b</sup> Splittings have a larger error than normal, ~100 Hz. <sup>c</sup> This phase contains 1.4 wt % methanol.

**Table III.** Nuclear Quadrupole Splittings Obtained from Nematic Phases Listed in Table I for Deuterium<sup>a</sup>

| Phase | $\Delta\nu_1 \sim \Delta\nu_3^b$ | $\Delta\nu_2^b$ | $\Delta\nu_4^b$    | $\Delta\nu_1^c \sim \Delta\nu_2^c$ | $\Delta\nu_3^c \sim \Delta\nu_4^c$ | $\Delta\nu_8^c$ | $\Delta\nu_9^c$    | $\Delta\nu_{10}^c$ | $\Delta\nu_{D_2O}$ | Ion              |
|-------|----------------------------------|-----------------|--------------------|------------------------------------|------------------------------------|-----------------|--------------------|--------------------|--------------------|------------------|
| 12    | 8,500                            |                 | 9,140 <sup>d</sup> |                                    |                                    |                 | 6,850              | 1,680              | 287                | $(NH_4)_2SO_4$   |
| 13    | 8,230 <sup>d</sup>               |                 | 8,760 <sup>d</sup> |                                    |                                    |                 | 7,060 <sup>d</sup> | 1,657              | 293                | $NH_4Cl$         |
| 14    | 10,390                           |                 | 11,340             |                                    |                                    |                 | 7,610              | 1,865              | 329                | $CH_3NH_3Cl$     |
| 15    | 11,990                           |                 | 13,130             |                                    |                                    |                 | 8,320              | 2,053              | 376                | $(CH_3)_2NH_2Cl$ |
| 16    | 12,840                           |                 | 13,950             |                                    |                                    |                 | 8,710              | 2,142              | 375                | $(CH_3)_2NH_2Cl$ |
| 17    |                                  |                 |                    | 15,480                             | 14,535                             | 10,930          | 8,320              | 2,056              | 293                | $(CH_3)_2NH_2Cl$ |
| 5     | 12,580                           | 13,820          |                    | 16,100                             | 15,060                             |                 | 8,460              | 2,080 <sup>d</sup> | 307                | $(CH_3)_2NH_2Cl$ |
| 6     | 13,090                           |                 | 14,280             | 17,090                             | 16,130 <sup>d</sup>                |                 |                    |                    | 363                | $(CH_3)_2NH_2Cl$ |
| 18    | 8,390                            |                 | 9,130              |                                    |                                    |                 | 6,430              | 1,573              | 308                | $(CH_3)_3NHCl$   |
| 8     | 9,580                            | 10,500          |                    |                                    |                                    |                 | 7,170              | 1,810 <sup>d</sup> | 260                | $(CH_3)_3NHCl$   |
| 9     |                                  |                 |                    | 11,180                             |                                    |                 |                    |                    | 291                | $(CH_3)_3NHCl$   |
| 19    | 8,180                            |                 | 8,730 <sup>d</sup> |                                    |                                    |                 | 6,550              | 1,590              | 256                | $(CH_3)_4NCl$    |
| Error | ~40                              | ~40             | ~40                | ~80                                | ~80                                | ~80             | ~15                | ~5                 | ~2                 |                  |

<sup>a</sup> In some cases coincidence of splittings is indicated by having two labeled positions at the head of the columns. <sup>b</sup> Splittings obtained from deuterated decylsulfate. <sup>c</sup> Splittings obtained from deuterated decanol. <sup>d</sup> Splittings have a larger error (~100 Hz).



**Figure 2.** Ratios of deuterium quadrupole splittings ( $\Delta\nu_x/\Delta\nu_{10}$ ) for decylsulfate and decanol chains from the phases containing dimethylammonium ion. The position "x" is plotted on the horizontal axis. Note that ratios are higher for any given carbon in decanol.

independent of the site in the chain. Such an approximation has a high degree of validity.<sup>29</sup>

Under the conditions that the asymmetry parameter,  $\eta$ , equals 0 and the C-D bond axis is the direction of the principal electric field gradient the degree of orientation of the C-D bond is obtained from the quadrupole splitting,  $\Delta\nu_D$ , by

$$\Delta\nu_D = \frac{3}{2} Q_D S_{CD} \quad (1)$$

$\Delta\nu_D$  is the observed splitting,  $Q_D$  is the quadrupole coupling constant taken as 170 Hz for C-D bonds.  $S_{C_2D}$  is the degree of orientation along the CD bond axis for a  $CD_2$  group,  $S_{C_3D}$  for a methyl group. The  $CD_2$  plane is perpendicular to the chain segment axis and parallel to the electrical double layer interface in a perfectly oriented repeated trans arrangement. The degree of orientation of the chain segment axis ( $S_{zz}$ )<sub>2</sub> perpendicular to the C-D bond is given by (2) since  $S_{C_2D} = \frac{1}{2}(3 \cos^2 90 - 1)(S_{zz})_2$ .

$$\Delta\nu_D = -\frac{3}{4} Q_D (S_{zz})_2 \quad (2)$$

If these nematic phases have a cylindrical superstructure perpendicular to the magnetic field ( $H_0$ ),  $S_{zz}$  is averaged over 360°. That is

$$\begin{aligned} \Delta\nu_D &= -\frac{3}{4} Q_D \frac{1}{2} \langle 3 \cos^2 \beta - 1 \rangle S_{zz}^0 \\ &= -\frac{3}{16} Q_D S_{zz}^0 \end{aligned} \quad (3)$$

where  $\beta$  ranges from 0° to 360°. Consequently  $S_{zz}^0$  is the degree of orientation of a segment axis corrected for rotation or diffusion around the cylindrical array.

The data from the tables (see also Figure 2) show that the degree of orientation of the C-D bond in the decylsulfate is roughly constant from positions 1 to 8 then falls off rapidly for the terminal groups. An alternating effect in the degree of order along the chain is observed. Position 1 has a C-D bond with a smaller degree of orientation than position 2 but about the same as 3. Position 4 has a degree of order only slightly less than that of position 2. Although not discussed previously, a similar but not so pronounced alternating effect has been found in bilayer systems, Figure 2 of ref 22a, and Figure 3 of ref 30. The region of near constant order parameter accompanied by a rapid decrease near the terminal positions has been found in bilayer systems.<sup>22,30,31</sup> These features have been interpreted in terms of complementary gauche interactions which introduce "kinks" and "jogs" which are in equilibrium along the chains.<sup>22,30</sup> These represent thermally excited imperfections in the perfect trans alignment and lead to some disorder with the creation of some free volume. In the region where the degree of order is nearly constant along the chain, then the kink-jog-extended equilibrium must be the same for all segments. Near the free chain end a single gauche conformer has increasing probability because the volume swept out by the

chain ends is not so large as the chain rotates. A rapid fall in degree of order at each succeeding segment near the chain end is observed for all bilayer systems so far studied. The great similarity in behavior between phospholipid bilayers<sup>22</sup> and the simpler detergent bilayers reported here is interesting since it indicates certain generalities in the state of order in bilayer membrane structures.

There are differences in the present detergent system connected with the alternation of the degree of order which goes at least up to position 4. Such an alternation is indicative of preferential points for the kink formation. A more rigidly fixed head group could be responsible for restricting kink formation at certain carbons or interfering with their motion along the chain. Without knowledge of the solvation structure at the electrical double layer interface it is difficult to suggest a model to explain this properly. However, the statistical mechanical approach to chain ordering has been able to reproduce the order pattern for the bilayer system of sodium octanoate-decanol-water.<sup>32</sup>

The quaternary phases prepared in this work contain selectively deuterated decanol as a minor component. Figure 2 shows that at any given carbon segment the degree of order along the C-D bonds is higher for the decanol than for the decylsulfate. As an example, from the tables a value  $\Delta\nu_2 = 16.1$  kHz for the splitting at the second carbon in decanol and  $\Delta\nu_2 = 13.82$  kHz for the second carbon in the decylsulfate chain can be selected (phase 5) to yield from eq 3  $S_{zz}^0 = 0.505$  for decanol and 0.434 for decylsulfate at the second segment position. The decanol has some 16% higher order at this position. The decylsulfate chain is longer than the decanol chain so that if the polar -OH group resides in the interface with the  $-SO_3^-$  group, then the first segment,  $-CD_2-$ , of the decanol still coincides with some position in the sulfate group. The higher degree of order imposed upon it therefore derives from the stronger binding forces of the interface layer which we have previously studied.<sup>8</sup> This displacement of corresponding segments of the decanol toward the surface cannot explain all aspects of the results. The degree of order at positions 3 and 4 of the decanol does not correspond to positions 1 and 2 of the decylsulfate chain where coincidence of position might be expected. The alternation of degree of order is not observed for the decanol chain and positions 3 and 4 have higher order than 1 and 2 of the decylsulfate. The results are novel in that they show conclusively for chains with different head groups the kink-jog-extended motions are different. The only difference between decanol and decylsulfate is in the head group so that the interface structure must be dominant in determining these differences. The electrical double layer interface has so far been ignored in considerations of factors affecting order in different types of molecules or ions, but it is clear that the interface has rather specific effects. The decylsulfate, being ionic, may have some extra freedom of motion into the aqueous region which the nonionic, more tightly bound decanol does not have.

**(b) Some Quantitative Considerations Regarding the Rapid Decrease in the Degree of Orientation of the Terminal Chain Segments.** The factors which lead to a rapid fall in degree of order at the end of the chain can be analyzed.<sup>8,9</sup> The discussion will be referring to the phases from which the spectra in Figure 1 were obtained. These do not differ significantly from the results obtained with other phases as seen in Tables IV and V. The  $-CD_2CD_3$  end group can be treated according to eq 1 to obtain  $S_{C_2D}$  and  $S_{C_3D}$  for the methylene and methyl deuteriums. Equation 2 gives the degree of order of the segment axis for the  $CD_2$  group. Equation 4, however, is required to obtain the degree of order of this segment axis from the methyl splitting since the methyl group sits in a different orientation with respect to the chain

Table IV. Ratios of Quadrupole Splittings for Various Specifically Deuterated Hydrocarbon Chain Positions from Values Listed in Table II<sup>a</sup>

| Phase           | Ratios of quadrupole splittings |                              |                              |                              |                              |                              |                                   |
|-----------------|---------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|-----------------------------------|
|                 | $\Delta\nu_2/\Delta\nu_1$       | $\Delta\nu_1/\Delta\nu_{10}$ | $\Delta\nu_2/\Delta\nu_{10}$ | $\Delta\nu_3/\Delta\nu_{10}$ | $\Delta\nu_8/\Delta\nu_{10}$ | $\Delta\nu_9/\Delta\nu_{10}$ | $\Delta\nu_{10}/\Delta\nu_{D_2O}$ |
| 1               | 1.067                           | 4.98                         | 5.32                         |                              | 4.12 <sup>b</sup>            | 3.17                         | 5.92                              |
| 2               | 1.060 <sup>b</sup>              | 4.99                         | 5.29                         |                              | 4.12                         | 3.17                         | 5.65                              |
| 3               | 1.100                           | 5.15                         | 5.66                         |                              | 4.09                         | 3.11                         | 7.15                              |
| 4               | 1.109                           | 5.26                         | 5.84                         |                              | 4.11                         | 3.11                         | 7.46                              |
| 5               |                                 |                              | 5.97                         | 5.44                         |                              | 3.14                         | 7.53                              |
| 6               |                                 |                              |                              | 5.37                         | 4.13                         | 3.12                         | 6.72                              |
| 7               | 1.099                           | 5.20                         | 5.71                         |                              | 4.08                         | 3.12                         | 6.01                              |
| 8               |                                 |                              | 5.68                         | 5.18                         | 4.08                         | 3.12                         | 7.12                              |
| 9               |                                 |                              |                              |                              | 4.11                         | 3.12                         | 5.54                              |
| 10              | 1.083                           | 5.10                         | 5.52 <sup>b</sup>            |                              |                              | 3.15                         | 6.62                              |
| 11 <sup>c</sup> | 1.083                           | 5.24                         | 5.67                         |                              | 4.14                         | 3.14                         | 6.46                              |
| Error           | 0.005                           | 0.03                         | 0.03                         | 0.03                         | 0.03                         | 0.02                         | 0.06                              |

<sup>a</sup> Splittings reported are for the deuterated decylsulfate. <sup>b</sup> Ratios have a larger error than normal. <sup>c</sup> This phase contains 1.4 wt % methanol and this could adequately account for some rather large changes in ratio as compared to phase 10 which is similar but contains no methanol.

Table V. Ratios of Quadrupole Splittings for Various Specifically Deuterated Hydrocarbon Chain Positions from Values Listed in Table III<sup>a</sup>

| Phase | Ratios of quadrupole splittings |   |                           |                                |                                |                                |                                |                                  |                                  |                                  |
|-------|---------------------------------|---|---------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|----------------------------------|----------------------------------|----------------------------------|
|       | $\Delta\nu_2/\Delta\nu_3$       | $\Delta\nu_4/\Delta\nu_1$                 | $\Delta\nu_4/\Delta\nu_3$ | $\Delta\nu_1/\Delta\nu_{10}^b$ | $\Delta\nu_3/\Delta\nu_{10}^b$ | $\Delta\nu_2/\Delta\nu_{10}^b$ | $\Delta\nu_4/\Delta\nu_{10}^b$ | $\Delta\nu_2^b/\Delta\nu_{10}^b$ | $\Delta\nu_3^b/\Delta\nu_{10}^b$ | $\Delta\nu_9^b/\Delta\nu_{10}^b$ |
| 12    |                                 | 1.076 <sup>c</sup>                        |                           | 5.06                           |                                |                                | 5.45 <sup>c</sup>              |                                  |                                  | 4.09                             |
| 13    |                                 | 1.064                                     |                           | 4.96                           |                                |                                | 5.29 <sup>c</sup>              |                                  |                                  | 4.26 <sup>c</sup>                |
| 14    |                                 | 1.091                                     |                           | 5.57                           |                                |                                | 5.95                           |                                  |                                  | 4.08                             |
| 15    |                                 | 1.095                                     |                           | 5.84                           |                                |                                | 6.40                           |                                  |                                  | 4.05                             |
| 16    |                                 |   | 1.086                     |                                | 6.00                           |                                | 6.51                           |                                  |                                  | 4.07                             |
| 17    |                                 |   |                           |                                |                                |                                |                                | 7.53                             | 7.07                             | 4.05                             |
| 5     | 1.098                           |   |                           |                                | 6.06 <sup>c</sup>              | 6.65 <sup>c</sup>              |                                | 7.74 <sup>c</sup>                | 7.24 <sup>c</sup>                | 4.07 <sup>c</sup>                |
| 6     |                                 |   | 1.091                     |                                |                                |                                |                                |                                  |                                  |                                  |
| 18    |                                 | 1.090                                     |                           | 5.32                           |                                |                                | 5.80                           |                                  |                                  | 4.08                             |
| 8     | 1.096                           |   |                           |                                | 5.29 <sup>c</sup>              | 5.80 <sup>c</sup>              |                                |                                  |                                  | 4.08 <sup>c</sup>                |
| 19    |                                 | 1.066 <sup>c</sup>                        |                           | 5.15                           |                                |                                | 5.49 <sup>c</sup>              |                                  |                                  | 4.12                             |
| Error | ~0.005                          | ~0.005                                    | ~0.005                    | ~0.03                          | ~0.03                          | ~0.03                          | ~0.03                          | ~0.05                            | ~0.05                            | ~0.02                            |
| 6     |                                 | $\Delta\nu_1^b/\Delta\nu_{10} = 7.00$     |                           |                                |                                |                                |                                |                                  |                                  |                                  |
| 9     |                                 | $\Delta\nu_{1,2}^b/\Delta\nu_{10} = 6.94$ |                           |                                |                                |                                |                                |                                  |                                  |                                  |
| 17    |                                 | $\Delta\nu_3^b/\Delta\nu_{10} = 5.32$     |                           |                                |                                |                                |                                |                                  |                                  |                                  |
| 5     |                                 | $\Delta\nu_{10}^b/\Delta\nu_{10} = 0.90$  |                           |                                |                                |                                |                                |                                  |                                  |                                  |

<sup>a</sup> Splittings obtained from deuterated decylsulfate. <sup>b</sup> Splittings obtained from deuterated decanol. <sup>c</sup> Splittings have a larger error ( $\sim \pm 50$  Hz).

segment axis.

$$S_{C_3D} = \frac{1}{2}(3 \cos^2 \theta - 1) \frac{1}{2}(3 \cos^2 \gamma - 1)(S_{zz})_3 \quad (4)$$

The angle  $\theta = 109.5^\circ$  is the C<sub>9</sub>-C<sub>10</sub>-D angle and the corresponding term transfers the order to the C-CD<sub>3</sub> bond axis.  $\gamma = 34^\circ$  is the angle between the C-C bonds and the segment axis as in normal hydrocarbons. Using these numerical values of the angles, eq 4 becomes

$$\Delta\nu_{C_3D} = -0.177 Q_D (S_{zz})_3 \quad (5)$$

If the -CD<sub>2</sub>CD<sub>3</sub> group moves as a unit in any motions, then the degree of orientation  $(S_{zz})_2$  from the -CD<sub>2</sub>- group and  $(S_{zz})_3$  from the -CD<sub>3</sub> group should be the same value and this implies a ratio  $\Delta\nu_9/\Delta\nu_{10} = 2.82$ . If, however, the -CD<sub>2</sub>- group rotates about the 9,10 axis or the methyl group rotates about the 8,9 axis, then the two computed degrees of order will not be the same. Examination of the quadrupole coupling ratios for deuterium in the 9 and 10 positions,  $(\Delta\nu_9/\Delta\nu_{10})$  in Tables IV and V, reveals that this theoretical ratio 2.82 is never observed.

Two possible motions can be invoked to explain the experimental ratios as indicated in Figure 3. In Figure 3A rotation occurs about the 8,9 carbon-carbon bond and in 3B about the 9,10 carbon-carbon bond. The latter process must be compensated at some other near point in the chain to avoid undue creation of free volume. In the conformational process 3A two contributions to the degree of order can be written:

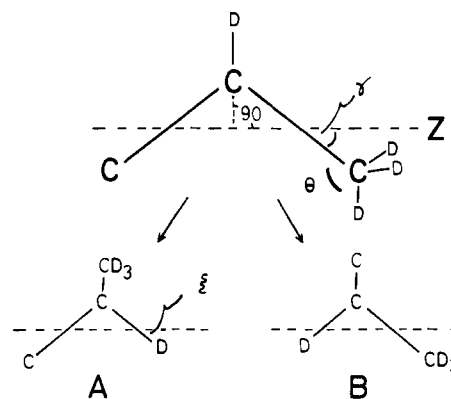


Figure 3. Conformational averaging involving the terminal positions of hydrocarbon chains. 3A represents a rotation about the 8,9 C-C bond and 3B represents the process of rotation about the 9,10 bond. This latter process must be accompanied by a reverse rotation close by in the chain to prevent the creation of large free volume.

$$S_{C_3D'} = \frac{1}{2}(3 \cos^2 \theta - 1) \frac{1}{2}(3 \cos^2 90 - 1)(S_{zz}')_3 \quad (6)$$

and

$$S_{C_2D'} = \frac{1}{2} \left[ \frac{1}{2}(3 \cos^2 90 - 1) + \frac{1}{2}(3 \cos^2 \xi - 1) \right] (S_{zz}')_2 \quad (7)$$

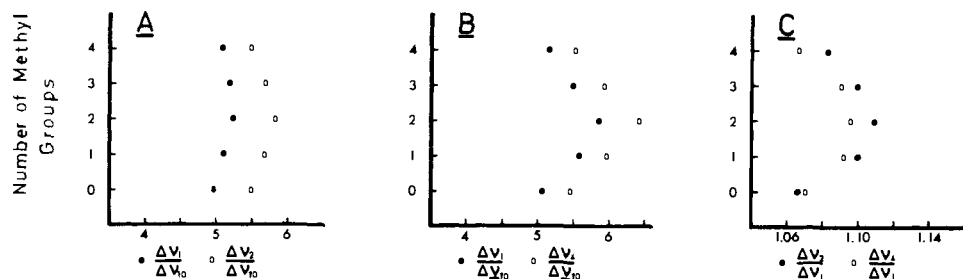


Figure 4. Ratio of quadrupole couplings as a function of counterion type from the phases described in Table I. A. Decylsulfate chains, first and second to terminal carbons. B. First and fourth carbons of decylsulfate to terminal carbons of decanol. C. Decylsulfate chains, second to first carbon and fourth to first carbon.

$(S_{zz'})_3$  and  $(S_{zz'})_2$  are the degrees of orientation of the segment axis bisecting carbon-carbon bonds 8,9 and 9,10 in the trans conformation taking into account motions of the type in Figure 3A only.  $S_{C_3D'}$  and  $S_{C_2D'}$  are degrees of orientation along the methyl and methylene C-D bonds computed from  $(S_{zz'})_3$  and  $(S_{zz'})_2$ . Substituting  $\xi = 36^\circ$ , the equations above become:

$$S_{C_3D'} = 0.166(S_{zz'})_3 \quad (8)$$

$$S_{C_2D'} = -0.01(S_{zz'})_2 \quad (9)$$

Assuming a fraction  $x$  of chains nonrotated and  $(1-x)$  in the rotated form, Figure 3A, the observed degree of order is the population weighted average of (8) and (9) with the earlier derived straight chain formulas, (2) and (5). The expressions 10 and 11 are now obtained

$$S_{C_3D} = [-0.177x + 0.166(1-x)]S_3 \quad (10)$$

$$S_{C_2D} = [-0.5x - 0.01(1-x)]S_2 \quad (11)$$

where  $S_3$  and  $S_2$  are equal. The ratio may be written:

$$S_{C_2D}/S_{C_3D} = -[0.01 + 0.49x]/[0.166 - 0.343x] \quad (12)$$

The factor on the right varies between 2.82 for  $x = 1$  to  $\sim 50$ , at  $x = 0.5$ . As a consequence the ratio on the left side of (12) must increase in absolute magnitude as the conformation of Figure 3A increases in population.

The conformational averaging described by Figure 3B affects the degree of order of the methylene  $CD_2$  only and

$$S_{C_3D} = -0.177S_3'$$

$$S_{C_2D} = [-0.5x + (-0.01)(1-x)]S_2' \quad (13)$$

corresponding to eq 10 and 11 for the process of Figure 3B. As  $x$  decreases from 1 in this case, the ratio ( $S_{C_3D}/S_{C_2D}$ ) decreases from the values for the completely extended chain. This case of conformational averaging has been reported by us for the  $^+ND_3CD_2^-$  head groups in the electrical double layer of a decylammonium phase.<sup>8</sup> The change in this degree of order ratio for increasing amounts of 3A or 3B has opposite senses. If measurable then a distinction between the two cases might be made for two values of  $x$ .

Written in terms of the orientation parameters along the C-D bonds,  $S_{C_2D}$  and  $S_{C_3D}$ , the ratio of quadrupole splittings becomes:

$$\frac{\Delta\nu_9}{\Delta\nu_{10}} = \frac{(S_{C_2D})_{3A}}{(S_{C_3D})_{3A}} = \frac{-[0.01 + 0.49x]}{[0.166 - 0.343x]} \quad (14)$$

for contributions involving the process in Figure 3A and

$$\frac{\Delta\nu_9}{\Delta\nu_{10}} = \frac{(S_{C_2D})_{3B}}{(S_{C_3D})_{3B}} = \frac{-[0.01 + 0.49x]}{-0.177} \quad (15)$$

for contributions from the process in Figure 3B. Since the value ( $\Delta\nu_9/\Delta\nu_{10}$ ) is 2.82 for an extended chain, then an increase above this ratio designates a dominance of process

3A in the segmental motions while ratios below 2.82 are associated with the dominance of process 3B. From examination of the experimental ratios in Table IV, it is evident that the conformational averaging of type 3A is dominant in population over 3B. If we assume that process 3A represents the entire extent of conformational averaging, then eq 14 may be used to compute " $x$ ", the fractional population in the extended form. It is found to have a value 0.91 for the decylsulfate chain for the phase used in Figure 1 to illustrate general results where the ratio  $\Delta\nu_9/\Delta\nu_{10} = 3.12$ . If the extended population 0.91 is used in an equilibrium constant and a free energy calculated, the value is 1.38 kcal mol<sup>-1</sup>, which, with the entropy change  $\Delta S \sim 0$ , corresponds to the enthalpy change. This is much too high compared with the value  $0.5 \pm 0.1$  kcal mol<sup>-1</sup> which is expected for a free hydrocarbon chain.<sup>33</sup> A definite contribution to the conformational averaging by the process shown in Figure 3B is indicated. Its neglect gives an erroneously high value of " $x$ ", the population in the extended form.

The ratio of quadrupole splittings on the terminal positions of the decanol indicates, from a typical value  $\Delta\nu_9/\Delta\nu_{10} = 4.1$ , that the motions at the decanol chain are distinctly different from those of the decylsulfate chain tail. From Table V, phase 8, having a value of 4.08 for the ratio, is selected as being typical and a computation made assuming that rotation about the 8,9 C-C bond (process 3A) is the only segmental motion. This ratio leads to a value  $x = 0.76$  for the fraction of chains in the extended form which in turn yields an enthalpy value 0.68 kcal mol<sup>-1</sup> for the trans/gauche process. This is somewhat high but it is evident that process 3B contributes little in the overall conformational averaging for the tails of decanol chains. The quadrupole splittings on the terminal decanol  $-CD_3$  are somewhat smaller than on the terminal decylsulfate chain in all cases. If  $x = 0.76$  in the extended form, then the observed quadrupole coupling at position 9 of the decanol chain can be corrected by this figure to an extended chain value

$$\Delta\nu_9^{\text{obsd}} = -2[0.01 + 0.49x]\Delta\nu_9^{\text{ext}} \quad (16)$$

$\Delta\nu_9^{\text{obsd}}$  is the observed quadrupole splitting on the 9 position of the decanol chain taken as 8460 Hz from a typical value in the tables (phase 5).  $\Delta\nu_9^{\text{ext}}$  is the value which would be observed for this position if the averaging motion of Figure 3A ceased. This can be calculated with  $x = 0.76$  as 11,000 Hz for phase 5. A comparison of this with the splitting of  $\sim 16,000$  Hz at the first positions of the chain near the head group indicates there are further averaging motions affecting the terminal but not the initial segments.

(c) **The Influence of Counterions in the Electrical Double Layer on the Motion of Hydrocarbon Chains.** The data in Tables IV and V do indicate small variations in ratios of quadrupole splittings from system to system. These small variations can be shown to be a function of the counterion which is present in the particular phase. The graph repre-

sented as Figure 4 shows that ratios of quadrupole coupling constants in the same chain have a regular dependence on the methyl substitution of the ammonium counterion. For Figure 4A the ratios of splittings ( $\Delta\nu_1/\Delta\nu_{10}$ ) and ( $\Delta\nu_2/\Delta\nu_{10}$ ) from the decylsulfate chain in these nematic phases show a maximum value for the dimethylammonium counterion and rather similar minimum values for the ammonium and tetramethylammonium counterions. As seen in Figure 4B the magnitude of the ratio is always larger for the decanol chain but again a maximum in the ratio occurs with two methyl groups. In Figure 4C the ratios ( $\Delta\nu_2/\Delta\nu_1$ ) and ( $\Delta\nu_4/\Delta\nu_1$ ) are much smaller but also illustrate a maximum at two methyl groups in the substituted ammonium counterion. An increase in these ratios with the counterion is interpreted in terms of greater structure building ability and penetration of the counterion into the surface and hydrophobic regions. It is suggested that the ammonium ion itself has unprotected positive charge and hence is very hydrophilic while the tetramethylammonium ion is too bulky to penetrate efficiently into the tight structurally bound superstructure. The balance between hydrophobic methyl groups and the charged  $-\text{NH}_2$  group of the dimethylammonium ion appears to represent an optimization of the structure building properties and therefore it interacts most efficiently with the double layer interface. The difference in the decanol and decylsulfate chain motions is quite clear in this counterion effect. In terms of the absolute magnitude of the quadrupole couplings the largest values at the initial carbons of a chain occur with the dimethylammonium counterion. This implies a structure building capacity for this ion with respect to other counterions. Actual magnitudes of couplings may be misleading when compared between phases since they are often sensitive to small variations in composition and temperature. This sensitivity, however, may turn out to be very useful for the investigation of such parameters.

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## Stable Organic Derivatives of Heteropoly Anions, Pentamolybdobisphosphonates

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**Abstract:** Heteropoly molybdates containing covalently bound organic moieties have been prepared and characterized by chemical analysis and spectroscopic measurements. Salts of the anions  $(\text{RP})_2\text{Mo}_5\text{O}_{21}^{4-}$ , where  $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5, \text{C}_2\text{H}_4\text{NH}_3^+$ , and  $p\text{-CH}_2\text{C}_6\text{H}_4\text{NH}_3^+$ , are stable in aqueous solution at pH 2.5–5. The new complexes have a structure related to that of  $\text{P}_2\text{Mo}_5\text{O}_{23}^{6-}$  and are not reducible to heteropoly blue species. The amino derivatives are the first examples of zwitterionic heteropoly complexes. Applications of organic derivatives of heteropoly complexes, of which the molybdobisphosphonates are the first examples, are briefly considered.

Heteropoly oxoanions of the transition metals of groups V and VI form a large class of complexes with a number of unusual properties.<sup>1</sup> To a large extent these discrete inorganic complexes may be viewed as fragments of close-packed metal oxide lattices, and they provide well-defined models for examining many of the properties of such lat-

tices including magnetic interactions, electron delocalization,<sup>2</sup> and heterogeneous catalysis. We have for some years been interested in the possibility of synthesizing heteropoly complexes containing organic groups. It seemed to us that such species would have several interesting properties and potentially important applications.