The supramolecular structure of water

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Abstract

This paper presents a dynamic model related to the supramolecular structure of water in dynamised solutions. The dynamic model is based on experimental data performed on water dynamised solutions in the presence of an active principle. The experimental data have been obtained by means of a nuclear magnetic resonance spectrometer, measuring nuclear spin relaxation times $T_1$ and $T_2$. The hypothesis advanced in this paper is based on the formation of dissipative structures, in the form of supramolecular structures of water, by virtue of its hydrogen bonds, structurally similar to a liquid crystal.

1 Introduction

A liquid crystal or liquid cluster can be defined as a substance that flows as a liquid but has some order in its arrangement of molecules and a phase of matter whose order is intermediate between that of a liquid and a crystalline solid. The molecules are typically rod-shaped and about 25Å in length. The ordering functions of these liquids crystal molecules is a function of temperature. According to S. Chandrasekhar [1] “The term liquid crystal signifies a state of aggregation that is intermediate between the crystalline solid and the amorphous liquid. As a rule, a substance in this state is strongly anisotropic in some of its properties and yet exhibits a certain degree of fluidity, which in some cases may be comparable to that of ordinary liquid”. The model described is based on the assumption of the formation of a network structure of the water-cluster mechanically strong: a low-density water with stronger hydrogen bonds and lower entropy.

Water is the most abundant substance on earth and has been very well studied with a number of different model stuctures. Notwithstanding this, it remains an anomalous liquid where no single model is able to explain all of its properties, as
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underlined by M.F. Chaplin [2].

The hypothesis advanced in this paper is based on the formation of dissipative structures [3, 4], in the form of supramolecular structures of water, by virtue of its hydrogen bonds, structurally similar to a liquid crystal. The supramolecular structure could be a macromolecule typical of a living organism (plant or animal), which as we know is ~80% water, with a complex conformation induced initially by the active principle and which remains, organizing itself as a result of an input of energy (dynamisation, electromagnetic wave or other).

2 Experimental

NMR spectra were recorded on a Varian XL-200 spectrometer. The spin-lattice relaxation rates were measured with the inversion recovery pulse sequence. The spin-spin relaxation rates were measured with the Carr-Purcell-Meiboom-Gill pulse sequence. The values of $1/T_1$ and $1/T_2$ were calculated from exponential regression analysis.

3 Theoretical background

Proton nuclear spin relaxation in the water molecule is described in terms of perturbation theory. The spin Hamiltonian for the single proton consists of two parts; the Zeeman energy $\mathcal{H}_0 = -\gamma_N \mathbf{I} \cdot \mathbf{H}_0$ in the steady external magnetic field, and a random perturbation term $V(t)$ due to the local field, which is represented by the matrix:

$$
\begin{pmatrix}
V_{\alpha\alpha}(t) & V_{\alpha\beta}(t) \\
V_{\beta\alpha}(t) & V_{\beta\beta}(t)
\end{pmatrix}
$$

The off-diagonal matrix elements of $V(t)$ depend on the $x$ and $y$ components of the local field, which can be thought of as containing many fluctuating components oscillating at different frequencies. The parts which oscillate at the nuclear resonance frequency $\omega_0$ induce transitions between the states and cause spin-lattice relaxation. By making a Fourier analysis of $V(t)$ and using time-dependent perturbation theory we find that:

$$
\frac{1}{T_1} = \frac{2}{\hbar^2} \int_{-\infty}^{T} V_{\alpha\beta}^*(t+\tau)V_{\alpha\beta}(t)e^{i\omega_0\tau} d\tau
$$

Here the integrand is an average of the off-diagonal matrix elements of $V$ taken over all values of the time $t$ and over a large number of samples of the molecular motion. The line width $1/T_2$ depends on the lifetimes of the $\alpha$ and $\beta$ spin states but it is also affected by fluctuations in the energy difference between the two levels, that is, by the $z$ components of the local field, or the diagonal matrix elements of $V(t)$. The expression for $T_2$ is:
where $T_2$ is defined as a time averaged product of the diagonal elements of $V$:

$$\frac{1}{T_2} = \frac{1}{T_2} + \frac{1}{2T_1}$$  \hspace{1cm} (3)

These perturbation formulae apply provided that the local field is reasonably small, so that both relaxation times are long compared with the period of the spin precession ($2\pi/\omega_0$). It is also necessary that the local fields fluctuate many times during the time $T_1$ or $T_2$. Water molecules do not so much rotate as “tumble” in a very irregular fashion, because the axis and the direction of motion are continually being altered by collisions. As a result the motion of one proton relative to another is a kind of random walk over the surface of a sphere. The theory is due to Debye.

The critical reader may well object that the Brownian motion in liquids cannot possibly so simple as it is pictured in Debye’s theory. This is certainly true, but Debye’s simple ideas have proved most useful for interpreting resonance line widths, and the more elaborated theories often lead to practically the same conclusions. All relaxation effects depend on the frequency spectrum of the local fields at the nucleus and there is almost always a definite characteristic time scale for the fluctuations, i.e., a correlation time $\tau_c$.

Finally the calculation of $T_1$ for the spin-lattice relaxation time leads to:

$$\frac{1}{T_1} = \frac{3}{20} \left( \frac{g_N^4 \beta_N^4}{\hbar^2 \tau^6} \right) \left\{ \frac{2\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{8\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right\}$$  \hspace{1cm} (5)

The calculation of $T_2$ is considerably more complicated than the one we have just performed for $T_1$. It is not possible to use the relation 3 which holds for a single spin of $\frac{1}{2}$, and the theory needs a more advanced mathematical approach. We merely quote the result:

$$\frac{1}{T_2} = \frac{3}{40} \left( \frac{g_N^4 \beta_N^4}{\hbar^2 \tau^6} \right) \left\{ 6\tau_c + \frac{10\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right\}$$  \hspace{1cm} (6)

We have neglected the magnetic fields of the protons on other water molecules which diffuse by, but these also produce relaxation and $T_1 = T_2$ under normal conditions. The theoretical expression must therefore be supplemented by a further term, which is:

$$\left( \frac{1}{T_1} \right)_{trans} = \frac{\pi}{5} \left( \frac{g_N^4 \beta_N^4}{\hbar^2} \right) \frac{N}{D_b}$$  \hspace{1cm} (7)

Here $D$ is the coefficient of self diffusion, $N$ the concentration of spins, and $b$ the distance of closest approach between spins on different molecules. Taking $D = 1.85 \times 10^{-5}$, $N = 6.75 \times 10^{22}$, $b = 1.74\text{Å}$ for water we estimate $(T_1)_{trans} = 12.6$ sec. The total relaxation rate is the sum of the rotational and translational parts:
4 Results and discussion

As long as $\tau_c$ is short, so that $\omega_0\tau_c \ll 1$, $T_1$ and $T_2$ remain equal. Both contributions to $1/T_1$ should be proportional to $(\eta/T)$, since the first depends on the correlation time $\tau_c = 4\pi \alpha^3 \eta / 3kT$ and the second on the diffusion coefficient, whose value calculated for a spherical molecule is $1/D = 6\pi \eta \alpha / kT$. This prediction is well tested by the experiments of Bloembergen on proton relaxation times in glycerin, a liquid whose viscosity varies very strongly with temperature. The experimental results are shown in Figure 1 where the logarithms of $T_1$ and $T_2$ are plotted against log($\eta/T$). The left side of the figure, where $\eta/T < 10^{-1}$, shows the expected straight lines with $T_1 = T_2$. However, at higher viscosities the curves for $T_1$ and $T_2$ diverge, and this requires some explanation.

As the liquid becomes more viscous and the correlation time increases, the component of the local field fluctuations at the resonance frequency $\omega_0$ decreases, tending to zero when $\omega_0\tau_c \gg 1$. The result is that the value of $T_2'$ decreases, being still proportional to $1/2\tau_c$ but the spin-lattice relaxation time now becomes very long, as it is proportional to $2\tau_c/(1 + \omega_0^2\tau_c^2)$. Hence in the limit of long correlation times
Theoretical behavior of $T_1$ and $T_2$ as a function of the correlation time. Calculated for protons in water at 29 Mc/s ($\omega_0 = 1.9 \times 10^8$ radians/sec.)

$T_1$ is proportional to $\tau_c$ instead of $1/\tau_c$ and begins to increase again. In the region between long and short correlation times $T_1$ goes through a minimum at the point $\omega_0 \tau_c = 1$, as we see in Figure 2. The line width $1/T_2$ continues to increase linearly with $\tau_c$ until the molecular motion slows down so much that it is completely frozen. At this stage we have a randomly oriented solid.

All our experimental NMR data performed on water dynamised solutions initially perturbed by different active principles present the behavior of the right side, before the solid dominion of Figure 2 (between the two dotted lines). The experimental behavior is in agreement with the theoretical model and with the formation of a low-entropy dissipative structure in the form of supramolecular structure of water, by virtue of its hydrogen bonds.

The phenomena observed lead to the conclusion that water and aqueous solutions should be regarded as continuous polymorphous self-organizing systems, far from thermodynamic equilibrium [3, 4].

**References**