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Original Scientific Paper

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—90° pulse method over a temperature range from —150 to + 120° 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° C. The comparative study of different starches indicates that the T_1 — minimum is caused by the rotation of —CH_2OH 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.*[1] drew some conclusions about the rotation of —OH and —CH_2OH groups in the starch molecule based on the temperature dependence of the second moment of the NMR absorption line, and Glazkov[2] 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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THEORETICAL

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

$$\frac{1}{T_1} + \frac{1}{10\,\pi^2}\,\gamma^2 h^2 I\,(I+1) \sum_k r_{jk}^{-6} \left(\frac{\tau_c}{1+\omega_o^2\ \tau_c^2} + \frac{4\,\tau_c}{1+4\,\omega_o^2\ \tau_c^2} \right) \tag{1}$$

where γ, h, I, τ_c, ω_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 minumum value, $T_{1\,min}$, for the correlation time $\tau_{c\,min}$ determined by the condition:

$$\tau_{c\,min}\,\omega_o = 0.6158 \tag{2}$$

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

$$\tau_c = \tau_0 \exp\left(\frac{E_a}{kT}\right) \tag{3}$$

where τ_0 is a constant characteristic of the system (the value of τ_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:

$$E_a = k\,\frac{\Delta\,(\ln T_1)}{\Delta\,(1/T)}\,. \tag{4}$$

EXPERIMENTAL

The spin-lattice relaxation time, T_1, was measured by the 90—90° pulse method[6] using a home-made NMR pulse spectrometer[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

$$M(t) = M_0\left[1 - \exp\left(-\frac{t}{T_1}\right)\right] \tag{5}$$

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° 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[8], and highly polymerized potato amylose was prepared from starch paste[9]. Amylose iodine complex was prepared by exposing the dry sample to iodine vapour[10]. The samples were deuterated by repeated dissolving in D_2O and slow evacuation[11] at 80° 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.

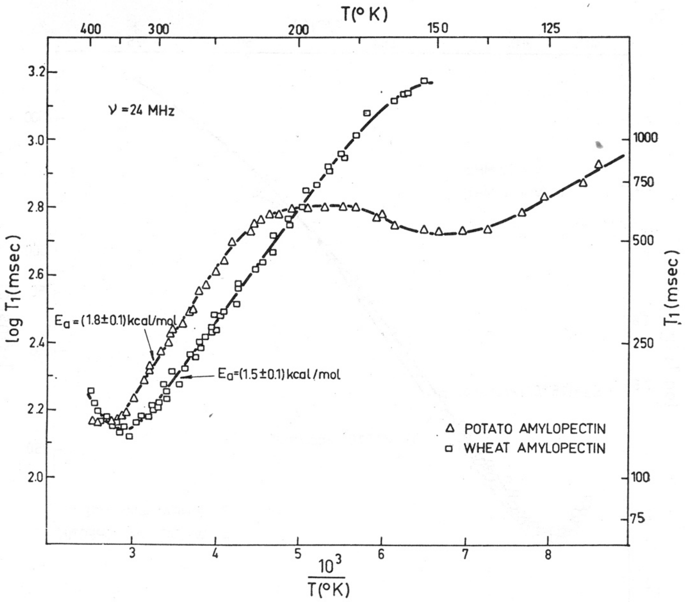

Fig. 1. The temperature dependence of T_1 for potato and wheat amylopectin.

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 amylose and amylopectin of the same starch, Fig. 2, are scarcely visible. A $T_{1\,\mathrm{min}} \approx 0.14$ sec, from $+ 50$ to $+ 100^0$ C is common to all the starches studied. According to Eq. (2) the correlation time $\tau_{c\,\mathrm{min}}$ related to this $T_{1\,\mathrm{min}}$ is 4.2×10^{-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— 125^0 C). For the other starches the change in low temperature slope only indicates the onset of another relaxation mechanism.

The iodine complex of potato amylose and soluble starch show the same behaviour of T_1 with respect to temperature as other starches but with slightly different $T_{1\,\mathrm{min}}$ (0.12 and 0.075 sec, respectively), T_{min} ($+ 16$ and $+ 5^0$ 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 ($T_{1\,\mathrm{min}}$ is 0.063 and 0.145 sec, respectively) and shifts the $T_{1\,\mathrm{min}}$ to lower temperatures (from $+ 97$ to $+ 62^0$ 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 ($T_{1\,\mathrm{min}}$ from 0.137 to 0.234 sec) and T_1-minimum is shifted to higher temperatures (from $+ 71$ to $+ 105^0$ C) by deuteration of the wheat amylopectin, but there are no differences in activation energy.

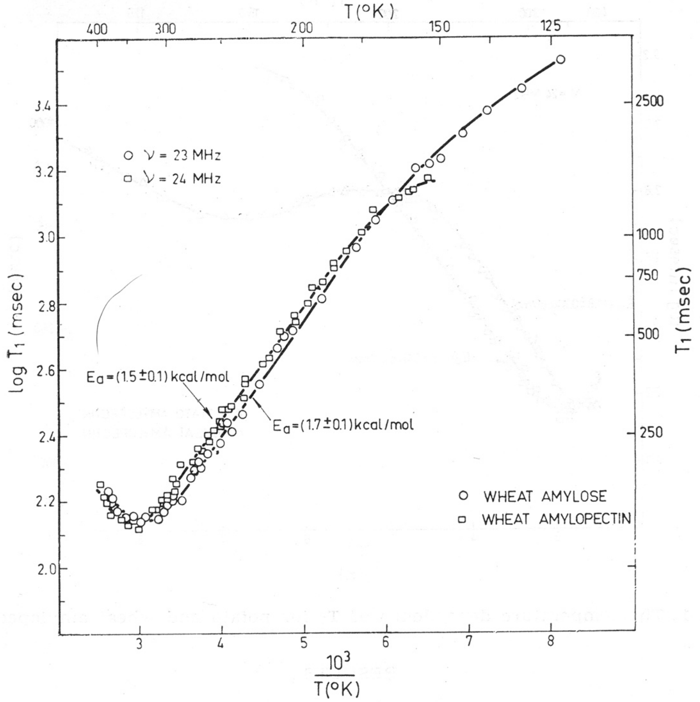

Fig. 2. The temperature dependence of T_1 for amylose and amylopectin fraction of wheat.

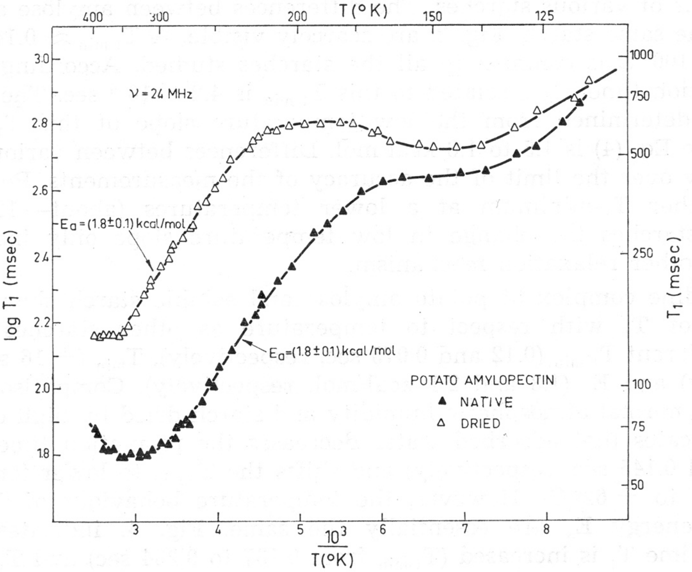

Fig. 3. The temperature dependence of T_1 for the native and dried potato amylopectin.

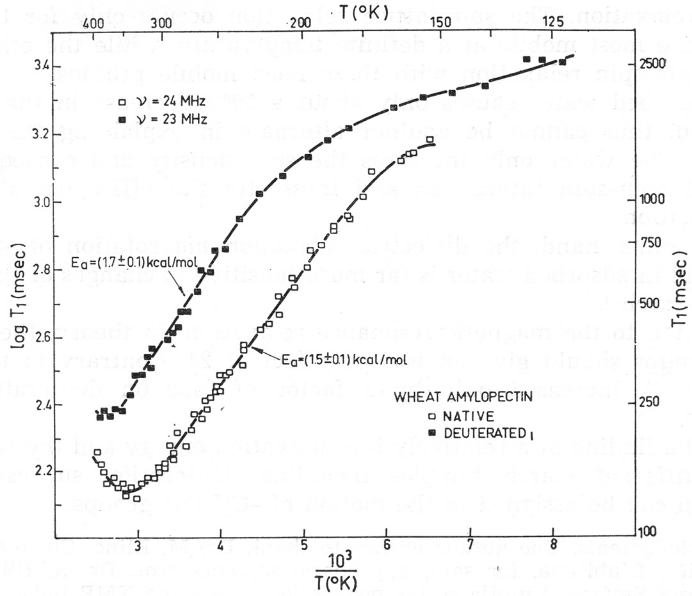

Fig. 4. The temperature dependence of T_1 for the native and deuterated wheat amylopectin. The deuterated sample was pressed for the purpose of better NMR signal.

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[12]

$$E_a\,(\text{cal/mol}) \approx 37\, T_{trans}\,(^0\text{K}) \qquad (6)$$

causes narrowing of the NMR line shape at a temperature T_{trans} lower than 77^0 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 τ_c could change the activation energy measured from the slope of the curve $\ln T_1 = f(1/T)$[13]. Our broad line NMR data indicate only 12% change in the second moment from 77 to 270^0 K for very dry starch and 86% for undried starch. It is possible that the narrowing of NMR line observed by Samec *et al.*[1] above 100^0 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 77^0 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 -CH_2OH 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 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[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_2OH groups.

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REFERENCES

1. M. Samec, R. Blinc, and M. Brenman, *J. Polymer Sci.* **56** (1962) S21.
2. V. I. Glazkov, *Dokl. Akad. Nauk SSSR* **142** (1962) 387.
3. N. Blombergen, E. M. Purcel, and R. V. Pound, *Phys. Rev.* **73** (1948) 679.
4. R. Kubo and K. Tomita, *J. Phys. Soc. Japan* **9** (1954) 888.
5. I. Solomon, *Phys. Rev.* **99** (1955) 559.
6. E. L. Hahn, *Phys. Rev.* **80** (1950) 580; *Phys. Today* **6**, No. 11 (1953) 4.
7. S. Vrščaj, *Elektroteh. vestnik* **16** (1962—3) 257.
8. M. Samec, *Kolloid-Z.* **94** (1941) 350.
9. J. Holo, J. Szejtli, and G. Gantner, *Mezögazd. Kém. Techn. Tansz. Közl.* **1958**, 39.
10. R. E. Rundle and D. French, *J. Am. Chem. Soc.* **65** (1943) 1707.
11. N. W. Taylor, *J. Phys. Chem.* **65** (1961) 1816.
12. J. S. Waugh and E. I. Fedin, *Fiz. Tverd. Tela* **4** (1962) 2233.
13. T. M. Connor, *Trans. Faraday Soc.* **60** (1964) 1574; **61** (1965) 1097.
14. S. Ono, T. Kuge, and N. Koizumi, *Bull. Chem. Soc. Japan* **31** (1958) 39, 40.

IZVOD

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

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Vrijeme T_1 za protonsku relaksaciju spin-rešetka mjereno je metodom pulseva 90—90° u škrobovima različitoga podrijetla i u objema frakcijama škroba, te u jodovom kompleksu amiloze, topivom škrobu i deuteriranim škrobovima, kao i u škrobovima različite vlažnosti. 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). Usporedni rezultati za različite škrobove ukazuju na to, da je taj minimum za T_1 uzrokovan rotacijom —CH_2OH grupa u škrobovoj molekuli.

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ZAGREB

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