Summary

From O-17-T\textsubscript{1} studies in D\textsubscript{2}O and H\textsubscript{2}O 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\textsubscript{1} in D\textsubscript{2}O solution and proton T\textsubscript{1} in H\textsubscript{2}O 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 D\textsubscript{2}O and H\textsubscript{2}O are compared.

In order to study these effects, we have investigated the O-17-T\textsubscript{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.\textsuperscript{1} Figure 1 compiles the ratio of the O-17-T\textsubscript{1} for a series of pressures.

This ratio increases significantly with falling temperature. Comparison of the \textsuperscript{17}O-T\textsubscript{1} and the \textsuperscript{2}H-T\textsubscript{1} in D\textsubscript{2}O\textsuperscript{3} shows an identical pressure and temperature dependence for both T\textsubscript{1}. Furthermore, identical correlation times \( \tau_{\theta} \) are obtained, when the quadrupole coupling constants of ice \( I_{\theta} \) are inserted in the relaxation equations. This shows that the rotational diffusion of the single water molecule is isotropic.

Studying the \textsuperscript{1}H-T\textsubscript{1} in H\textsubscript{2}O enriched with O-17 permits the analysis of the complete proton relaxation rate in the temperature and pressure range, where
the O-17–T₁ becomes too short to be measurable. The interaction between O-17 and the protons is practically an additional intramolecular relaxation path:

\[
\frac{1}{T_1} = K \sum <r_{X-H}^6> f(\tau_0)
\]

\[
H_2^{16}O: \left( \frac{1}{T_1} \right)_H = \left( \frac{1}{T_1} \right)_{\text{intra}} + \left( \frac{1}{T_1} \right)_{\text{inter}}
\]

\[
H_2^{17}O: \left( \frac{1}{T_1} \right)_H = \left( \frac{1}{T_1} \right)_{\text{intra}} + \left( \frac{X}{T_1} \right)_{\text{intra}}^{17O-H} + \left( \frac{1}{T_1} \right)_{\text{inter}}^{17O}
\]

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

Analysis of the data shows that in the supercooled liquid the \(^1H\)-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 \(^1H–T_1\) obtained in the aqueous solution of biopolymers it is thus preferable to include into the study \(^{17}O–T_1\) data obtained in light water.
References