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Water Mobility in Multicomponent Model Media As Studied by ^{2}H and ^{17}O NMR

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Molecular mobility of water was studied in a microbiological media containing complex and heterogeneous mixtures of cellulose, l-sorbose, and orange serum broth (OSB) using ^{2}H and ^{17}O high-resolution NMR. All mixtures showed Lorentian ^{17}O NMR spectra but complex ^{2}H NMR line shapes. Sorbose, when solubilized, caused line-narrowing where as cellulose−OSB mixtures showed wide peaks with flat plateaus. Presence of liquid or solvent water had a profound effect on a marked increase in T_2 relaxation time observed in sorbose-containing samples. ^{17}O NMR data were not composition dependent, while ^{2}H NMR data were highly sorbose dependent.

KEYWORDS: Water mobility; NMR; microbiological media

INTRODUCTION

Water mobility of a system depends on the physicochemical properties of nonaqueous constituents and their interactions with water and among themselves. Presence of molecules of different molecular weight and solubility in water can have a profound influence on water mobility. For instance, solid moistened starch powder can become a liquid paste simply by an addition of sucrose crystals (*1*). Osmotic dehydration of starch from greater osmotic gradient between the sucrose crystals and starch leads to a redistribution or migration of water from the inside of starch granules to the outside. The extragranular water dissolves the sucrose crystals becoming an integral part of a solution where water increases significantly in flowability. As a result, the solid powder turns into a liquid state (*2*−*4*). Understanding of changes in location and mobility of water is particularly important considering that water molecular mobility profoundly influences the chemical, physical, and microbiological quality of foods. In food formulation, substitution of an ingredient with others may affect product quality and stability through a change in water mobility. Although the relationship between molecular mobility and food formulation and safety is of primary importance, we are still far from a fundamental understanding of the problem and further research in the area should be strongly encouraged.

Water molecular mobility can be analyzed by nuclear magnetic resonance (NMR) spectroscopy (*3*, *5*). Proton (^{1}H), deuterium (^{2}H), and oxygen-17 (^{17}O) NMR can be used to characterize water mobility in heterogeneous and complex systems.

The proton (^{1}H) nucleus is the most abundant NMR detectable species hence its signal acquisition is relatively easy. However, interpretation of proton relaxation data is complex since, in mixtures, protons are present in the molecular structure of most components and they can exchange. Additionally, a cross-relaxation between neighbor protons in the water and the solids can greatly influence (even dominate) the relaxation process (*6*−*8*). Interpretation of ^{1}H NMR is complicated as the contribution of the exchange and the cross relaxation processes are very complex.

Deuterium (^{2}H) is less abundant (0.02%) than proton causing a more difficult signal acquisition. Deuterium NMR relaxation is strongly affected by quadrupolar interactions (because of its quadrupolar moment with spin quantum number (I) of 1) and, since it does not involve dipole−dipole interaction, it is not affected by cross relaxation as in the case of ^{1}H NMR (*4*, *9*, *10*). ^{2}H NMR, however, does not escape the contribution from the chemical exchange either with other exchangeable deuterons or protons on the solids (*4*, *9*).

Oxygen-17 (^{17}O) NMR data are free from the effect of cross relaxation and ^{17}O does not likely exhibit a significant oxygen exchange (*3*, *4*, *11*−*13*). Therefore, ^{17}O NMR data are more easily interpreted, but the low ^{17}O abundance, (0.037%) accompanied with a strong quadrupolar moment, ($I = 5/2$) make ^{17}O signal acquisition quite difficult. The application of ^{17}O NMR to the study of water mobility is mainly limited to a high moisture environment where bulk water is present. For lower moisture (solid and semisolid systems) water mobility can be investigated using ^{1}H and ^{2}H NMR. Enrichment with $H_2{}^{17}O$

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Table 1. Samples' Composition[a]

cellulose, g	sorbose, g	OSB, g	S/[C + S], g
1.00	0.00	0.04	0
0.67	0.33	0.04	33
0.50	0.50	0.04	50
0.33	0.67	0.04	67
0.00	1.00	0.04	100

[a] Ratios by weight and sorbose/(cellulose + sorbose) ratio (% S/[C +S])

and/or D_2O_2 can further improve the signals allowing application in lower moisture with a wider range of substrates.

In an earlier report (*14*), a microbiological media containing cellulose, sorbose, and orange serum broth (OSB) has shown an increasing water sorption behavior with added sorbose. Solubilization of sorbose was suggested to play an important role in shifting the water distribution increasing its molecular mobility which could have played a key role in mold germination. Therefore, presence of large and small molecules in complex systems can influence water molecular dynamics and this may have an impact on biological functions of cells. The objective of this study was to further apply NMR to analyze these microbiological media containing variable amounts of cellulose, sorbose, and OSB. The NMR results are presented and evaluated with respect to the water mobility as influenced by media composition and moisture.

MATERIALS AND METHODS

Sample Preparation. Cellulose, l-sorbose (SIGMA Chemical Co., St. Louis, MO), and OSB (Difco Lab., Detroit, MI) were used. Their mixtures were prepared at various ratios as shown in **Table 1**. OSB was purchased in liquid form (4% solids) and when added as such to a mixture caused liquefaction of the system. Dry samples (40 g total) were mixed with OSB and, eventually, enough double distilled water to obtain a slurry (for homogeneity with liquid samples). All the samples were quench-cooled with liquid nitrogen and freeze-dried (15 °C, 15 atm vacuum; Unitop 100, Freeze Mobile 6, Virtis, Gardiner, NY) for 48 h. Freeze-dried samples (~2% moisture content) were then adjusted to 0−350% moisture content (dry basis) by equilibrating against saturated salt solutions over a 0.06−0.97 a_w at 25 °C (*15*). The water used to prepare the saturated salt solutions was enriched with either 50% deuterium (D_2O) or 1% oxygen-17 ($H_2{}^{17}O$) depending on the NMR experiment. Variation in a_w of the saturated salt solutions made with D_2O or $H_2{}^{17}O$ from the reference values reported by Greenspan, (*15*) were possible (*16*) but expected to be very small (within 1%). Equilibration time of most cases (<0.90 a_w) was approximately 5 days. For samples at $a_w > 0.90$ a known amount of water was added directly followed by a 3-day equilibration over appropriate saturated salt solutions to avoid mold growth. Samples were prepared in duplicate, and the equilibrated moisture content was within 5−8% error.

NMR Analysis. *Deuterium High-Resolution NMR.* ^{2}H NMR determination was carried out at 46.7 MHz, using a MSL 300 spectrometer (Bruker Instruments, Inc., Billerica, MA). A 0.2−0.3 g of sample were packed into 10 mm NMR tubes and compressed down to 8−10 mm in height.

WALTZ pulse sequence (*17*) was applied using a 90° pulse width of 7.45−7.80 μs. The data were acquired with a number of scans of 256, spectral width of 1500−20000 Hz, acquisition time of 166−12 ms. Recycle delay was set typically at 0.5−1 s, depending on sample moisture content and composition and it was, in all cases, $\geq 5T_1$. Samples were run unlocked and spun at 16 rps. The FID was exported to WIN NMR (Bruker Instruments, Inc., Billerica, MA) software where it was Fourier transformed, phase corrected and baseline corrected. Spectra were deconvoluted into their constituent peaks by Peakfit (Jandel Scientific, San Rafael, CA) analysis. All samples were run at least in duplicate and each experiment was repeated twice.

Spin−spin relaxation time (T_2) was determined with a Carr Purcell Meiboom Gill (CPMG) pulse sequence (*18*, *19*). The interpulse spacing covered a 5−500 μs range. At least eight different NMR determinations were used for each T_2 determination. Peak height was obtained as a function of time. The recycle delay was set to $\geq 5T_1$. Single (eq 1) and double (eq 2) exponential curve fittings were performed using a nonlinear curve fitting program (SYSTAT. Inc., Evanston, IL).

$$M_t = M_0 \exp(-\text{time}/T_2) \quad (1)$$

$$M_t = M_{0a} \exp(-\text{time}/T_{2a}) + M_{0b} \exp(-\text{time}/T_{2b}) \quad (2)$$

where, M_t = peak height; M_0, M_{1a}, and M_{1b}= equilibrium magnetization; time = τ (interpulse spacing) * n (number of echoes). The a and b subscripts refer to the two components of the relaxation process. T_2 analyses were done in at least duplicated samples and duplicated experiments.

Oxygen-17 High-Resolution NMR. ^{17}O NMR spectra were obtained at 40.6 MHz using a Bruker MSL-300 spectrometer (Bruker Instruments, Terrance, MA). A 90° pulse width (15 μs) and a spectral width of 100 kHz were used. Acquisition time of 0.02 s and 32 768 scans were used. The rolling baseline effect was reduced by using a 200 μs delay (dead time) between pulse and acquisition. Thus, the signal detected was assigned to highly mobile water (*20*).

Ten percent ^{17}O-enriched water (Cambridge Isotope, Inc.) was diluted with deionized distilled water to obtain a 1% ^{17}O-enriched water. This was then used for NMR calibration and sample preparation as described above. The NMR signals from variable amounts (100−1100 mg) of enriched water were measured in intensity which was used for calibrating signal intensities (*20*). A standard curve was constructed to avoid day to day variation of measurement affected by the expected variation in probe tuning. Sample size for a 10 mm NMR tube was ≈ 1 g, which was within the calibration curve for the instrument and the active region of the instrument receiver coil. All samples were measured in duplicate and the experiments were repeated for each sample type.

A Fourier transformed NMR spectrum yielded line widths, LW (measured as width in hertz at half peak height), which could be used to calculate the transverse relaxation time (T_2) provided a Lorentzian shape function [$T_2 = 1/(\pi \text{LW})$]. T_2 values obtained with this procedure could be affected by field inhomogeneity (*21*, *22*) and, therefore, the terminology T_2^* was used in the remaining of the paper. The total intensity of the ^{17}O NMR signal was determined by integration of the area (mobile water fraction) calculated as the amount of water detected (*20*, *23*).

RESULTS AND DISCUSSION

NMR Water Molecular Mobility. *Deuterium NMR. (a) Individual Components (Cellulose, Sorbose, and Orange Serum Broth).* Series of ^{2}H NMR spectra for freeze-dried cellulose, sorbose, and OSB at various moisture contents are shown in **Figure 1, panels A, B,** and **C**, respectively.

In cellulose, a single Lorentzian peak at moisture content ≥11.1% dry basis was observed (**Figure 1A**) indicating a fast exchange regime. At 8.9% moisture content dry basis, a duplex spectrum was observed suggesting slow exchanging deuterium spin populations. The splitted peak observed at 8.9% moisture content (dry basis) has been earlier reported to be a macroscopic manifestation of the existence of two deuterium spin populations, i.e., possibly physically separated in space or in orientation on the cellulose fiber (*24*). The splitting of the peak disappeared at higher moisture content possibly due to a more rapid exchange regime resulting in a motion-averaged spectrum. At moisture content ≤8.3% (dry basis) one broad peak was observed (**Figure 1A**), and it was, possibly, composed of two overlapping broad peaks. Detailed discussion of the origins and moisture content dependence of the splitting phenomenon were previously reported (*24*).

In sorbose, the main spectrum experienced a line narrowing effect at higher moisture (≥20.7%, **Figure 1B**). An emergence of a second peak was observed at moisture content where

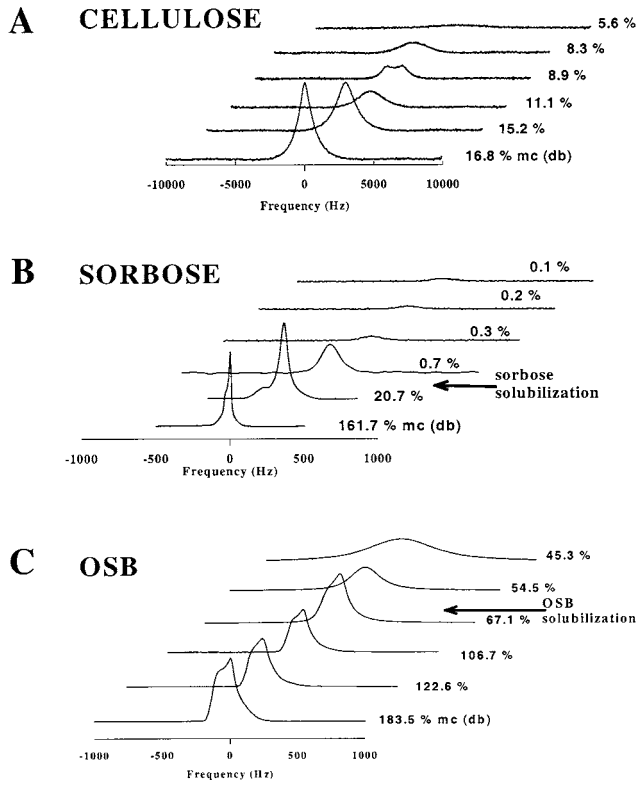

Figure 1. Series of ^{2}H high-resolution NMR spectra for freeze-dried cellulose (A), sorbose (B), and OSB (C) at variable moisture contents. Arbitrary Y scale was used.

sorbose became solubilized ($a_w \geq 0.91$; *14*), suggesting a contribution of sorbose deuterons.

The OSB spectra (**Figure 1C**) showed multiple peaks at moisture contents ≥67.1% (dry basis) but a single peak for moisture contents ≤54.5% (dry basis). Similarly to the case of sorbose, the transition from a single to multiple peaks occurred at moisture contents where OSB became liquid ($a_w \geq 0.84$, earlier reported, *14*) suggesting some contributions from dissolved OSB deuterons.

To verify that the additional peaks observed in the higher moisture contents of sorbose and OSB samples were contributed by deuterons on dissolved solids, sorbose and OSB were each mixed with deuterium enriched water (50% D_2O) to obtain 40, 60, 100% moisture dry basis (sorbose) and 330% moisture dry basis (OSB). These samples were then quench cooled with liquid nitrogen, freeze-dried and hydrated with H_2O to the same initial moisture content (i.e., 40, 60, 100, and 330% for sorbose and OSB, respectively). Samples were analyzed for ^{2}H NMR before and after freeze-drying. Upon freeze-drying, almost all the D_2O was removed and any remaining deuteron should be located on the solids only as result of deuterium exchange. Once the freeze-dried sample was rehydrated with H_2O, detection of deuterium in the sample would originate from deuterons on the solids. Indeed, the deuterium peaks were detected in both samples (before and after freeze-drying), supporting the deuterium exchange hypothesis.

The minimum moisture contents for detection of a ^{2}H NMR signal varied from system to system; ∼5%, (dry basis) for cellulose, ∼0.1%, (dry basis) for sorbose and ∼40%, (dry basis) for OSB. The high moisture limit for observed ^{2}H NMR mobility was possibly because of strong intermolecular interactions and other physical factors leading to higher local viscosity.

(b) Effect of Sorbose on Water Mobility in Mixtures. Spectra of the cellulose and OSB mixtures containing no sorbose (0% S/[C + S], **Figure 2A**) had a peculiar shape characterized by a wide peak and flat plateau over 7.4−18.9% moisture contents dry basis. The flat-top line broadening observed was a consequence of the addition of OSB to the cellulose. This reflects complex contributions from multiple water populations varying in exchange rates within the NMR time frame, chemical shift anisotropy, and contributions from non aqueous components.

In the case of 100% sorbose (no cellulose, 100% S/[C + S]; **Figure 2D**) multiple peaks were observed at moisture contents ≥ 47.7% (dry basis) while at lower moisture contents, single Lorentzian spectra were observed. Since at 47.7% moisture contents both sorbose and OSB dissolved in water (based on water sorption isotherm; 14), the additional ^{2}H peaks at moisture above this level were attributed at least in part to the deuterons of the dissolved solutes.

In mixtures containing cellulose, OSB and sorbose, e.g., at 33% S/[C + S] (**Figure 2B**), a Lorentzian line shape was observed in the entire range of moisture contents studied. Significant line narrowing was observed above the sorbose solubilization point (25% moisture content, dry basis, **Figure 2B**), suggesting that sorbose solubilization resulted in increased mobility averaging with no evidence of multiple peaks. In spectra of lower moisture below sorbose solubilization point (e.g., 6.8 and 7.1% water) multiple peaks were observed (**Figure 2B,C**). At some intermediate moisture (e.g., 6−8% moisture content for 33% sorbose, **Figure 2B**), the spectra could be deconvoluted into at least two Lorentzian peaks ($R^2 \geq 0.97$) as earlier reported for ^{17}O NMR data (*3*). The narrow peak could be attributed to liquid water in a sugar solution and the broader peak to that associating with the polymers (*3*).

The NMR line shapes observed revealed a great degree of complex nature of the samples. Broader, overlapping peaks observed in semisolid or solid states were transformed into line-narrowed spectra once the moisture content was raised to dissolve sorbose.

Oxygen-17 NMR. ^{17}O NMR data showed typical single Lorentzian spectra for all samples (**Figure 3A**). The peak was observed at moisture above 20% (dry basis) and its intensity linearly increased proportionally with water content. Calculated ^{17}O NMR intensity agreed with the quantity of water in the sample (according to method by Stengle and Chinachoti; *20*). There was no contribution from nonaqueous oxygen (i.e., nondetectable ^{17}O nuclei exchange; *3*, *12*, *13*, *25*).

Deuterium and Oxygen-17 NMR Mobility. Transverse relaxation time (T_2) was obtained in case of ^{2}H NMR using a Carr Purcell Meiboom and Gill (CPMG) method (*18*, *19*), and in case of ^{17}O NMR using line width at half-height (T_2^*; *3*, *20*). For the case of ^{2}H NMR, the FID showed a single-exponential function (a typical ^{2}H T_2 decay is shown in **Figure 3B**) with calculated T_2 shown in **Figure 4B**.

NMR T_2^* and T_2 relaxation times of both nuclei (as shown in **Figure 4A,B**) increased with increasing moisture in some cases reaching some plateau levels corresponding to values for pure water. ^{2}H T_2 and ^{17}O T_2^* relaxation times were in a few milliseconds and tens of milliseconds range, respectively. This fell within a range of T_2's generally observed in food systems (*5*). Due to the different detectability limits of the two nuclei, ^{17}O NMR transverse relaxation analysis was done on samples with moisture contents higher than those for ^{2}H NMR. T_2 relaxation times measured by ^{17}O NMR were ∼10 times shorter than those by ^{2}H NMR (**Figure 4A,B**) because of its stronger quadrupolar moment that caused a faster dissipation of the energy (through spin−spin interactions) absorbed during the 90 degree pulse.

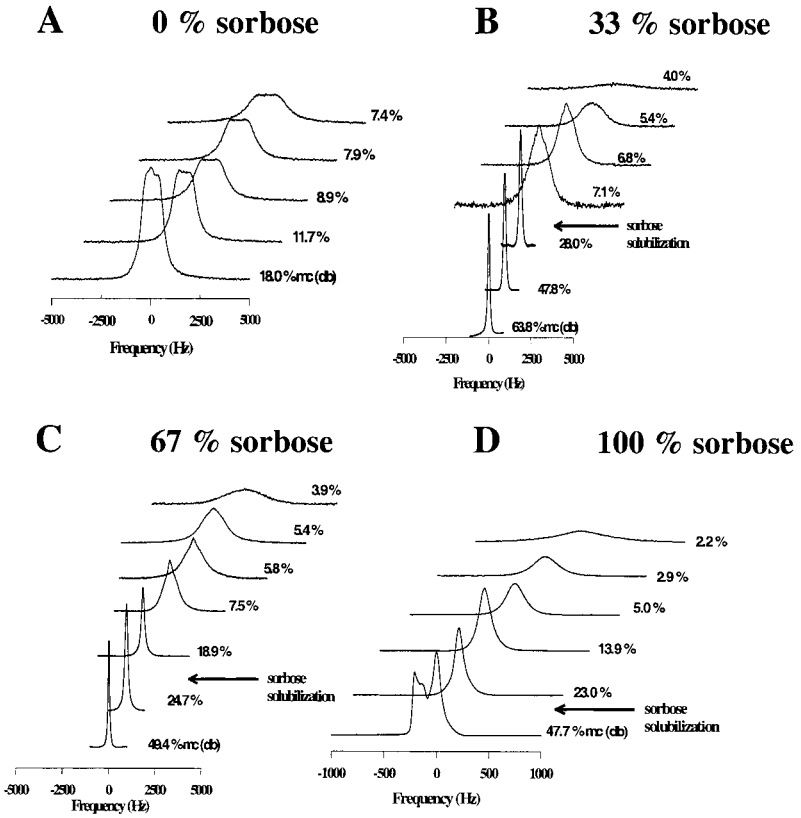

Figure 2. ^{2}H high-resolution NMR spectra at varying moisture contents of freeze-dried cellulose, L-sorbose, and OSB mixtures. Arbitrary *Y* scale was used.

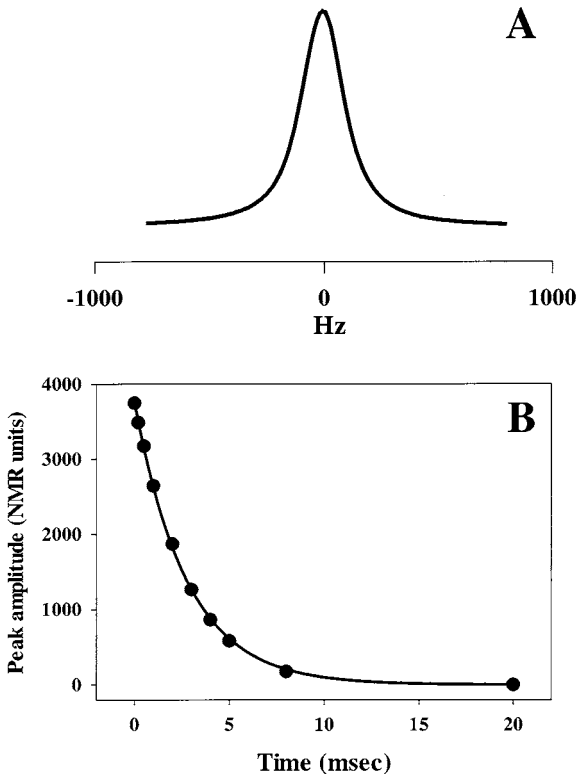

Figure 3. (A) Typical ^{17}O NMR spectrum; (B) Typical ^{2}H NMR T_2 calculation. Original data (circles) and monoexponential fit (line).

^{2}H NMR T_2 at a given moisture was dependent on sorbose level (> 95% confidence) while ^{17}O NMR T_2^* was not. The contrast in sorbose dependence of ^{17}O T_2^* and ^{2}H NMR T_2 can be explained by a contribution of deuterium exchange between

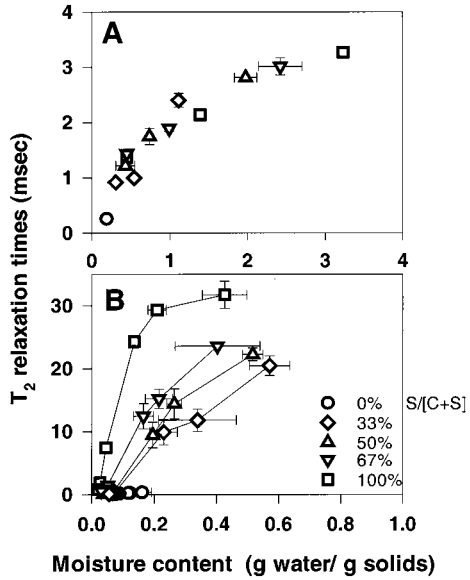

Figure 4. Transverse relaxation times obtained from ^{17}O (A) and ^{2}H (B) NMR as functions of moisture and sorbose contents of mixtures containing cellulose, L-sorbose, and OSB. % S/[C + S] is percent sorbose on a cellulose + sorbose basis.

D_2O and the solids (cellulose and/or sorbose) that did not take place with ^{17}O nuclei. The measured ^{2}H T_2's are thus averaged T_2 among those of observable deuterons (on the solids and on D_2O) in the sample. In a low moisture (solid) regime, the relaxation was dominated by cellulose and solid sorbose and in a high moisture (liquid) regime, it was dominated by dissolved sorbose resulting in line narrowing. Since ^{17}O T_2^* relaxation times were calculated from peak LW, they might be influenced by static magnetic field inhomogeneity, chemical shift anisotropy

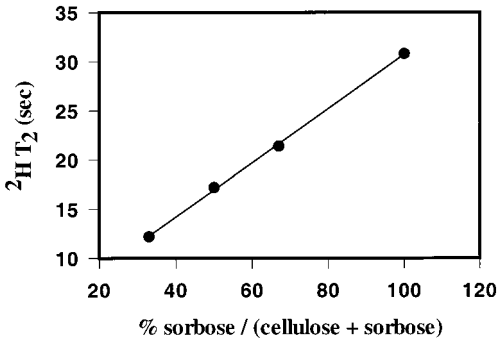

Figure 5. ^{2}H NMR T_2 as a function of sorbose content (% S/[C + S]) at 35% moisture content (dry basis).

(leading to apparent line-broadening) and quadrupolar interactions (causing some signal loss). Therefore, the application of ^{17}O NMR to investigate water mobility is limited to a higher moisture regime (>0.5% dry basis in this case).

To demonstrate the significance of dissolved sorbose contribution to ^{2}H NMR T_2, a plot between T_2 and sorbose content at a given moisture content was analyzed (**Figure 5**). At this moisture content, the increase of dissolved sorbose largely increased the system mobility as observed by the increase in T_2. The mobility increase resulted from the sorbose phase transition dissolving and associating with the water molecules. When dissolved, sorbose and water become an entity inseparable in mobility in the ^{2}H NMR relaxation time frame. As a result, T_2 measured for all peaks observed in spectra shown in **Figure 2** (which are contributed by water and nonaqueous solids) were almost identical.

For the case of ^{17}O NMR T_2^* (**Figure 4A**), T_2 was entirely dependent on moisture content irrespectively of sorbose content. Since ^{17}O NMR relaxation measures only the contribution of water, the information obtained is useful in more definitive characterization of water mobility free of contribution from nonaqueous component. However, ^{17}O NMR is limited to liquid systems.

To demonstrate the range of applications, R_2 relaxation rates were calculated and plotted against solid concentrations as shown in **Figure 6**. At a low solid concentration (0−100 g of solids/mol of water or a_w > 0.91), R_2^* of both ^{17}O and R_2 of ^{2}H slightly increased with an initial increase in solid concentration. The system in this lower solid concentration range was in a fast exchange regime and water molecules could move freely. At higher solid concentrations (>100 g of solids/mol of water), ^{2}H R_2 more drastically increased deviating from linearity. As earlier described (*2*, *12*, *26*) this indicated an additional contribution to the relaxation (i.e., some interaction between water and the solids) which became more significant at higher solid contents. Deviation form linearity was only observed in ^{2}H NMR because ^{17}O NMR only limited to low solid contents. At g of solid/mol of water > 100, ^{2}H R_2 was inversionally proportional to the amount of sorbose present in the sample. A lowered amount of sorbose implied the presence of a larger amount of cellulose and led to a decreased average mobility and limited diffusive phenomena. In other words, at a given moisture or solid concentration, a higher amount of sorbose resulted in a more liquid state (*14*) and less dramatic increase in R_2 as water present was more mobile and not in a diffusion-limited condition.

This work demonstrates the use of two powerful techniques to characterize water mobility in complex systems containing water soluble solutes. Line shape analysis of ^{2}H and ^{17}O NMR spectra provide qualitative description of the complex relaxation

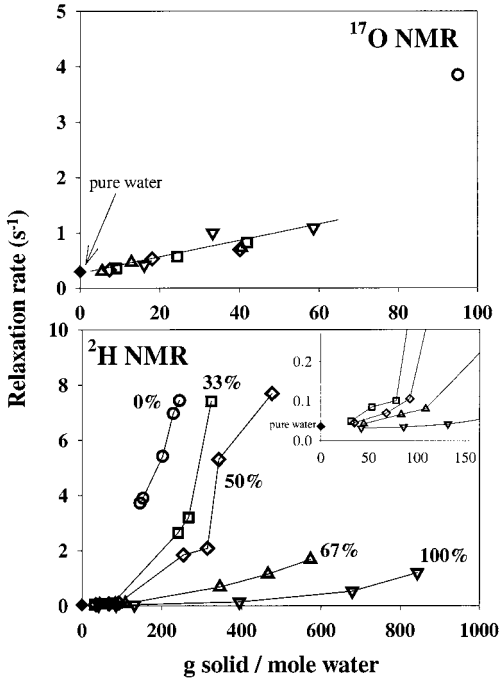

Figure 6. ^{17}O (A) and ^{2}H (B) transverse relaxation rates (R_2) as functions of moisture content for binary and tertiary mixtures of cellulose, sorbose, and OSB.

and exchange behavior whereas relaxometry provides quantitative mobility parameters. For ^{17}O NMR, approximation of water mobility can be obtained with no or little contributions from the solids but it is limited to a more liquid system. For ^{2}H NMR, the observed mobility is contributed from both aqueous and nonaqueous water soluble components. It also provides a means to investigate mobility changes in semisolid and solid systems that is not possible in ^{17}O NMR.

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