An NMR Measurement of the Diffusion Anisotropy in a Nematic Liquid Crystal

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An NMR Measurement of the Diffusion Anisotropy in a Nematic Liquid Crystal††

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Abstract—We have measured the anisotropy of the diffusion constant for the solute molecule, tetramethylsilane, dissolved in the nematic liquid crystal, *p*-methoxybenzylidene-*p'*-*n*-butylaniline. We measure a diffusion constant of $D = 3.2 \pm 0.3 \times 10^{-5}$ cm²/sec for diffusion parallel to the preferred direction of alignment, while a value of $D = 0.8 \pm 0.3 \times 10^{-5}$ cm²/sec is obtained for diffusion perpendicular to the preferred direction.

Pulsed NMR techniques are well known for their use in diffusion studies in solids and liquids. In some cases, the diffusion constant can be determined directly. One such technique,[1] used primarily in the case of liquids, involves measuring the transverse nuclear polarization or intensity of the spin-echo from a sample placed in a linear magnetic field gradient. The translational movement of the nuclear spins into different regions of the sample and hence into different magnetic field strengths alters their phase relationship and destroys the transverse polarization. If one applies a 90° pulse followed by n 180° pulses appropriately phased[2] and spaced, the intensity of the resulting spin-echo, M_y, as a function of time follows

$$M_y(t) = M_0 \exp\left[-t/T_2 + (-\gamma^2 G^2 D t^3 / 12n^2)\right] \qquad (1)$$

Where γ is the gyromagnetic ratio of the nuclear spin, G the linear field gradient, D the diffusion constant and T_2 the transverse relaxation time. It is readily seen from the above expression that if the

diffusion constant is to be measured, the condition $T_2^3 \gtrsim 12n^2/\gamma^2 G^2 D$ must be met. Further, if one applies a continuous field gradient across the sample, one must restrict the value of G to be less than ~ 1 gauss/cm in order that Eq. (1) be valid. This places severe restrictions on T_2. As a matter of fact, if one applies a continuous gradient, it completely precludes the measurement of D for a liquid crystal molecule as $T_2 \sim 10^{-4}$ sec for these partially ordered systems.

In order to circumvent this problem, we have dissolved a " spherical " molecule, tetramethylsilane (TMS), into the liquid crystal p-methoxybenzylidene-p'-n-butylaniline (MBBA). As this molecule is only slightly ordered[3] by the nematic matrix, it shows a large T_2 (0.30 sec at room temperature). This value is large enough for the measurement of the diffusion constant for diffusion rates typical of liquids. Because of the large disparity of times for T_2 between the solute and the liquid crystal, one sees only the proton spin-echo from the solute.

Using a Bruker Model No. B-KR-322s pulsed NMR system, we have measured $M_y(t)$ for TMS dissolved in MBBA at different magnitudes of G in a direction parallel to the nematic director $\mathbf{N}$ and for one value of G perpendicular to $\mathbf{N}$. The gradients were created by introducing opposing fields with a circuit placed in the magnet and with use of inhomogenieties inherent in the magnet itself. A check on the linearity as well as the magnitude of the gradient was determined by the use of two small capillaries inserted in the gradient and observing the resulting beats of the two echos. A further check on the gradient was made by measuring the diffusion constant of water.

The value of T_2 was determined in the usual manner of the Carr–Purcell sequence by making the number n, in Eq. (1), large. The diffusion constant was then obtained from the $90°$–$180°$ sequence and plotting $\ln M_y/M_0 + t/T_2$ vs t^3. A straight line was obtained and the slope of the line was used to determine D. The values measured were :

$$D_\parallel = 3.2 \pm 0.3 \times 10^{-5} \text{ cm}^2/\text{sec} \quad \text{and} \quad D_\perp = 0.8 \pm .03 \times 10^{-5} \text{ cm}^2/\text{sec}.$$

The value of the measured ratio, $D_\parallel/D_\perp = 4$, is not unreasonable in view of previous viscosity measurements. From simple considerations, one might expect $D_\parallel/D_\perp \sim n_\perp/n_\parallel$. It is interesting to note that measured values[4] of $\eta_\perp/\eta_\parallel$ for p-azoxyanisole give a value of

3.8 for this ratio. More significantly, the measured value of $D_{\parallel}/D_{\perp}$ has been found to be in accord with a more detailed calculation based upon a modified Kirkwood diffusion theory.[5]

Since the diffusion constants were measured for a solute molecule and not the liquid crystal solvent, their absolute values might be difficult to predict from theory. However, it is generally believed that the diffusion rate of an impurity in normal liquids is equal to that of the solvent provided the size of the impurity molecule is equal to or somewhat smaller than the solvent molecule.[6]

Finally, it should be noted that the mole fraction of solute TMS to the liquid crystal host was quite large, $\sim 5\%$. This large concentration was necessary in order to have sufficient signal strength to make the measurement.

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