

O-17 and proton spin-lattice relaxation time studies in supercooled H₂O and D₂O enriched with O-17

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Summary

From O-17- T_1 studies in D₂O and H₂O in supercooled water emulsion the dynamic isotope effect is derived. It is shown that the isotope effect increases significantly in the supercooled range.

It is common practice, to use a combination of deuterium T_1 in D₂O solution and proton T_1 in H₂O solution to separate the different contributions to the proton relaxation in aqueous solutions of biopolymers. However, the presence of hydrophobic solutes in the aqueous phase influences the mobility of the water molecules in the immediate vicinity of the solute, and one must expect that these effects are quantitatively different when D₂O and H₂O are compared.

In order to study these effects, we have investigated the O-17- T_1 in light and heavy water in a wide range of temperatures and have included pressure as an additional parameter.

The complete O-17 data are in print.¹ Figure 1 compiles the ratio of the O-17- T_1 for a series of pressures.

This ratio increases significantly with falling temperature. Comparison of the ¹⁷O- T_1 and the ²H- T_1 in D₂O³ shows an identical pressure and temperature dependence for both T_1 . Furthermore, identical correlation times τ_θ are obtained, when the quadrupole coupling constants of ice I_h are inserted in the relaxation equations. This shows that the rotational diffusion of the single water molecule is isotropic.

Studying the ¹H- T_1 in H₂O enriched with O-17 permits the analysis of the complete proton relaxation rate in the temperature and pressure range, where

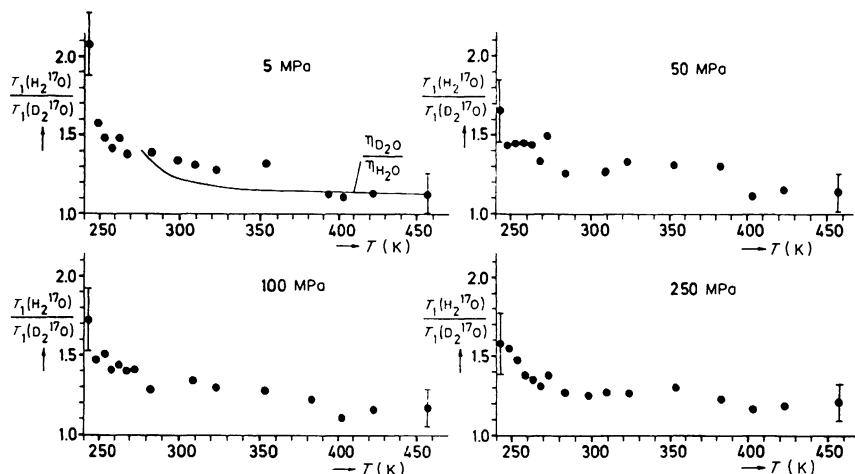


Figure 1 Ratio of the $^{17}\text{O}-T_1$ obtained in H_2O and D_2O as function of temperature for the pressures indicated in the diagrams. Solid line in the 5 MPa-diagram: Ratio of the viscosities at 0.1 MPa²

the O-17- T_1 becomes too short to be measurable. The interaction between O-17 and the protons is practically an additional *intramolecular* relaxation path:

$$\frac{1}{T_1} = K \sum \langle r_{X-H}^6 \rangle f(\tau_\theta)$$

$$\text{H}_2^{16}\text{O}: \left(\frac{1}{T_1}\right)_{\text{H}} = \left(\frac{1}{T_1}\right)_{\text{HH}}^{\text{intra}} + \left(\frac{1}{T_1}\right)_{\text{HH}}^{\text{inter}}$$

$$\text{H}_2^{17}\text{O}: \left(\frac{1}{T_1}\right)_{\text{H}} = \left(\frac{1}{T_1}\right)_{\text{HH}}^{\text{intra}} + \left(\frac{X}{T_1}\right)_{^{17}\text{O}-\text{H}}^{\text{intra}} + \left(\frac{1}{T_1}\right)_{\text{HH}}^{\text{inter}}$$

X is the mole fraction of ^{17}O -isotope.

Analysis of the data shows that in the supercooled liquid the $\{^1\text{H}$ -relaxation is almost completely described by the intramolecular contribution, and this result leads to the conclusion that in the supercooled liquid the next neighbour geometry of a given water molecule is essentially tetrahedral.

The data presented in Figure 1 show that the dynamic isotope effect between light and heavy water at $T < 300$ K cannot be scaled by a constant factor.

For the analysis of $\{^1\text{H}-T_1$ obtained in the aqueous solution of biopolymers it is thus preferable to include into the study $^{17}\text{O}-T_1$ data obtained in light water.

References

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