Molecular Motion in Starch by Proton Spin-Lattice Relaxation

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Relaxation time $T_1$ for proton spin-lattice relaxation was measured by the $90^\circ-90^\circ$ pulse method over a temperature range from $-150$ to $+120^\circ$C in starches of various origin, and in both starch fractions, in soluble starch, in the amylose iodine complex, and in deuterated starches and starches of different humidity. At 24 MHz resonant frequency a common $T_1$ — minimum of about 0.1 sec with a relatively low activation energy (1.3 to 2.1 kcal/mol) is found at temperatures above $0^\circ$C. The comparative study of different starches indicates that the $T_1$ — minimum is caused by the rotation of $-\text{CH}_2\text{OH}$ groups in the starch molecule.

INTRODUCTION

The use of nuclear magnetic resonance (NMR) for the study of molecular motion in solids is possible because the relaxation processes can be explained in terms of molecular motion. The spin-lattice relaxation is directly dependent on the dynamic parameters of the lattice. An adequate theory is necessary to relate the quantities experimentally measurable by the phenomenon of magnetic resonance with the parameters of the lattice in a manner which allows predictions about the behaviour of the lattice.

In this work proton spin-lattice relaxation times ($T_1$) were measured with the purpose of identification of the molecular motion in different starches. Previously, Samec $et$ $al.$ drew some conclusions about the rotation of $-\text{OH}$ and $-\text{CH}_2\text{OH}$ groups in the starch molecule based on the temperature dependence of the second moment of the NMR absorption line, and Glazkov compared the effect of molecular motion on NMR spectra of different polysaccharides.

Pulsed measurement of spin-lattice relaxation provide more direct approach to molecular motion from a NMR point of view. Starches of various origin (potato, corn, wheat), both fractions (amylose and amylopectin), soluble starch and amylose iodine complex were studied in an attempt to determine the effect of structural differences on the spin-lattice relaxation time. The same samples were studied both in the atmospheric conditions of humidity and as dried in order to find the influence of the adsorbed water. Deuterated samples were also studied in obtaining additional information for the identification of the detected molecular motions.

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The simple theory of magnetic relaxation, the so-called BPP theory (Bloembergen, Purcell and Pound\textsuperscript{3}; corrected by Kubo and Tomita\textsuperscript{4} and Solomon\textsuperscript{5}) assumes a uniform relaxation mechanism via isotropic motion of spin pairs and gives for the spin-lattice relaxation time, $T_1$:

$$\frac{1}{T_1} + \frac{1}{10 \pi^2} \gamma^2 \hbar^2 I (I + 1) \sum_k r^{-6}_{jk} \left( \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4 \tau_c}{1 + 4 \omega_0^2 \tau_c^2} \right)$$

(1)

where $\gamma$, $\hbar$, $I$, $\tau_c$, $\omega_0$, and $r_{jk}$ are gyromagnetic ratio, Planck constant, spin, correlation time, resonant frequency and distance between spin $j$ and $k$, respectively. According to Eq. (1) the curve $T_1 = T_1(\tau_c)$ is V-shaped with a minimum value, $T_{1\text{ min}}$, for the correlation time $\tau_{c\text{ min}}$ determined by the condition:

$$\tau_{c\text{ min}} \omega_0 = 0.6158$$

(2)

Assuming the spin motion is a thermally activated process with activation energy $E_a$,

$$\tau_c = \tau_0 \exp \left( \frac{E_a}{kT} \right)$$

(3)

where $\tau_0$ is a constant characteristic of the system (the value of $\tau_c$ for infinite temperature), $k$ is the Boltzman constant and $T$ is absolute temperature. Consequently, the curve $\ln T_1 = f(1/T)$ has a symmetric V-shape with the slopes directly proportional to the activation energy:

$$E_a = k \frac{\Delta (\ln T_1)}{\Delta (1/T)}$$

(4)

EXPERIMENTAL

The spin-lattice relaxation time, $T_1$, was measured by the 90–90° pulse method\textsuperscript{6} using a home-made NMR pulse spectrometer\textsuperscript{7}. The signals of free precession after 90° pulses were compared on the oscilloscope screen and the calculation of relaxation time $T_1$ were based on the relation

$$M(t) = M_0 \left[ 1 - \exp \left( - \frac{t}{T_1} \right) \right]$$

(5)

where $M_0$ is the thermal equilibrium magnetization, $M(t)$ is the magnetization in a time $t$ after the first 90° pulse. The relaxation time $T_1$ was measured over a temperature range from $-150$ to $+120^\circ$C, and the activation energy $E_a$ was calculated by Eq. (4). With respect to the relatively large number of experimental points, the diagrams $\ln T_1 = f(1/T_1)$ are well defined and the activation energy $E_a$ was determined to an accuracy better than $\pm 10\%$.

The samples were both commercial and specially prepared starches and starch fractions. Amylose and amylopectin were prepared by the method of electrodialysis\textsuperscript{8}, and highly polymerized potato amylose was prepared from starch paste\textsuperscript{9}. Amylose iodine complex was prepared by exposing the dry sample to iodine vapour\textsuperscript{10}. The samples were deuterated by repeated dissolving in $D_2O$ and slow evacuation\textsuperscript{11} at $80^\circ$C. The efficiency of deuteration of the hydroxyl groups (at least $90\%$) was determined from the infrared spectra.

All the samples studied were fine powders. The samples were dried by high evacuation (up to $10^{-5}$ mm Hg) and were under vacuum during the NMR measurements, except for the samples used for the investigation of the effect of moisture.
RESULTS

Figs. 1—4 give the relaxation time $T_1$ as a function of temperature for some of the samples studied. Fig. 1 shows appreciable differences in the magnitude of $T_1$ and the behaviour of $T_1$ with respect to temperature between amylopectins of various starches. The differences between amylase and amylopectin of the same starch, Fig. 2, are scarcely visible. A $T_{1\text{min}} \approx 0.14$ sec, from $+50$ to $+100^\circ$C is common to all the starches studied. According to Eq. (2) the correlation time $\tau_{c \text{min}}$ related to this $T_{1\text{min}}$ is $4.2 \times 10^{-9}$ sec. The activation energy $E_a$ determined from the low temperature slope of this $T_1$-minimum according to Eq. (4) is 1.5 to 1.8 kcal/mol. Differences between various starches are unlikely over the limit of the accuracy of the measurements. Potato starch shows another $T_1$-minimum at a lower temperatures (about $-125^\circ$C). For the other starches the change in low temperature slope only indicates the onset of another relaxation mechanism.

The iodine complex of potato amylase and soluble starch show the same behaviour of $T_1$ with respect to temperature as other starches but with slightly different $T_{1 \text{min}}$ (0.12 and 0.075 sec, respectively), $T_{\text{min}}$ (+16 and +5$^\circ$C, respectively) and $E_a$ (1.3 and 2.1 kcal/mol, respectively). Comparison between starch with normal atmospheric humidity and starch dried by high evacuation, Fig. 3, indicates that adsorbed water decreases the relaxation time $T_1$ ($T_{1 \text{min}}$ is 0.063 and 0.145 sec, respectively) and shifts the $T_{1 \text{min}}$ to lower temperatures (from $+97$ to $+62^\circ$C). However, the temperature behaviour of $T_1$ and the activation energy $E_a$ are essentially the same. Fig. 4, indicates that the relaxation time $T_1$ is increased ($T_{1 \text{min}}$ from 0.137 to 0.234 sec) and $T_1$-minimum is shifted to higher temperatures (from $+71$ to $+105^\circ$C) by deuteration of the wheat amylopectin, but there are no differences in activation energy.
Fig. 2. The temperature dependence of $T_1$ for amylose and amylopectin fraction of wheat.

Fig. 3. The temperature dependence of $T_1$ for the native and dried potato amylopectin.
Fig. 4. The temperature dependence of $T_1$ for the native and deuterated wheat amylopectin. The deuterated sample was pressed for the purpose of better NMR signal.

DISCUSSION

The molecular motion responsible for the $T_1$-minimum is characterized by relatively low activation energy (1.5 to 1.8 kcal/mol). A molecular motion with such a low activation energy according to the approximate relation

$$E_a (\text{cal/mol}) \approx 37 T_{\text{trans}} \,(^0\text{K})$$

(6)

causes narrowing of the NMR line shape at a temperature $T_{\text{trans}}$ lower than $77^\circ$K. However, the absolute values of the activation energy $E_a$ in the present work are questionable, because it is unlikely that the simple basis of the BPP theory (eq. 6) is valid for a solid polymer like starch. The introduction of an adequate distribution of correlation times in place of the BPP single correlation time $\tau_c$ could change the activation energy measured from the slope of the curve $\ln T_1 = f (1/T)$. Our broad line NMR data indicate only $120/0$ change in the second moment from 77 to $270^\circ$K for very dry starch and $86/0$ for undried starch. It is possible that the narrowing of NMR line observed by Samec et al. above $100^\circ$K is due to »unfreezing« the motion of adsorbed water, while the narrowing expected due to the molecular motion responsible for observed $T_1$-minimum in our measurements is really below $77^\circ$K ($E_a < 3$ kcal/mole).

It is possible to assign the low activation energy to potentially the most movable part of the starch molecule, the $-\text{CH}_2\text{OH}$ group, for the following reasons.

If motion of a larger segment of the molecules were the cause of $T_1$-minima then the differences in molecular and crystal structure should be expressed by differences in $T_1$-minima. There are no essential differences in the observed $T_1$-minima for various starches. The existence of a molecular group remarkably more movable than the rest of the molecule determines the manner of magnetic interaction.
resonance relaxation. The spin-lattice relaxation occurs only for the protons which are the most mobile at a definite temperature, while the other protons relax via spin-spin relaxation with these most mobile protons.

The adsorbed water causes only about a 50% decrease in the relaxation time $T_1$ and, thus cannot be another alternate in explaining the relaxation mechanism. The water only increases the spin density and consequently the intensity of spin-spin interaction and indirectly the efficiency of the spin-lattice relaxation.

On the other hand, the dielectric relaxation via rotation of -OH groups in starch and in adsorbed water is far more sensitive to changes of the moisture content in starch\textsuperscript{14}.

In relation to the magnetic resonance relaxation, in theory, the motion of the -OD groups should give an isotope effect of 24. Contrary to this, in our experiments $T_1$ increased only by a factor of four on deuteration of the -OH groups.

Thus, the finding of a relatively low activation energy and the comparative study of different starch samples including deuteration suggest that the $T_1$-minimum can be assigned to the motion of -CH$_2$OH groups.

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REFERENCES


IZVOD

Molekularno gibanje u škrobu na osnovu protonjske magnetske relaksacije (spin-rešetka)

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Vrijeme $T_1$ za protonsku relaksaciju spin-rešetka mjerno je metodom pulseva 90—90° u škrovima različitih podrijetla i u objema frakcijama škroba, te u jednom kompleksu amiloze, topivom škrobu i deuteriranim škrobovima, kao i u škrovima različite vlaznosti. Na rezonantnoj frekvenciji 24 MHz za sve ispitivane uzorke zajednička je vrijednost minimalna $T_1$ od oko 0,1 sek na temperaturama iznad 0°C. Relaksacijski proces je karakteriziran relativno niskom energijom aktivacije (1,3 do 2,1 kcal/mol). Uspoređni rezultati za različite škrobe ukazuju na to, da je taj minimum za $T_1$ uzrokovana rotacijom —CH$_2$OH grupa u škrobovoj molekuli.