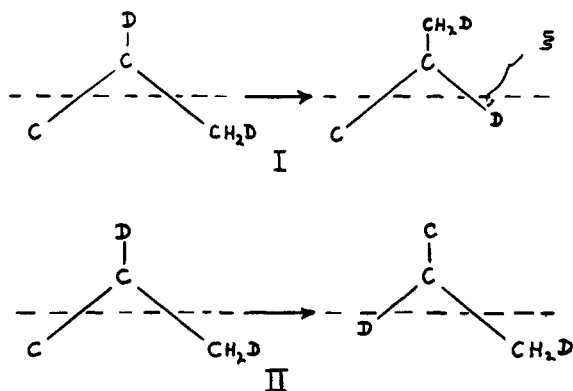methylene group is more highly ordered than the methyl group. The ratio should be 1 if the two are ordered the same. The difference in ordering may result from motions such as that shown below.

Clearly I would result in the methylene group being more highly ordered. Neglecting II we have the following additional contributions to the ordering.

$$S_{C_3D}' = {}^1/_2(3\cos^2\theta - 1){}^1/_2(3\cos^2 90 - 1)S_{zz}{}^0 =$$

$$0.1664 S_{zz}{}^0 \quad (2)$$

$$S_{C_2D} = {}^1/_2({}^1/_2(3\cos^2 90 - 1)S_{zz}{}^0 +$$

$${}^1/_2(3\cos^2\xi - 1)S_{zz}{}^0) = -0.01 \ S_{zz}{}^0 \quad (3)$$

where $\xi = 36°$ and $S_{zz}{}^0$ is along the zz axis. Weighting the contributions according to the fractional population x for non-rotated and $(1 - x)$ for rotated chains we have

$$S_{C_3D} = -0.1767 x S_{zz}{}^0 + (1 - x)0.1664 S_{zz}{}^0 \quad (4)$$

$$S_{C_2D} = -0.5 x S_{zz}{}^0 + (1 - x)(-0.01)S_{zz}{}^0 \quad (5)$$

Using our previously obtained values for S_{C_3D} and S_{C_2D}, it follows that $x = 0.74$, that is 74% of the population is in the extended conformation. Expressed in terms of energy differences between conformers this value leads to a ΔH of 0.64 kcal mol^{-1} at 33° and an $S_{zz}{}^0$ of 0.0565. A ΔH of 640 cal mol^{-1} seems a reasonable figure considering that a gauche rotamer in a normal hydrocarbon is about 0.50 ± 0.10 kcal mol^{-1} [26] higher in energy than that for the extended chain.

During the course of this study measurements were made on a cationic middle detergent phase of composition 59 wt % D_2O (0.1 N HCl), 36.9% decylammonium chloride, and 4.1% ammonium chloride.[4] The deuterium quadrupole splitting of the D_2O in this phase at 34° was 237 Hz whereas the ^{17}O spectrum in natural abundance gave first-order quadrupole splittings of 2.4 kHz separation. The degree of orientation of the deuterium in the water is 0.016 resolved along the C_2 axis if the asymmetry parameter is zero and the quadrupole coupling constant for D in D_2O is 180 kHz. The ^{17}O spectrum yields the degree of orientation 2.0 × 10^{-3} along the C_2 axis if the quadrupole coupling constant is 8.0 mHz[14] for ^{17}O and the principal field gradient is along the C_2 axis. The difference in ordering of deuterium and oxygen indicates the preferential effect of chemical exchange of deuterium over oxygen with more highly ordered parts of the electrical double layer.

Of particular interest in this study is the fact that the $ND_4{}^+$ ion is ordered by this phase where the ordered

superstructure itself carries a positive charge. The deuterium quadrupole splitting is only a factor of about four less than that obtained when the ordered superstructure has a negative charge.[11] The ordering of the ammonium ion in the cationic phase raises questions about the ordering process itself and bears significance in the studies of membrane and related processes.

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Studies of Membrane Processes. V. The Distortion of Tetrahedral Ions in the Electrical Double Layer of a Model Membrane

Sir:

In recent studies of model membranes based on the lyotropic liquid crystal systems, we have pointed out the advantages of a multinuclear, nuclear magnetic resonance (nmr) approach from the study of both the aqueous and lipophilic regions of these phases.[1–9] Middle nematic phases[10,11] orient homogeneously in the magnetic field and provide a highly oriented electrical double layer (edl) suitable for nmr studies without signal enhancement techniques. In addition all isotropic and aniostropic parts of nmr parameters are potentially valuable in giving information about the membrane systems from high resolution spectra. In contrast the lamellar mesophases are not homogeneously oriented by the magnetic field because of their higher viscosity and the powder type spectra obtained

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are of much lower quality and resolution.[12–20] From high resolution proton and deuterium magnetic resonance studies of the ND_4^+, ND_3H^+, and NH_4^+ ions in acidified middle phases of the decylsulfate detergent, we were able to demonstrate the distortion of the ammonium ion from T_d symmetry in the oriented edl.[4] In this present study we report results for BF_4^- and NH_4^+ simultaneously oriented in the edl of a cationic detergent system and resolve four quartets for the fluorine nuclei in BF_4^-. A middle phase of the following composition is typical of those studied, 45.5 wt % D_2O (0.1 M HCl), 49.2% decylammonium tetrafluoroborate, and 5.3% ammonium tetrafluoroborate. The previous study[4] of ammonium ions in an anionic detergent employs opposite charges for the mobile and relatively immobile detergent ions. In the present work the cationic detergent middle phase is shown to cause ordering of both small tetrahedral cations (NH_4^+) and anions (BF_4^-).

In Figure 1 the fluorine and boron magnetic resonance spectra of the BF_4^- ion in the middle phase described above is presented for a probe temperature of 29.7°. All the spectral parameters measured from ^{11}B, ^{19}F, ^1H, and ^2H nmr spectra are listed in the legend to the figure. Of special note are the following. (a) The $\Delta \nu_{Q_D}$ of the ND_4^+ cation in a cationic phase is larger than previously measured in the anionic middle phase[4] and this indicates, surprisingly, a higher degree of distortion. (b) There is a separation in the ^{19}F spectrum of $+18.0$ Hz at 41° between isotropic and nematic phases. (c) When the isotropic micellar and middle nematic phases coexist between 41 and 44°, the value $|(J + D)_{BF}|$ remains constant at 3.16 ± 0.05 Hz but this value increases linearly to 7.05 ± 0.05 Hz as the temperature is lowered to 17.5° through the nematic range. (d) The $|J_{BF}|$ is 0.61 ± 0.05 Hz in normal isotropic or micellular solution.

There is now considerable evidence from spectra of the oriented ND_3H^+ ion in the present work that the assignment of the magnitude of D_{NH} in this ion was incorrectly reported in the previous study.[4] Comparing the dependence of $|(J + D)_{NH}|$ on phase composition with relative variations in $\Delta \nu_{Q_D}(ND_4^+)$, $\Delta \nu_{Q_D}(D_2O)$, $\Delta \nu_{Q_{11B}}(BF_4^-)$, and $\Delta \nu_{Q_D}(-ND_3^+)$,[21] it is clear that D_{NH} is of opposite sign to the absolutely positive J_{NH} and takes the small values rather than values around -100 Hz. Taking $(D + J)_{NH} = 50.55 \pm 0.05$ Hz from the figure legend and $J_{NH} = +52.23$ Hz, D_{NH} becomes -1.68 Hz. A full report on distortion of tetrahedral ions will be published soon.

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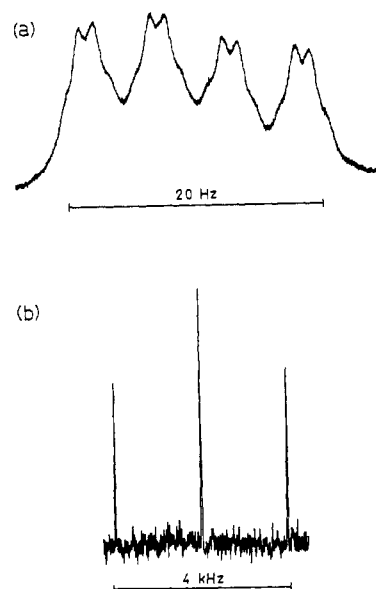(21) F. Fujiwara and L. W. Reeves, unpublished results.

Figure 1. (a) ^{19}F nmr spectrum of the BF_4^- ion in the cationic detergent middle phase mentioned in the text. The main observable $1:1:1:1$ quadruplet with separation $|(J + D)_{BF}|$ is the sum of the scalar and dipole–dipole coupling between ^{11}B and ^{19}F in the ion. The further splitting into $1:3:3:1$ quadruplets arises because of an average distortion of the tetrahedron. The separations give D_{FF}, the dipole–dipole coupling between fluorine atoms in the ion. Intensities are distorted in the low field side of the spectrum because of underlying isotopically shifted $^{10}BF_4^-$ signals. (b) The ^{11}B spectrum of the same sample at the same temperature demonstrates a typical $3:4:3$ first-order quadrupole splitting, which arises because of anisotropic tumbling and distortion of the local T_d symmetry at the ^{11}B nucleus. Spectal parameters are: $|(J + D)_{BF}| = 5.75 \pm 0.02$ Hz, $\delta_F = 1554.3$ (downfield from external C_6F_6 capillary), $|D_{FF}| = 0.71 \pm 0.05$ Hz, $2 \Delta \nu_{Q_{B11}} = 3.77 \pm 0.01$ kHz (separation of outer components of ^{11}B $3:4:3$ triplet), $\Delta \nu_{Q_D}(-ND_3^-) = 7.14 \pm 0.05$ kHz (quadrupole splitting for terminal ionic head deuterium nuclei in the edl of the cationic detergent), $|(D + J)_{NH}| = 50.55 \pm 0.05$ Hz (scalar plus dipole–dipole coupling of the ND_3H^+ ion from proton spectrum), $\Delta \nu_{1/2} = 12$ Hz (half width of components of ND_3H^+ proton spectrum), $\Delta \nu_{Q_D}(ND_4^+) = 87 \pm 1$ Hz (quadrupole splitting for deuterium in ND_4^+ ions), and $\Delta \nu_{Q_D}(D_2O) = 239 \pm 1$ Hz (quadrupole coupling for deuterium in the water).

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Studies of Membrane Processes. VI.
Monatomic Ions in the Electrical Double Layer

Sir:

It is now well known from work on alkali metal and deuterium magnetic resonance[1–9] studies in biological

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