An NMR Study of Structure Formation in Maltodextrin Systems

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ABSTRACT

Water mobility in the solutions of maltodextrin during the structure formation was studied by the Proton Pulse NMR technique. The comparison of the two-component spin–spin relaxation of the maltodextrin non-exchanging CH-protons with the relaxation properties of water protons in maltodextrin–water systems in sol–gel transition mode leads to the assumption that maltodextrin gel networking involves the formation of stable clusters whose lifetime is comparable with the relaxation time of water molecules.

INTRODUCTION

As has been shown earlier (German *et al.*, 1988), at starch concentrations close to the critical gelation concentration (C_0) the spin–spin relaxation of water molecules is characterized by two time values. The idea of the complex relaxation of water molecules (Lillford *et al.*, 1980) has been useful in showing that gel network formation involves the formation of stable clusters whose lifetime is comparable with the water molecule relaxation time. However, the problem concerning the existence of clusters whose lifetime is shorter than this time is still open.

The process of structure formation in starch is known (Kerr, 1950) to occur through intermolecular hydrogen bonding. As this takes place, as stated elsewhere (Maklakov *et al.*, 1985) with particular reference to agarose, there are changes in the macromolecule mobility. However, it is quite natural that not all macromolecules are involved in the gel network. It can be assumed that the spin–spin relaxation of the protons associated with the macromolecules participating and not participating in the network will be characterized by different times. The relaxation times of

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non-exchanging CH-protons can be readily determined by preliminary deuteration of the polymer and the use of D_2O as the solvent. In this case the changes in the spin–spin relaxation time (T_2) of the starch CH-protons depends on the state of the system, sol or gel. A comparison of the relaxation time properties of the systems starch–H_2O and starch–D_2O in the concentration region preceding the critical gelation concentration provides an answer to the question concerning the existence of clusters whose lifetime is much shorter than the water molecule relaxation time.

The purpose of this work is to study the changes in the T_2 values for the non-exchanging CH-protons in the sol–gel transition mode and also to compare the relaxation properties of the systems starch–H_2O and starch–D_2O. The study was made on a gelling maltodextrin produced by enzyme hydrolysis of potato starch.

EXPERIMENTAL

The maltodextrin for the experimental purposes was produced by enzyme hydrolysis of potato starch as described elsewhere (Richter *et al.*, 1972) at the Central Institute of Nutrition of the GDR Academy of Sciences. The deuterated sample was obtained as follows.

(1) Preparation of a 6% dispersion of native maltodextrin in D_2O.
(2) Heating the dispersion with stirring to 95°C, holding at this temperature for 5 min and cooling slowly down to 25°C.
(3) Thermostatting the solution obtained at 25°C for 24 h.
(4) Freeze-drying of the sample.

To solutions in the concentration range 0·8–32·4%, the freeze-dried and deuterated maltodextrin sample was dispersed in D_2O, heated to 95°C, held for 5 min at this temperature and then slowly cooled down to 25°C and thermostatted at this temperature for 24 h.

The critical gelation concentration or gel point (C_0) was determined as proposed elsewhere (Grinberg *et al.*, 1980).

The spin–spin relaxation time T_2 was measured with a Minispec pC-120 pulsed NMR spectrometer (Bruker, FRG) with an operating frequency of 20 MHz at 25 ± 2°C. At least 200 scans were made in each case. The experimental echo envelope in the Carr–Parcell–Meiboom–Gill sequence (Carr & Parcell, 1954; Meiboom & Gill, 1958) is expanded into the individual components on a Duet-16 personal computer (Parafacon, Japan) using IBM programs. The error in T_2 was estimated to be *c.* 2%.

RESULTS AND DISCUSSION

In the determination of the boundary conditions for the gelation of the maltodextrin–D_2O system the C_0 value was found to be 11%. A comparison of the derived C_0 value with the published data ($C_0 = 17\%$) (Shierbaum *et al.*, 1977; German *et al.*, 1988), that were obtained in experiments with *distilled water* as the solvent, shows the derived value to be somewhat smaller.

Figure 1 shows the dependence of the maltodextrin CH-proton spin–spin relaxation time on the reduced concentration C ($\tilde{C} = C_p/C_0$), where C_p is the maltodextrin concentration). It is evident that in the entire concentration range the relaxation is characterized by two time values, viz., T_{2a} and T_{2b}. It can be assumed that the observed values of the spin–spin relaxation (Fig. 1) are typical of the CH-protons entering and not entering into the gel structural elements, respectively. It is evident that the former are distinguished by a shorter relaxation time T_{2b}. Variations in the fraction of such protons (P_b) with respect to the reduced maltodextrin concentration is illustrated in Fig. 2.

The T_{2a}–$\tilde{C}$ dependence has a fairly sophisticated nature. As is seen from Fig. 1, in the polymer concentration range close to the critical
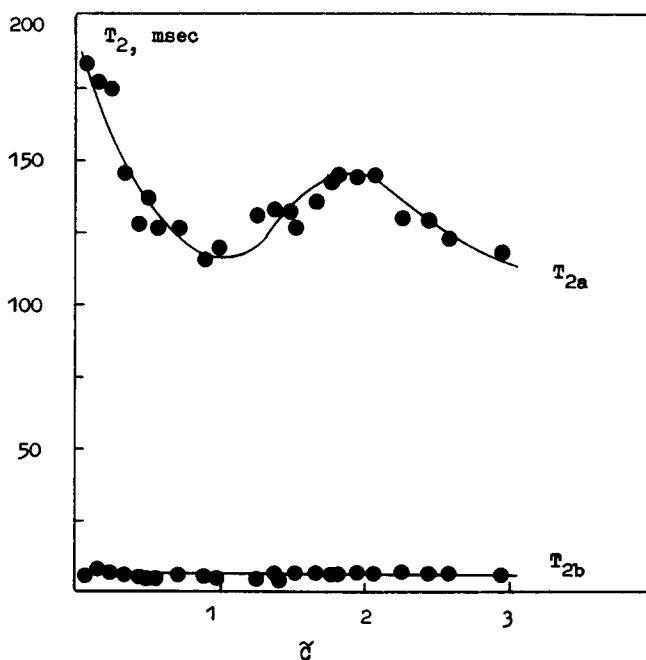

Fig. 1. Dependence of the maltodextrin CH-proton spin–spin relaxation time on the reduced concentration.

concentrations $(1 < \tilde{C} < 2)$, i.e. when passing from the finite clusters to infinite clusters, an anomalous behaviour of the function $T_{2a} = f(\tilde{C})$ may be observed. This anomaly seems to be due to the fact that at the initial stage of the formation of a maltodextrin gel network the fraction of the CH-protons entering into the structural elements increases. Figure 2 illustrates the validity of this assumption at $1 < \tilde{C} < 2$. A similar result has been obtained in studies of the translational mobility of agarose macro-molecules (Maklakov et al., 1985).

Thus the relaxation properties of the CH-protons not entering into the structural gel elements are controlled by the process of network formation.

As opposed to the dependence $T_{2a} = f(\tilde{C})$, the dependence $T_{2b} = f(\tilde{C})$ is rather simple (Fig. 1). It is evident that the maltodextrin proton spin–spin relaxation time is independent of the reduced concentration. Bearing in mind that the concentration range under study covers the sol–gel transition region, it can be assumed that the process of the space gel networking does not lead to any T_{2b} changes. In other words, the transition from the finite to the infinite clusters brings about no changes
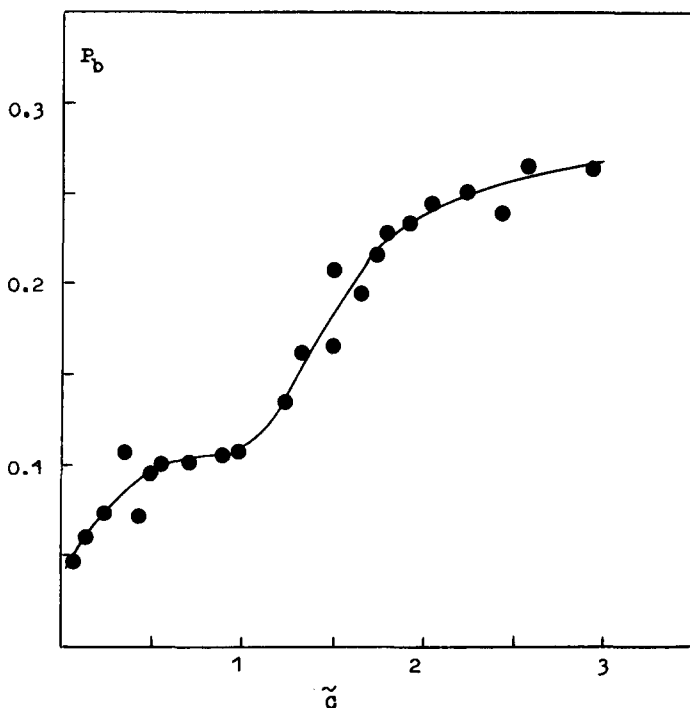

Fig. 2. Dependence of the fraction of the maltodextrin CH-protons entering into the gel structural elements on the reduced concentration.

in the relaxational properties of the protons entering into the structural elements.

It is known that the spin–spin relaxation rate variation is proportional to viscosity, i.e., $1/T_2 \propto \eta$ (Abraham, 1963). Due to the fact that the T_{2b} values characterize the relaxational properties of the protons entering into the structural elements, it is quite probable that the parameter $1/T_{2b}$ characterizes their internal viscosity. Since T_{2b} is independent of the reduced concentration (Fig. 1), the internal viscosity of the structural gel elements is independent of polymer concentration. Hence, as suggested elsewhere (Grinberg *et al.*, 1985), maltodextrin gels have a micro-inhomogeneous structure. Such gels are composed of structural elements interacting with one another in the nodal points only, the relaxation properties of such a structure (Bikbov *et al.*, 1981) being governed by the internal viscosity of the elements.

As is known (Hermans, 1965; Cohen & Bedenek, 1982; Grinberg *et al.*, 1985), the degree of crosslink formation due to intermolecular inter-action is proportional to the polymer concentration. It is also known (De Gennes, 1979) that an increase in the polymer concentration when $C_p < C_0$ results in the appearance of larger clusters. At a critical value of the reaction coordinate (p_0), i.e. at $C_p = C_0$ or $\tilde{C} = 1$ the finite clusters merge to form an infinite cluster. According to the percolation gelation model (De Gennes, 1979), the fraction of monomers belonging to the infinite cluster (S_∞) increases with increasing $\Delta p = p - p_0$ according to the equation

$$S_\infty \cong (\Delta p)^\beta \tag{1}$$

where β the critical index is equal to 0.39. It can be assumed that the fraction of the CH-protons entering into the infinite cluster (P_b) at $C_p > C_0$ is proportional to that of the monomers belonging to the infinite cluster, i.e.

$$S_\infty \propto P_{b, \tilde{C} \geqslant 1}$$

Moreover, taking into account that, as stated elsewhere (Cohen & Bedenek, 1982; Grinberg *et al.*, 1985; Hermans, 1965),

$$P \propto C_p$$

$$P_0 \propto C_0$$

eqn (1) can be written as

$$P_{b, \tilde{C} \geqslant 1} \cong (\tilde{C} - 1)^\beta \tag{2}$$

or

$$\log P_{b, \tilde{C} \geqslant 1} \cong \beta \log(\tilde{C} - 1) \tag{3}$$

Figure 3 shows a change in the fraction of the maltodextrin CH-protons at $\check{C} > 1$ in the coordinates of eqn (3). It is evident that this equation provides a fairly good description of the experimental data and the derived critical index equal to 0.32 ± 0.04 practically coincides with the theoretical value. Hence it follows that the percolation model describes the process of maltodextrin gelation well.

Figure 4 presents $T_{2b} - \check{C}$ dependences for two systems, viz. maltodextrin-H_2O and maltodextrin-D_2O. As can be seen from this figure, the two systems are distinguished by the existence of T_{2b} at values of $\check{C} < 1$ in the D_2O system but not for H_2O. It has been shown by other authors (German et al., 1988) in studies of the system maltodextrin-H_2O that the appearance of the time T_{2b} is due to the formation of stable clusters whose lifetime is comparable to the water molecule relaxation time. However, it does not mean that at lower polymer concentrations no finite clusters exist. It is quite probable that, in the maltodextrin region when $\check{C} < 1$ and the water molecule spin-spin relaxation is characterized by a single T_{2a} value (German et al., 1988), they do exist, although their
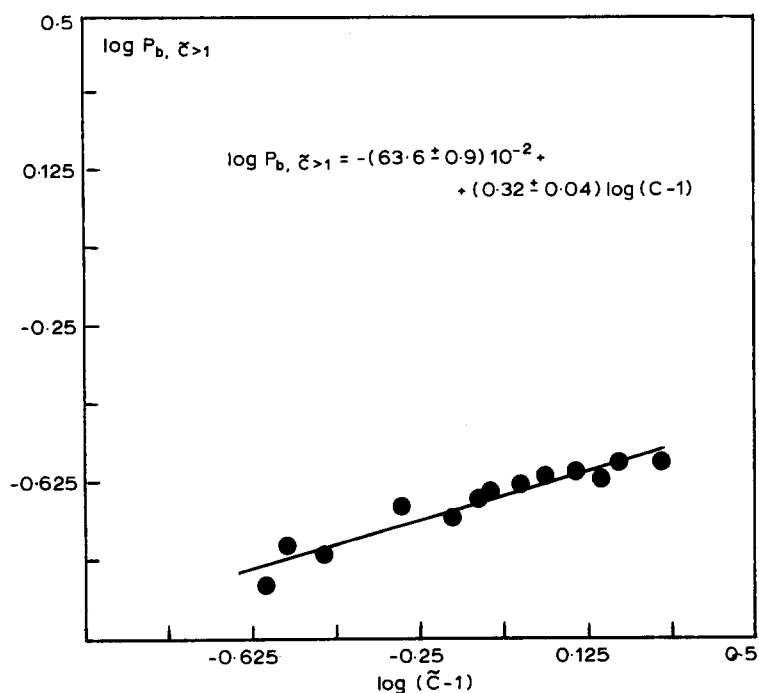

The plot shows $\log P_{b}$, $\check{C}_{>1}$ on the y-axis (values 0.5, 0.125, -0.25, -0.625) versus $\log (\tilde{C}-1)$ on the x-axis (values -0.625, -0.25, 0.125, 0.5).

$$\log P_{b}, \check{C}_{>1} = -(63.6 \pm 0.9) 10^{-2} + (0.32 \pm 0.04) \log (C-1)$$

Fig. 3.   Concentration dependence of the fraction of the maltodextrin CH-protons entering the gel structural element at $\check{C} > 1$.

lifetime is much shorter than this relaxation time. In fact, as can be seen from Fig. 4, the $\tilde{C}$ value at which the appearance of T_{2b} can be observed for the system maltodextrin–D_2O is one tenth as large as that for the system maltodextrin–H_2O. Hence it is quite probable that the formation of stable clusters is preceded by the formation of clusters whose lifetime is much shorter than the water molecule relaxation time.

Thus the process of maltodextrin gel network formation can be represented as follows.

(1) At $\tilde{C} < 0.7$ (Fig. 4) finite clusters are formed, whose lifetime is much shorter than the water molecule relaxation time.
(2) At $0.7 < \tilde{C} < 1$ finite clusters are formed, whose lifetime is comparable with the water relaxation time.
(3) At $\tilde{C} > 1$ the process of gel networking is described by the percolation model.

Thus the totality of the results obtained points to the validity of the authors' assumption by which the times T_{2a} and T_{2b} characterize the relaxational properties of the CH-protons entering and not entering the maltodextrin gel structural elements.
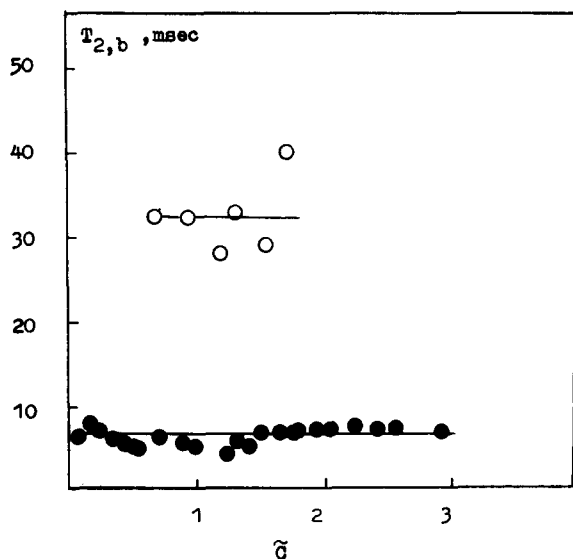

Fig. 4. Dependence of the spin–spin relaxation short time T_{2b} on the reduced concentration for the systems maltodextrin–H_2O (●) and maltodextrin–D_2O (○).

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REFERENCES

Abraham, A. (1963). *Nuclear Magnetic Resonance,* ed. G. V. Skrotsky. Inostrannaya Literature, Moscow.

Bikbov, T., Grinberg, V. Ya., Smandke, H., Chaika, T. S., Vaintraub, J. A. & Tolstoguzov, V. B. (1981). *Colloid. Polym. Sci.,* **259**, 536.

Carr, H. Y. & Parcell, E. M. (1954). *Phys. Rev.,* **94**, 630.

Cohen, R. J. & Bedenek, G. B. (1982). *J. Phys. Chem.,* **86**, 3696.

De Gennes, P. G. (1979). *Scaling Concepts in Polymer Physics.* Cornell University Press, Ithaca and London.

German, M. L., Gotlib, A. M., Blumental, A. L., Yuryev, V. P., Braudo, E. E., Fedin, E. I., Eichoff, U. & Tolstoguzov, V. B. (1988). *Zh. Fiz. Khim.,* **62**(4), 1054.

Grinberg, N. V., Plashchina, I. G., Braudo, E. E. & Tolstoguzov, V. B. (1980). *Colloid. Polym. Sci.,* **258**(9), 103.

Grinberg, V. Ya., Bikbov, T. M., Grinberg, N. V. & Tolstoguzov, V. B. (1985). In *Gelatinization Processes in Polymer Systems,* Part I. Saratov University, Saratov, p. 96.

Hermans, J. T. (1965). *J. Polym. Sci.,* **A3**, 1895.

Kerr, R. W. (1950). *Chemistry and Industry of Starch.* Academic Press, NY.

Lillford, P. J., Clark, A. H. & Jones, D. V. (1980). In *Water in Polymers,* ed. S. P. Rowland. American Chemical Society, Washington, DC.

Maklakov, A. I., Pimenov, G. G. & Skirda, V. D. (1985). In *Gelatinization Processes in Polymer Systems,* Part I. Saratov, p. 28.

Meiboom, S. & Gill, D. (1958). *Rev. Sci. Inst.,* **29**, 688.

Richter, M., Schierbaum, F., Augustat, S. & Knoch, K. D. (1972). DDR Patent, W. P. 126992, Vertahren zur enzymatischen Herstellung von Starkehydrolysenprodukten.

Schierbaum, F., Richter, M., Augustat, S. & Radosta, S. (1977). *Deutsche Lebensm.-Rundsch. (Stuttgart),* **73**, 390.