Hydration of Potato Starch in Aqueous Suspensions Determined from Nuclear Magnetic Relaxation Studies by ^{17}O, ^{2}H, and ^{1}H NMR: Relaxation Mechanisms and Quantitative Analysis

Phillip I. Yakubu, Eiichi M. Ozu, and Ion C. Baianu*

Department of Food Science, Nuclear Magnetic Resonance Facility, College of Agriculture, University of Illinois at Urbana, Urbana, Illinois 61801

Paul H. Orr

Potato Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture, East Grand Forks, Minnesota 56721

Nuclear magnetic relaxation (^{17}O, ^{2}H, and ^{1}H NMR) measurements were employed to investigate the hydration properties of potato starch in relation to functionality in food systems. A comparison of ^{17}O, ^{2}H, and ^{1}H NMR data allowed us to resolve the contributions to water relaxation made by water binding, chemical exchange, and intermolecular dipolar interaction cross-relaxation, respectively. Weakly bound water in potato starch suspensions has an average correlation time of about 20 ± 0.6 ps (determined by ^{17}O, NMR), compared with 5 ps for bulk water (D_2O) at 20 °C. Three hydration regions were observed between 0.02 and 0.90 g of starch/g of D_2O, respectively. The first hydration region extends from 0.02 to 0.4 g of starch/g of H_2O, whereas the second region occurred between 0.40 and 0.65 g of starch/g H_2O. Deuterium and proton NMR allowed us to resolve three water populations "bulk (or free)" water, "weakly bound" water, and trapped water in potato starch suspensions. Deuterium NMR resolved a slowly exchangeable anisotropically bound water population within the potato starch granule structure. We find, therefore, that potato starch has a potential for utilization as a stable functional ingredient in food formulations to increase stability and storage life.

INTRODUCTION

Potato starch has the potential for wide utilization as a stable functional ingredient in food formulations to increase the stability and storage/shelf life of foods (Baianu et al., 1990a). Previous deuterium nuclear magnetic resonance (NMR) studies of potato starch hydration properties showed that these are unique since they were not found in corn or wheat starches (Lechert et al., 1980; Lechert, 1981; Baianu et al., 1990b; Yakubu et al., 1990a,b). Potato starch contains about 34 ± 1% water (Schierbaum and Taufel, 1962), which we found to be trapped, or anisotropically bound, within the potato starch granule structure (Baianu et al., 1990a; Yakubu et al., 1990b,c). The X-ray diffraction studies of starches, on the other hand, classified fully hydrated potato starch as B-starch (Zobel, 1988a). It has also been recently suggested that the hydration properties of potato starch and potatoes may be due to the presence of B-type structure (Reuther et al., 1984; Zobel, 1988b), that is, the hexagonal arrangement of double helices of very large amylose molecules (Yakubu et al., 1990b). The ability of potato starch to bind, or trap, water within its granule structure makes potato starch more desirable than other (cereal) starches as a functional ingredient for improving and increasing the rigidity and firmness of gels in a number of food systems (Baianu, 1986; Lanier, 1986; Lee, 1986; Baianu et al., 1990a).

The role of water in influencing the physicochemical, hydration, and functional properties of carbohydrates and proteins has been quantitated by NMR techniques (Tait

et al., 1972; Lèlievre and Mitchell, 1975; Halle and Lindman, 1978; Baianu, 1982, 1985, 1989, 1992; Baianu and Förster, 1980; Kakalis and Baianu, 1988; Mora-Gutierrez and Baianu, 1989, 1991). The NMR techniques, being nondestructive, are widely utilized to monitor the molecular dynamics of water in foods, water binding, and diffusion rates (Baianu et al., 1992). Such information is useful for the prediction of stability and storage life of foods (Baianu, 1986; Baianu et al., 1990a,b).

Oxygen-17, deuterium, and proton NMR measurements were recently employed to investigate the hydration properties of starches (Baianu et al., 1990a) and proteins (Lioutas et al., 1986; Kakalis and Baianu, 1988; Baianu, 1989). Such studies are here extended to the hydration of potato starch suspensions.

MATERIALS AND METHODS

Potato Starch. Potato starch was obtained from Sigma Chemical Co. (St. Louis, MO) and was specified to contain 25% amylose and 75% amylopectin.

Moisture and pH. Moisture content was determined according to the AOAC (1981) method and was found to be about 14%. The pH values of potato starch suspensions in H_2O and D_2O were determined with a laboratory pH meter (Hana Instruments, H18417). For pD = pH + 0.45 (Covington et al., 1968), most values were close to pD = 7.45 (pH 7.0).

Sample Preparation. Potato starch suspensions were prepared by mixing appropriate amounts of solids with deuterium oxide for ^{17}O and ^{2}H NMR or deionized water for ^{1}H NMR. Samples were transferred to 5- or 10-mm o.d. NMR tubes and were allowed to equilibrate on ice.

^{1}H NMR Measurements. ^{1}H NMR measurements were carried out at 10 MHz with a PC-10 process analyzer (Bruker/ IBM Instruments, Danbury, CT). The Carr–Purcell–Meiboom-Gill (CPMG) sequence was employed for T_2 measurements. The decay of the transverse magnetization was monitored with a dual-beam Tektronix storage oscilloscope (Model 5113). Measurements were carried out in triplicate at 20 ± 1 °C.

* Address correspondence to this author at Department of Food Science, Physical Chemistry and NMR Laboratories, University of Illinois at Urbana–Champaign, 580 Bevier Hall, 905 S. Goodwin Ave., Urbana, IL 61801 [telephone (217) 244-6630, 333-4443].
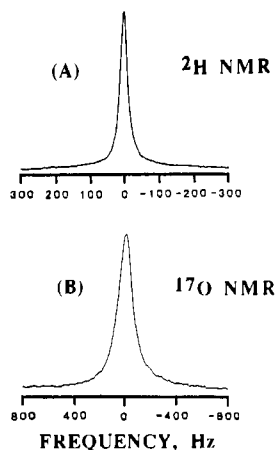
Hydration of Potato Starch

J. Agric. Food Chem., Vol. 41, No. 2, 1993 **163**

Figure 1. Fourier transform NMR spectra of D_2O in potato starch suspensions at 20 ± 1 °C. (A) ^2H NMR spectrum of D_2O in potato starch suspensions; (B) ^{17}O NMR spectrum of D_2O in potato starch suspensions.

Oxygen-17 and Deuterium NMR Measurements. A CXP 200, high-field, multinuclear NMR spectrometer (Bruker Instruments Inc., Billerica, MA), operating at 4.7 T, was used for both ^{17}O and ^2H NMR. Measurements were carried out at resonance frequencies of 27.12 and 30.71 MHz, respectively. For oxygen-17 NMR, spectral widths were selected in the range from 50 to 200 kHz, the 90° pulse width was 16 µs, and the recycling time was 0.16 s. The number of scans was varied from 500 in dilute suspensions to 10 000 in hydrated powders. The deuterium NMR spectral widths were selected in the range from 40 kHz to 2 MHz, the 90° pulse width was 16 µs, and recycling time was 0.16 s. The number of scans was varied from 500 in dilute suspensions to 10 000 in hydrated powders. A signal-to-noise ratio of 1000:1 was selected to observe the deuterium powder pattern of "tightly bound" D_2O within the potato starch granules. The Fourier transforms were carried out on-line with a Bruker Aspect 2000A (24 bit) computer equipped with a CDC 90-MB drive.

Oxygen-17 and ^2H NMR Theory. The oxygen-17 nucleus has a spin quantum number $I = 5/2$. Therefore, it has five transitions between six spin energy levels. The ^{17}O nuclear spin relaxation is dominated by the quadrupolar interaction (Abragam, 1961; Halle, 1981; Kintzinger, 1983). The strong quadrupolar interaction causes a large relaxation effect, permitting the study of hydration even for a small number of hydration sites (Baianu et al., 1992).

Both the reorientation of the water molecules at the binding sites on a biopolymer, or a particle, and the exchange between "bound" and "free" or "bulk" water cause the narrowing of the ^{17}O NMR absorption peak of water. When the exchange between bound and free water is fast on the time scale of the NMR measurements (that is, when the water-exchange rate is faster than the bound water nuclear spin relaxation rate), the measured relaxation rate is the weighted average of the relaxation rates of bound (R_{2B}) and free (R_{2F}) water populations (Zimmerman and Brittin, 1957; Derbyshire, 1982; Mora-Gutierrez and Baianu, 1989). Such a relationship is expressed as

$$R_{2obs} = P_B R_{2B} + P_F R_{2F} \tag{1}$$

where P_B and P_F are fractions of bound and free water in the system, respectively, and R_{2obs} is the measured transverse relaxation rate of the samples at various hydration levels. A single Lorentzian ^{17}O NMR peak was observed in potato search suspensions in D_2O from 0.02 to 0.6 g of starch/g of D_2O. Our observations are consistent with a fast-exchange, two-state model between bound and free water populations, as shown in Figure 1 (spectra A and B). The two-state model was previously employed to analyze ^{17}O NMR data for water (D_2O) in dilute lysozyme solutions (Lioutas et al., 1986; Kakalis and Baianu, 1988), corn maltodextrins (Mora-Gutierrez and Baianu, 1990), and wheat starch (Baianu and Mora-Gutierrez, 1985; Baianu, 1986).

In the case of ^2H NMR studies of potato starch suspensions in D_2O, the analysis with the fast-exchange model applies only

to the water populations responsible for the central Lorentzian peak. The relevant deuterium NMR theory for water (D_2O in potato starch suspensions and hydrated powders) was outlined in several recent papers (Baianu et al., 1990a, 1992; Yakubu et al., 1990a–c). Deuterium NMR quadrupole splittings of about 1 kHz were resolved in potato starch suspensions ranging from 12% starch (88% water) to hydrated powders (down to ≤2% water).

In the case of water (D_2O) molecules that undergo anisotropic reorientation, there is a partial ordering of the water molecules (Mantsch et al., 1977; Smith, 1983). This is characterized by an order parameter, S, defined by the expression

$$\Delta\nu_Q = (3e^2qQ/4\hbar)S \tag{2}$$

where $S_D = [(3\cos^2\theta - 1)/2]$ is the order parameter, eq is the electric field gradient at the deuterium nucleus, eQ is the deuterium quadrupole moment, θ is the angle made by the direction of the oxygen–deuterium bond with the applied magnetic field, H_o, and $\hbar$ is Planck's constant devided by 2π. The order parameter, S_D, is equal to 1.0 for a perfectly ordered system, whereas it is zero for a completely disordered system. This property, S_D, makes deuterium NMR an excellent technique for the study of the degree of water ordering in foods and other biological systems (Baianu et al., 1984). The order parameter, S_O, in the case of the oxygen-17 NMR of water has twice the value of S_D measured for D_2O by deuterium NMR. This is mainly because of the different orientations of the oxygen-17 and deuterium quadrupole tensors with respect to the magnetic field (Abragam, 1961).

The transverse relaxation rates, R_2 (s^{-1}), for both oxygen-17 and deuterium NMR were calculated at each concentration with (Dwek, 1973; Mora-Gutierrez and Baianu, 1989)

$$T_2^{-1} = R_{2Corr} (s^{-1}) \propto \pi\Delta\nu_{obs}^{Corr} \tag{3}$$

where $\Delta\nu_{obs}^{Corr}$ is the line width at half-height for each spectrum, after correcting for a small inhomogeneity broadening of the order of 2% or smaller.

The ^{17}O NMR relaxation data were fitted with a Systat nonlinear regression program on a 32-bit Macintosh II microcomputer equipped with a 68020 CPU, a 68882 mathematical coprocessor, 5-Mb RAM, and an 80-Mb hard drive. Both Simplex and quasi-Newton algorithms were employed.

For calculations of correlation times, the "excess", or differential transverse relaxation rates, ΔR_2 (s^{-1}), were employed in

$$\Delta R_2 (s^{-1}) = (\Delta\nu_{obs}^{Corr} - \Delta\nu_{free}) \tag{4}$$

where $\Delta\nu_{free}$ is the line width at half-height for water (D_2O).

Nuclear Magnetic Relaxation Mechanisms of Water in Potato Starch Suspensions. Oxygen-17 nuclear spin relaxation is essentially quadrupolar, and in the case of "heavy" water (D_2O), it is not altered to any significant degree by either cross-relaxation (Kakalis and Baianu, 1988) or chemical exchange (Dwek, 1973; Kintzinger, 1983).

Deuterium nuclear spin relaxation mechanism is also quadrupolar in solutions, but the ^2H NMR relaxation rate is affected by the chemical exchange between bound and free water protons. The ^2H NMR is, therefore, quite useful for separating, or resolving, "liquidlike" from "solidlike" behaviors in biological systems where mixed phases are present (Baianu et al., 1984); other major uses of NMR, in general, and deuterium NMR in particular, are concerned with the conformational changes induced by heat treatments of biopolymers (Lechert et al., 1980; Baianu et al., 1982; Baianu, 1989, 1992; Mora-Gutierrez and Baianu, 1989; Yukubu et al., 1989).

The proton with a spin $1/2$ has a large magnetic moment, and in the absence of paramagnetic species, its nuclear spin relaxation is dominated by *dipolar interactions* (Abragam, 1961). In protonated or partially deuterated biopolymers, the dipolar-coupled spin group behavior in solids becomes important (Baianu et al., 1981). Major concerns in ^1H NMR spin–lattice relaxation studies are the contributions of cross-relaxation and chemical-exchange processes to the relaxation of water protons. Cross-relaxation is essentially a spin diffusion process (Edzes and Samulski, 1978) involving a magnetic energy transfer across a "solid" particle–liquid water interface. This process can only occur if the relaxing water molecules are closer than about 5 Å,
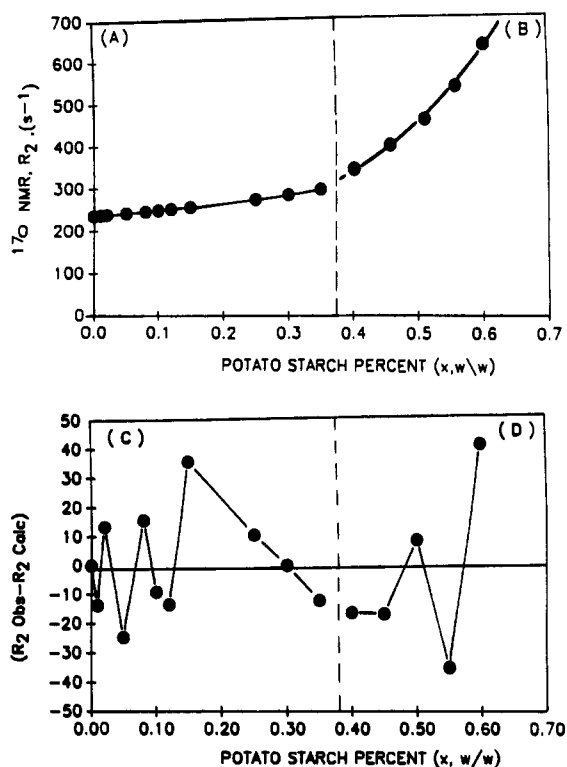
Figure 2. ^{17}O NMR transverse relaxation rates, R_2^* (s^{-1}), of water in potato starch suspensions. (A) Dependence of the transverse relaxation rates, R_2^* (s^{-1}), on potato starch-to-water ratios from 0.02 to 0.4 g of starch/g of D$_2$O; (B) dependence of the transverse relaxation rates, R_2^* (s^{-1}), on potato starch-to-water ratios from 0.4 to 0.6 g of starch/g of D$_2$O; (C) residual plots of ^{17}O NMR transverse relaxation rates, R_2^* (s^{-1}), for potato starch-to-water ratios [(A) 0.02–0.4 g of starch/g of D$_2$O, SD = 17.31; (B) 0.4–0.6 g of starch/g of D$_2$O, SD = 26.13].

or less, to the particle surface. Because of the marked effect of the protons attached to the biopolymer on the rate of water proton cross-relaxation, the ^{1}H nucleus is useful for the investigation of aggregation and denaturation of proteins (Baianu, 1989; Myers-Betts and Baianu, 1990a,b) and gelatinization and retrogradation of starch (Baianu and Mora-Gutierrez, 1985; Baianu, 1986; Mora-Gutierrez and Baianu, 1989, 1990).

RESULTS

Oxygen-17 and deuterium NMR spectra of potato starch suspensions in D$_2$O are presented in Figure 1A,B. In both spectra, a single Lorentzian peak is observed for a highly mobile water population in fast exchange with bulk water, observed in the hydration range from 0.02 to ~0.5 g of potato starch/g of D$_2$O. This is consistent with the two-state, fast-exchange model between bound and free water populations (eq 1).

The dependence of the ^{17}O NMR transverse relaxation rate, R_2^{*Corr}, potato starch suspensions on the starch-to-D$_2$O ratio is shown in Figure 2A; the ^{17}O NMR line width increases linearly with the starch-to-water ratio for low to intermediate values, as predicted by eq 1. Deviations from linearity were observed above 0.4 g of starch/g of D$_2$O (Figure 2B). Previous studies on other systems have attributed such deviations from linearity to either (1) a change in the hydration of macromolecules (Baianu, 1989), (2) a change in the relaxation rate of bound water (Baianu et al., 1990b), or (3) restricted diffusion of water molecules between tightly packed starch granules in hydrated powders (Baianu, 1986; Mora-Gutierrez and Baianu, 1989, 1990; Yakubu et al., 1990b,c). Note also the marked increase in the relaxation rate gradient above 0.4 g of starch/g of D$_2$O (Figure 2B).

Table I. Hydration Parameters of Sigma Potato Starch for the Weakly Bound Water Population, Derived from ^{17}O NMR Measurements

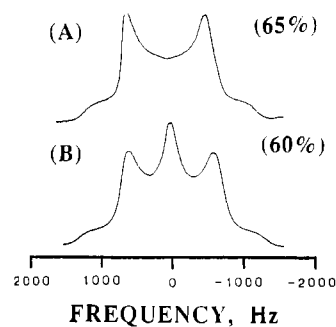| calcd parameters	correl coeff	suspension range, g of starch/g of D$_2$O
$n_H^w = 0.31 \pm 0.04$	0.999	0.00–0.35
$R_{2B}^w = 1000 \pm 20$ s^{-1}		
$\tau_c^{wb} = 20 \pm 0.6$ ps		
$R_{2F} = 236 \pm 9$ s^{-1}		

FREQUENCY, Hz

Figure 3. Fourier transform ^{2}H NMR spectra of D$_2$O in potato starch suspensions and powders at 20 °C. (A) Anisotropic slowly exchangeable water population within the potato granule structure at 0.65 g of starch/g of D$_2$O; (B) spectrum of a 0.6 g of starch/g of D$_2$O suspension showing a Lorentzian peak on top of the doublet. The water population within the potato starch granule structure does not exchange rapidly with the other water populations.

The residual plot of ($R_{2obs} - R_{2calc}$) vs potato starch-to-water ratio for values below 0.4 g of starch/g of D$_2$O and above this value, are presented in parts C and D, respectively, of Figure 2. In such a plot, a "run" is defined as a series of consecutive points with a residual of the same sign, positive or negative (Motulsky and Ransnas, 1987). At lower starch-to-water ratios from 0.02 to 0.4 g of starch/g of D$_2$O, there are seven runs for a total of 11 points, whereas in the range of higher starch-to-water rations from 0.4 to 0.60 g of starch/g of D$_2$O, there are four runs for a total of 5 points.

Nonlinear regression analysis of ^{17}O NMR transverse relaxation data for potato starch in the low (0.2–0.4 g of starch/g of D$_2$O) and high (0.4–0.6 g of starch/g of D$_2$O) solid ranges are presented in Table I. The value of the correlation time of weakly bound water to potato starch granule surface in a low concentration range ($\leq$0.4 g of starch/g of D$_2$O) is also given in the same table.

In addition to the single Lorentzian peak observed by both ^{17}O and ^{2}H NMR, deuterium NMR resolved a bound water population with anisotropic motions within the potato starch granule structure (Figure 3A,B). The "tightly" bound water is the only population remaining in potato starch powders above 0.6 g of starch/g of D$_2$O, as shown in Figure 3A. Quadrupole splittings of about 1 kHz were resolved in potato starch even in dilute starch suspensions (88% water). Deuterium NMR resolved a (35%) slowly exchangeable water population (D$_2$O) which is trapped within the potato starch granule and has strongly anisotropic motions.

A comparison of the normalized, or scaled, ^{17}O and ^{2}H NMR transverse relaxation rates, $R_{2obs}^{Corr}/R_{2free}$, is presented in Figure 4A as a function of potato starch-to-water ratio. Oxygen-17 and ^{2}H NMR relaxation rates have *different*, unscaled values because of the difference(s) between the magnitudes of the nuclear quadrupole moments of the two nuclei (Kakalis and Baianu, 1988; Mora-Gutierrez and Gaianu, 1990). The *difference* in the *normalized* ^{17}O and ^{2}H NMR transverse relaxation rates as a function of potato starch-to-water ratio is presented
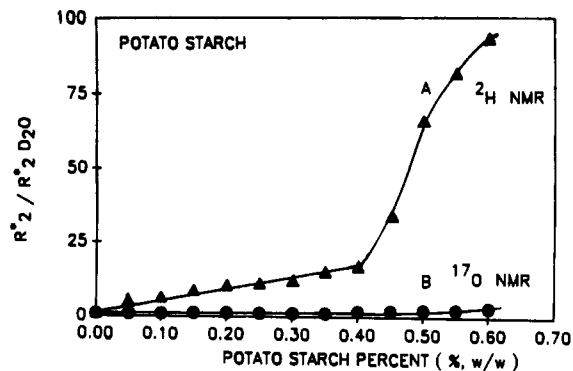
Figure 4. (A) Dependence of the normalized ^{17}O and ^{2}H NMR transverse relaxation rates, R_2^* (s^{-1}), on the starch-to-water ratios. Normalized rates were calculated with the following Rd_2^* values of D$_2$O: $R_2^*(^{17}O) = 235$ s^{-1} and $R_2^*(^{2}H) = 1.86$ s^{-1}. (B) Dependence of the difference between normalized ^{17}O and ^{2}H NMR transverse relaxation rates, R_2^* (s^{-1}), on potato starch-to-water ratios. Normalized rates were calculated with the same R_2^* values as in (A).
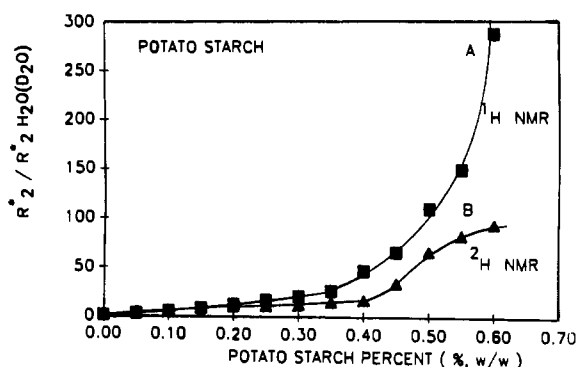

Figure 5. (A) Dependence of the normalized ^{2}H and ^{1}H NMR transverse relaxation rates, R_2 (s^{-1}), on the potato starch-to-water ratios. Normalized rates were calculated with the following R_2^* values of D$_2$O (^{2}H) and H$_2$O (^{1}H): $R_2^*(^{2}H) = 1.86$ s^{-1} and $R_2^*(^{1}H) = 0.33$ s^{-1}. (B) Dependence of the difference between the normalized ^{2}H and ^{1}H NMR transverse relaxation rates, (R_2), on potato starch-to-water ratios. Normalized rates were calculated with the same R_2^* values in (A).

in Figure 4B. This plot reflects the effect of *chemical exchange* on the ^{2}H NMR transverse relaxation rates of potato starch hydration.

The dependences of the normalized, or scaled, ^{2}H and ^{1}H NMR transverse relaxation rates on the potato starch-to-water ratio are shown in Figure 5A. ^{1}H NMR transverse relaxation rates vary more rapidly than the scaled ^{2}H NMR relaxation rates (Figure 5B), as a result of proton intermolecular dipolar interactions (PIDI), which contributes only to ^{1}H. The difference between the scaled ^{2}H and ^{1}H NMR transverse relaxation rates is shown in Figure 5B as a function of the starch-to-water ratio and reflects the effects of PIDI or cross-relaxation; note that the effect of PIDI cross-relaxation on the ^{1}H NMR relaxation rates is more marked above 0.2 g of potato starch/g of D$_2$O (Figure 5B). Comparing the relaxation contributions to ^{2}H and ^{1}H NMR relaxation rates presented in Figures 5 and 6, one notes that PIDI cross-relaxation *contributes significantly more* than proton/deuterium *chemical exchange* to the transverse relaxation rates of H$_2$O/D$_2$O in potato starch suspensions with less than 45% water (w/w).

DISCUSSION

Oxygen-17 NMR observations help resolve two hydration regions and three water populations in potato starch. The first region, which is linear, extends from 0.02 to 0.4 g of starch/g of D$_2$O (Figure 2A). In this region, the free,
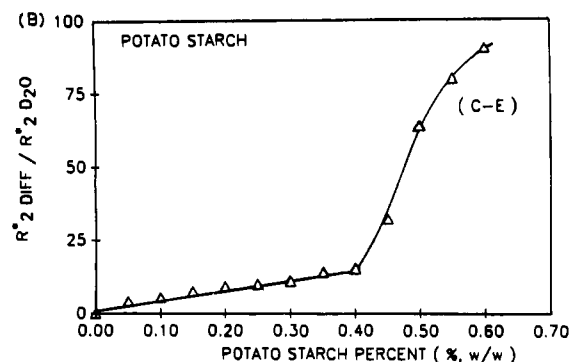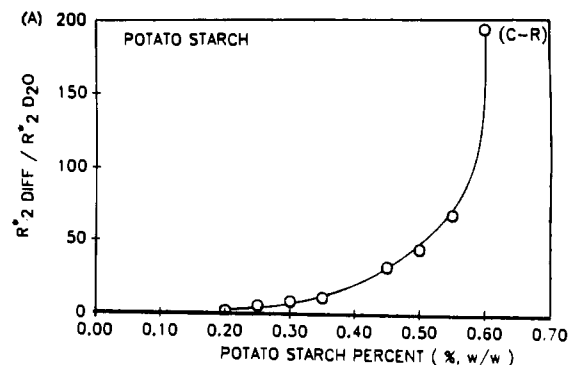

Figure 6. Dependence of the difference between normalized $^{17}O/^{2}H$ and $^{2}H/^{1}H$ NMR transverse relaxation rates, R_2^* (s^{-1}), on potato starch-to-water ratios. (A) Effect of PIDI cross-relaxation; (B) effects of chemical exchange.

or bulk, water and the *surface-bound* water populations make the major contributions to the observed transverse relaxation rates of water in potato starch suspensions. The second hydration region extends from 0.4 to 0.6 g of starch/g of D$_2$O (Figure 2B); this is also the beginning of aggregation and trapped water region in hydrated potato starch powders. A complete loss ("disappearance") of the oxygen-17 NMR peak was observed above 0.6 g of starch/g of D$_2$O. The water present within this region could only be observed by ^{2}H and ^{1}H NMR.

The percentage of weakly bound water to potato starch is about 31.1 ± 4.3%, whereas the value of R_2^{wb} for ^{17}O NMR of weakly bound water to potato starch is about 1000 ± 29 s^{-1}. Previous ^{2}H NMR hydration studies of hydrated potato starch granules resolved the slowly exchangeable water population trapped within the potato starch granule, which is about 35% w/w (Baianu et al., 1990a,b; Yakubu et al., 1990a,b). The percentage of weakly bound water to potato starch suspensions is less than that of the water population within the potato starch granule (35%). The weakly bound water and the bulk water populations contribute to the linear relaxation rate within the first hydration region (from 0.02 to 0.04 g of starch/g of D$_2$O). The percentage of trapped water between the potato starch granules is about 9.1 ± 0.07%, whereas the ^{17}O NMR transverse relaxation rate, R_2, of the trapped water is about 2000 ± 48 s^{-1}.

Three hydration regions and four water populations were resolved by ^{2}H NMR in conjunction with ^{17}O and ^{1}H NMR data. The first hydration region extended from 0.02 to 0.4 g of starch/g of D$_2$O, comprising a bulk water population, a weakly bound water fraction, and an anisotropic (slowly exchangeable) water population. In the third hydration region, above 0.6 g of starch/g of D$_2$O, only the anisotropic water (D$_2$O) population in hydrated potato starch remains consistent with previous continuous wave ^{2}H NMR studies on potato starch powders (Lechert et al., 1980; Lechert, 1981). The latter, continuous wave, ^{2}H NMR studies were also carried out on other starches
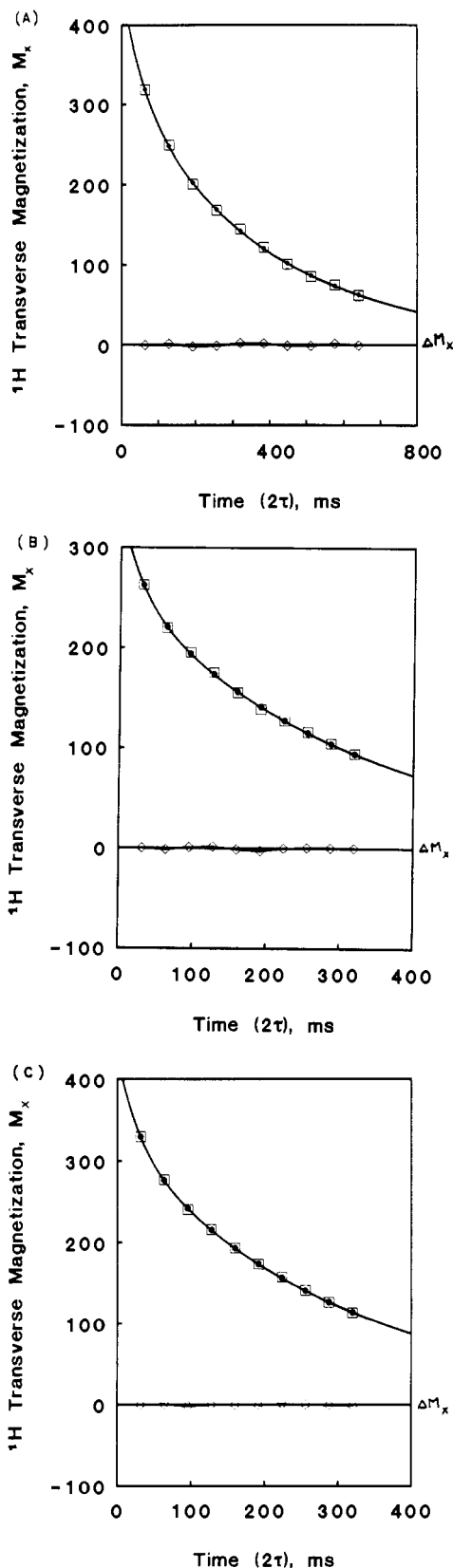
Figure 7. Two-component fittings of ^{1}H transverse magnetization decays in a 0.235-T magnetic field for water protons in potato starch suspensions at ~80% water content, 25 °C, and pH ~7. (A) Starch samples prepared from LaSoda (cultivars) potatoes (1991 and 1990 harvests; raw, 20%)); (B) starch samples prepared from Norchip (cultivars) potatoes (1991 and 1990 harvests; raw, 20%); (C) data for commercial potato starch samples from Sigma (raw, 20% w/w). (□) M_{obs}; (◊) residuals; (●) M_{est}.

and revealed that bound water in potato starch powders had a resolved ^{2}H NMR "powder pattern". On the other hand, water (D_2O) in corn, wheat, and pea starch powders gave essentially only a single Lorentzian isotropic water peak.

Determination of the Average Correlation Time, $\bar{\tau}_c^w$, of Weakly Bound Water. The average correlation time of weakly bound water at the potato starch granule surface can be calculated in the extreme narrowing limit ($\omega_0\tau_c \ll 1$) with

$$\bar{\tau}_c = R_2^{wb}/[K(e^2qQ/\hbar)^2(1 + \eta^2/3 - S^2)] \qquad (5)$$

where $K(^{17}O) = 12\,\pi^2/125$ and $K(^2H) = 3\pi/2$; $e^2qQ/\hbar$ is the quadrupole coupling constant expressed in hertz (Abragam, 1961); for oxygen (^{17}O), $e^2qQ/\hbar = 6.67$ MHz (Halle et al., 1981), and for deuterium (^2H), $e^2qQ/\hbar = 0.214$ MHz (Boden and Mortimer, 1978) or 0.216 MHz (Pessen and Kumosinski, 1985); and η is the asymmetry parameter. R_2^{wb} was found to be 1000.2 s^{-1} for ^{17}O and 300 s^{-1} for ^2H NMR relaxation, respectively. The correlation time, $\bar{\tau}_c^w$, for weakly bound water at the potato starch granule surface was calculated with eq 5 and with the above R_2^{wb} value from ^{17}O NMR measurements. The value of the correlation time, $\bar{\tau}_c^w$, was thus found to be about 20 ± 0.6 ps.

Conclusions. Oxygen-17, deuterium, and proton transverse, nuclear spin relaxation measurements were employed to quantitate the hydration properties of potato starch from dilute starch suspensions to hydrated powders. The weakly bound water at the potato starch granule surface has an average correlation time, $\bar{\tau}_c^w$, of about 20 ps in the range from 0.02 to 0.4 g of starch/g of D_2O. Deuterium NMR, on the other hand, resolved a slowly exchangeable anisotropic water population in the range from 0.12 g of starch/g of D_2O to 2% (g of D_2O/g of total) hydrated powders. Proton NMR was successful in monitoring the beginning of aggregation of potato starch suspensions at a low concentration (0.2 g of starch/g of H_2O), because of the effects of proton intermolecular dipolar interactions cross-relaxation on the ^{1}H NMR relaxation (Figures 6A and 7). The presence of a slowly exchangeable, anisotropically bound water population with highly restricted motions within the starch granules (even in dilute potato starch suspensions) makes potato starch a suitable functional ingredient in food formulations for increasing their stability and storage life.

LITERATURE CITED

Abragam, A. *Principles of Nuclear Magnetism*; Oxford University Press: London, 1961.

AOAC. *Official Methods of Analysis*, 13th ed.; Association of Official Analytical Chemists: Washington, DC, 1981.

Baianu, I. C. NMR relaxation studies of starch structure, hydration, gelatinization and retrogradation. Presented at the American Cereal Chemists Society Conference, Vancouver, Canada, 1986.

Baianu, I. C. High resolution NMR studies of food proteins. In *Nuclear Magnetic Resonance in Agriculture*; Pfeffer, P. E., Gerasimowicz, W. V., Eds.; CRC Press: Boca Raton, FL, 1989; pp 167–218.

Baianu, I. C. In *Physical Chemistry of Food Processes*; Van Nostrand Reinhold: New York, 1992; Vol. I, Chapters 5 and 6.

Baianu, I. C.; Förster, H. Cross-polarization, high-field carbon-13 nuclear magnetic resonance techniques for studying phys-

Hydration of Potato Starch

J. Agric. Food Chem., Vol. 41, No. 2, 1993 **167**

icochemical properties of wheat grain, flour, starch, gluten and wheat protein powders. *J. Appl. Biochem.* **1980**, *2*, 347–354.

Baianu, I. C.; Mora-Gutierrez, A. High field nuclear magnetic resonance studies of corn starch, chemically modified starch and maltodextrins. Presented at the Starch Science and Technology Conference, Orlando, FL, 1985.

Baianu, I. C.; Boden, N.; Lightowlers, D. NMR spin-echo responses of dipolar-coupled spin-1/2 triads in solids. *J. Magn. Reson.* **1981**, *43*, 101–111.

Baianu, I. C.; Gutowsky, H. S.; Oldfield, E. Origin and behavior of deuteron NMR spin echoes in selectively labeled amino acids, myoglobin microcrystals and purple membranes. *Biochemistry* **1984**, *23*, 3105–3111.

Baianu, I. C.; Orr, P. H.; Yakubu, P. I.; Lee, C. J. Unique properties of potato starch and potatoes for utilization in foods. Nuclear magnetic resonance and rheological characterization of functional properties of potato starch. Presented at the Potato Starch Utilization Conference, USDA-ARS Potato Research Laboratory, East Grand Forks, MN, Jan 26, 1990a.

Baianu, I. C.; Kumosinski, T. F.; Bechtel, P. J.; Myers-Betts, P. A.; Yakubu, P. I.; Mora-Gutierrez, A. Multinuclear spin relaxation and high-resolution nuclear magnetic resonance studies of food proteins, agriculturally important materials and related systems. In *NMR Applications in Biopolymers*; Finley, J. W., Ed.; Plenum Press: New York, 1990b.

Baianu, I. C.; Ozu, E.; Kumosinski, T. F.; Wei, T. C.; Lee, J. R. Molecular dynamics and local structure of simple monoatomic liquids, liquid/supercooled/glassy water and the liquid water-vapor interface. In *Interfacial Water in Dispersed Systems*; Drost-Hansen, W., Ed.; Springer-Verlag: Coral Gables, FL, 1992.

Boden, N.; Mortimer, M. Reorientation of D_2O in concentrated aqueous solutions of lithium chloride studies by nuclear magnetic relaxation. *J. Faraday Trans. Chem. Soc.* **1978**, *74* (2), 354–360.

Covington, A. K.; Paabo, M.; Robinson, R. A.; Bates, R. G. Use of a glass electrode in deuterium oxide and the relation between the standardized pD (pa$_D$) scale and the operational pH in heavy water. *Anal. Chem.* **1968**, *40*, 700–705.

Derbyshire, W. The dynamics of water in heterogeneous systems with emphasis on subzero temperatures. In *Water—A Comprehensive Treatise*; Franks, F., Ed.; Plenum Press: New York, 1982; Vol. 7, p 339.

Dwek, R. A. *Nuclear Magnetic Resonance in Biochemistry*; Oxford University Press (Clarendon): London, 1973; p 76.

Edzes, H. T.; Samulski, E. T. The measurement of cross-relaxation effects in the proton NMR spin-lattice relaxation of water in biological systems: Hydrated collagen and muscle. *J. Magn. Reson.* **1978**, *31*, 207–229.

Halle, B.; Lindman, B. Chloride ion binding to human plasma albumin from chloride-35 quadrupole relaxation. *Biochemistry* **1978**, *17*, 3774–3780.

Halle, B.; Anderson, T.; Forsen, S.; Lindman, B. Protein hydration from water oxygen-17 nuclear magnetic resonance relaxation. *J. Am. Chem. Soc.* **1981**, *103*, 500–508.

Kakalis, L. T.; Baianu, I. C. Oxygen-17 and deuterium nuclear magnetic relaxation studies of lysozyme hydration in solution: Field dispersion, concentration, pH/pD and protein activity dependencies. *Arch. Biochem. Biophys.* **1988**, *286*, 1–10.

Kintzinger, J. P. Oxygen-17 NMR. In *NMR of Newly Accessible Nuclei*; Laszlo, P. Ed.; Academic Press: New York, 1983; Vol. 2, Chapter 4, pp 79–104.

Kumosinski, T. F.; Pessen, H. A deuteron and proton magnetic resonance relaxation study of β-lactoglobulin A association. Some approaches to the Scatchard hydration of globular proteins. *Arch. Biochem. Biophys.* **1982**, *218*, 286–302.

Lanier, T. C. Functional properties of surimi. *Food Technol.* **1986**, *3*, 107–114.

Lechert, H. T. Water binding on starch: nuclear magnetic resonance studies on native and gelatinized starch. In *Water Activity: Influences on Food Quality*; Rockland, L. B., Stewart, G. F., Eds.; Academic Press: New York, 1981; pp 223–245.

Lechert, H. T.; Maiwald, W.; Kothe, R.; Basler, W. D. Nuclear magnetic resonance study of water in some starches and vegetables. *J. Food Process. Preserv.* **1980**, *3*, 275–279.

Lee, C. M. Surimi manufacturing and fabrication of surimi-based products. *J. Food Technol.* **1986**, *3*, 115–124.

Lèlievre, J.; Mitchell, J. A pulse NMR study of some aspects of starch gelatinization. *Starch* **1975**, *27* (4), 113–115.

Lioutas, T. S.; Baianu, I. C.; Steinberg, M. P. Oxygen-17 and deuterium nuclear magnetic resonance studies of lysozyme hydration. *Arch. Biochem. Biophys.* **1986**, *244*, 68–75.

Mantsch, H. H.; Saito, H.; Smith, I. C. P. Deuterium nuclear magnetic resonance applications in chemistry, physics and biology. *Int. Rev. J. Prog. NMR Spectrosc.* **1977**, *11* (4), 211–272.

Myers-Betts, P. A.; Baianu, I. C. Approaches to protein hydration and water activity in food proteins by nuclear magnetic relaxation and vapor pressure equilibration techniques. *J. Agric. Food Chem.* **1990a**, *38*, 1171–1177.

Myers-Betts, P. A.; Baianu, I. C. Determination of the protein activity of corn zeins in alkaline solutions from ^1H spin nuclear spin relaxation data as a function of concentration and heat treatments. *J. Agric. Food Chem.* **1990b**, *38*, 447–483.

Mora-Gutierrez, A.; Baianu, I. C. ^1H NMR and viscosity measurements on suspensions of carbohydrates and starch from corn. Relationship to oxygen-17 and carbon-13 NMR data. *J. Agric. Food Chem.* **1989**, *37*, 1459–1465.

Mora-Gutierrez, A.; Baianu, I. C. Carbon-13 nuclear magnetic resonance studies on chemically modified maize starch, corn syrups, and maltodextrins. Comparisons with potato starch and potato maltodextrins. *J. Agric. Food Sci.* **1991a**, *39*, 1057–1062.

Mora-Gutierrez, A.; Baianu, I. C. Hydration studies of maltodextrins by proton, deuterium and oxygen-17 nuclear magnetic resonance. *J. Food Sci.* **1991b**, *55* (2), 462–465.

Mot·ulsky, H. J.; Ransnas. Fitting curves to data using nonlinear regression: A practical and nonmathematical review. *FASEB J.* **1987**, *1*, 365–374.

Pessen, H.; Kumosinski, T. F. Measurement of protein hydration by various techniques. *Methods Enzymol.* **1985**, *117*, 219–255.

Reuther, F.; Damaschun, G.; Gernat, C.; Schierbaum, F.; Kettlitz, B.; Radosta, S.; Nothnagel, A. Molecular gelation mechanism of maltodextrins investigated by wide-angle X-ray scattering. *Colloid Polym. Sci.* **1984**, *262*, 643–647.

Schierbaum, F.; Taufel, K. The dependence of heat absorption of starches on their hydration. *Starch* **1962**, *14*, 233–236.

Smith, I. C. P. Deuterium NMR. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 1, pp 1–26.

Tait, M. J.; Sugget, A.; Franks, F.; Abblet, S.; Quickenden, P. A. Hydration of monosaccharides: A study of dielectric and nuclear magnetic relaxation. *J. Solution Chem.* **1972**, *1* (2), 131–151.

Yakubu, P. I.; Baianu, I. C.; Osman, E. Structural and hydration changes in potatoes induced by steaming. Proton and deuterium NMR investigations (Abstract). Presented at the National IFT Annual Meeting, Chicago, IL, June 25–29, 1989.

Yakubu, P. I.; Baianu, I. C.; Orr, P. H. Unique hydration behavior of potato starch as determined by deuterium nuclear magnetic resonance. *J. Food Sci.* **1990a**, *55* (2), 458–461.

Yakubu, P. I.; Baianu, I. C.; Orr, P. H. Deuterium nuclear magnetic resonance studies of potato starch hydration. In *Water Relations in Foods*; Levine, H., Slade, L., Eds.; Plenum Press: New York, 1990b, Vol. 1.

Yakubu, P. I.; Baianu, I. C.; Orr, P. H. First oxygen-17 NMR determination of potato starch hydration in relation to functionality in foods (Abstract). Presented at the National IFT Annual Meeting, Anaheim, CA, June 16–20, 1990c.

Zimmerman, J. R.; Brittin, W. E. Nuclear magnetic resonance studies in multiple phase systems: Lifetime of a water molecule in an adsorbing phase on silica gel. *J. Phys. Chem.* **1957**, *61*, 1328–1333.

Zobel, H. F. Starch crystal transformations and their industrial importance. *Starch* **1988a**, *40*, 1–7.

Zobel, H. F. Molecules to granules: A comprehensive starch review. *Starch* **1988b**, *40*, 44–50.