

Studies of Membrane Processes. III. Deuterium Magnetic Resonance as a Tool in Studies of the Lipophilic Region of Membrane Systems

Sir:

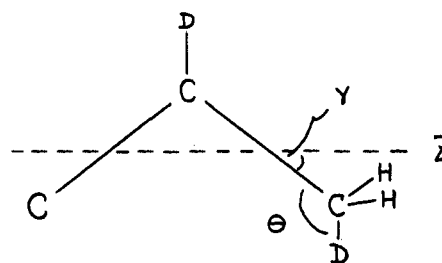
Many recent investigations have illustrated the power of the nuclear magnetic resonance (nmr) method in studies of water and ions in model membrane systems.¹⁻¹³ These studies have for the most part taken advantage of the first-order secular perturbation of nuclear Zeeman levels by a partially averaged dipole-dipole or nuclear quadrupole perturbation in a homogeneously or randomly oriented system.^{14,15} The first-order nuclear quadrupole perturbation is highly sensitive to local degrees of orientation and commends itself admirably in studies of orientation of lipophilic hydrocarbon chains in membranes through examination of the deuterium magnetic resonance spectra from the $-CD_2-$ groups in the specifically or massively deuterated systems of interest.^{16,17} We shall show in this communication that specific deuteration of two adjacent segments in a hydrocarbon chain, which forms part of a model membrane, leads to interpretable information regarding the local micro degree of orientation of the chain segment and that this can be extended in a massively deuterated chain to describe the detailed motions of each segment of the chain. The method indicated here has an elegance denied "spin labels"¹⁸⁻²⁰ because of the possibility of local perturbations by the spin label itself and is much more direct than measurements of ^{13}C nuclear spin relaxation times.²¹⁻²³

The model system described here has been discussed in previous studies from this laboratory^{1,4,5,10-12} and

is derived from the quaternary nematic middle soap region of water, sodium sulfate, decanol, and sodium decyl sulfate. The composition of the phase used was 53.7% H_2O by weight, 1.0% D_2O , 7.0% 9,10-dideuterio-decan-1-ol, 36.3% sodium decyl sulfate, and 2.0% sodium sulfate. 9,10-Dideuterio-decan-1-ol was prepared by reducing 9,10-decen-1-ol with deuterium over Adams catalyst.

Deuterium magnetic resonance spectra were observed on an XL-100 Varian spectrometer using 1000 transients and a spectral width of 12,835 Hz. The spectra consist of three quadrupole derived doublets (a) $\Delta\nu_{Q_{D_2O}} = 233 \pm 1$ Hz from the 1% D_2O , (b) $\Delta\nu_{Q_{CD}} = 1289 \pm 5$ Hz for the terminal methyl deuterium ($-CDH_2$) on the decanol chain, and (c) $\Delta\nu_{Q_{CD}} = 5416 \pm 15$ Hz for the adjacent methylene deuterium. The decanol chain in these systems is arranged with the $-OH$ group near the electrical double layer and with the hydrocarbon chain extended into the lipophilic interior.²⁴ The model is appropriate therefore in consideration of motions in the lipid regions of membranes.

Consider the terminal groups of the decanol chain arranged as below



The axis z is in the direction of orientation of an extended chain and therefore perpendicular to the $D-C-H$ plane. The angle θ is the $C-C-D$ angle (109.5°) and the angle γ (34°) is that between the $C-C$ bond and the z axis, the angles being obtained using values listed for various hydrocarbons in interatomic distances tables.²⁵ Utilizing the equation

$$\Delta\nu_{QD} = \frac{3}{2} Q_D S_D$$

and the value of $Q_D = 170$ kHz for hydrocarbons,²⁶ the degrees of orientations obtained are $S_{CD} = 2.12 \times 10^{-2}$ and $S_{CD} = 5.05 \times 10^{-3}$ for the $-CDH-$ and CDH_2- groups, respectively. Referring the above degrees of order to the "zz" axes which lie at an angle γ to the "z" axis but oscillate about this axis, we obtain the expressions

$$S_{CD} = \frac{1}{2}(3 \cos^2 \theta - 1)^{1/2}(3 \cos^2 \gamma - 1) S_{zz}^3 \quad (1)$$

$$S_{CD} = \frac{1}{2}(3 \cos^2 90 - 1) S_{zz}^2$$

Substituting the values $\theta = 109.5^\circ$ and $\gamma = 34^\circ$, the values $S_{zz}^3 = \pm 0.0286$ and $S_{zz}^2 = \pm 0.0425$ are obtained for the $-CDH_2$ and $-CDH-$ groups, respectively. From these values the ratio $S_{zz}^3/S_{zz}^2 = 0.672$ may be obtained indicating that along the common axis zz the

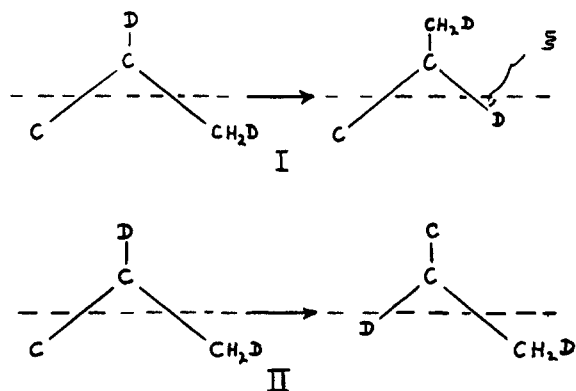
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methylene group is more highly ordered than the methyl group. The ratio should be 1 if the two are ordered the same. The difference in ordering may result from motions such as that shown below.



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

$$S_{C_3D'} = \frac{1}{2}(3 \cos^2 \theta - 1) \frac{1}{2}(3 \cos^2 90 - 1) S_{zz}^0 = 0.1664 S_{zz}^0 \quad (2)$$

$$S_{C_2D} = \frac{1}{2}(\frac{1}{2}(3 \cos^2 90 - 1) S_{zz}^0 + \frac{1}{2}(3 \cos^2 \xi - 1) S_{zz}^0) = -0.01 S_{zz}^0 \quad (3)$$

where $\xi = 36^\circ$ 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

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

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

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 % D₂O (0.1 N HCl), 36.9% decylammonium chloride, and 4.1% ammonium chloride.⁴ The deuterium quadrupole splitting of the D₂O in this phase at 34° was 237 Hz whereas the ¹⁷O 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 C₂ axis if the asymmetry parameter is zero and the quadrupole coupling constant for D in D₂O is 180 kHz. The ¹⁷O spectrum yields the degree of orientation 2.0×10^{-3} along the C₂ axis if the quadrupole coupling constant is 8.0 mHz¹⁴ for ¹⁷O and the principal field gradient is along the C₂ 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 ND₄⁺ 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 anisotropic 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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