Non-enzymatic browning kinetics analysed through water–solids interactions and water mobility in dehydrated potato

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Abstract

Non-enzymatic browning (NEB) development was studied in dehydrated potato at 70 °C. It was related to the macroscopic and molecular properties and to water–solid interactions over a wide range of water activities. Time resolved ^{1}H NMR, thermal transitions and water sorption isotherms were evaluated. Although non-enzymatic browning could be detected in the glassy state; colour development was higher in the supercooled state. The reaction rate increased up to a water content of 26 g/100 g of solids ($a_w = 0.84$) and then decreased at higher water contents, concomitantly with the increase of water proton mobility. The joint analyses of NEB kinetics, water sorption isotherm and proton relaxation behaviour made it evident that the point at which the reaction rate decreased, after a maximum value, could be related to the appearance of highly mobile water. The results obtained in this work indicate that the prediction of chemical reaction kinetics can be performed through the integrated analysis of water sorption, water and solids mobility and the physical state of the matrix.
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Keywords: Molecular mobility; Non-enzymatic browning; Glass transition; Water sorption properties

1. Introduction

Non-enzymatic browning (NEB) is one of the most important chemical phenomena, which may affect food quality during processing and storage. It may contribute to food palatability by improving flavour and colour. However, in dehydrated foods, browning results in deterioration, mainly by producing off-flavours and off-colours, and it may cause a loss of nutritional value (Labuza & Baiser, 1992). Therefore, the control of the mechanisms that determine this reaction rate has been given much attention. Several studies have investigated various stages of the non-enzymatic browning reaction and shown that the rate of the reaction is strongly dependent on concentra-

tion, ratio and chemical nature of reactants, temperature, time of heating, water content, and pH (Buera, Chirife, Resnik, & Wetzler, 1987). Subsequent studies have evaluated the impact of water activity (a_w) and the glass transition on chemical reactivity (Bell, 1995). Diffusion-controlled chemical and enzymatic reactions are particularly dependent on translational diffusivity of the reactants (or on the viscosity of the matrix material), and are thus susceptible to the physical state of the system (Slade & Levine, 1995). Some studies revealed that the rate of browning of several vegetables and food models is very slow in the glassy state, but at temperatures above the glass transition, in addition to the decreasing viscosity and increasing rate, other changes such as crystallisation and collapse affect the browning rate (Karmas, Buera, & Karel, 1992). In some food systems at high temperatures, it is the temperature *per se* rather than the physical state, which determines the possibility of a significant extent of browning (Schebor, Buera, Karel, & Chirife, 1999).

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Rather than water affecting chemical reactions via a_w or by plasticising amorphous systems, and considering the inhibitory effect of water as a reaction product of Maillard condensations, water mobility itself may have a direct impact on chemical reactivity in low and intermediate moisture systems. NMR is a powerful spectroscopic technique that allows water and food solids mobility to be studied independently (Gil, Belton, & Hills, 1996). Therefore, NMR spectroscopy has been used as a complementary technique to differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA), with the aim of obtaining a better understanding of the mobility of the water and food solids in food systems (Kalichevsky, Jaroszkiewicz, Ablett, Blanshard, & Lillford, 1992; Kou, Dickinson, & Chinachoti, 2000). It is possible to use ^1H NMR to probe the water dynamics in low-moisture samples. The slowing of water motion in low-moisture samples reflects strong water–solid interactions through hydrogen bonding (Chen, Long, Ruan, & Labuza, 1997), which corresponds to the water molecules that are strongly influenced by their proximity to the solids components. The difficulty in interpretation of ^1H NMR data of low-moisture samples is usually associated with structural complexity of samples with corresponding heterogeneous proton environments.

There have been a number of NMR studies on proton relaxations in potato starch, however the relationship between NEB kinetics and solids mobility in dried potato products is still limited.

The objective of the present work was to analyse the influence of water–solids interactions and water mobility on the kinetics of NEB in freeze-dried potato.

2. Materials and methods

2.1. Potato system

Fresh white potatoes (Spunta variety) were obtained from the local market and stored at 4 °C until the moment of the experiment. Peeled potatoes were washed and cut into discs (23 mm diameter and 0.5 mm thickness). The cut material was washed, in order to remove cellular debris on surfaces and immediately frozen at −20 °C.

2.2. Freeze-drying

Potato discs were covered with liquid nitrogen before freeze-drying for 48 h. After freeze-drying, several pieces were powdered in a mortar in a dry chamber and distributed into vials for the determination of water content, thermal transitions and molecular mobility. The remaining samples where used to determine NEB.

Dehydrated potato powder and discs were equilibrated over saturated salt solutions (in a range of 11–93% RH) in vacuum desiccators for 13 days at 23 °C, to obtain the desired water contents (Greenspan, 1977). With the purpose of studying the sorption isotherm at very high water activities (0.93–0.98), some mixtures were prepared by the addition of distilled water to the potato powder. In order to ensure a uniform water distribution these samples were equilibrated overnight. The water activities of the mixtures were measured using an electronic dew-point water activity meter, Aqualab Series 3 (Decagon Devices, Pullman, WA). The equipment was calibrated with saturated salt solutions over the a_w range of interest (Favetto, Resnik, Chirife, & Ferro Fontán, 1983).

2.3. Water content

The water content was determined (in duplicate samples) gravimetrically, by difference in weight before and after vacuum drying over magnesium perchlorate at 96 °C for 48 h.

2.4. Heat treatment

After equilibration, potato discs were placed inside rubber o-rings which in turn were sandwiched between two glass plates held hermetically with metal clamps to avoid water loss, as previously described (Acevedo, Briones, Buera, & Aguilera, 2008). The glass sample holder was then placed in an air-convection oven operated at 70 ± 1 °C. At suitable intervals, samples were removed from the oven; colour was measured and the samples were placed back in the oven to continue with the heat treatment.

2.5. Thermal transitions

Glass transitions were determined by differential scanning calorimetry (DSC; onset values) using a DSC 822^e Mettler Toledo calorimeter (Schwerzenbach, Switzerland). The instrument was calibrated with indium (156.6 °C), lead (327.5 °C) and zinc (419.6 °C). All measurements were performed at a heating rate of 10 °C/min. Hermetically sealed 40 μl medium pressure pans were used, (an empty pan served as a reference). Thermograms were evaluated using Mettler Star^e program. An average value of at least two replicates was reported.

2.6. Molecular mobility

A Bruker PC 120 Minispec pulsed nuclear magnetic resonance (NMR) instrument, with a 0.47 T magnetic field operating at resonance frequency of 20 MHz, was used for measurements (Bruker Biospin GmbH, Rheinstetten, Germany). Equilibrated powdered samples were removed from the desiccators, placed into 10 mm diameter glass tubes and returned to the desiccators for an additional 24 h prior to analysis.

The spin–spin relaxation time (t_2) associated with the fast relaxing protons (related to the solid matrix and to water interacting tightly with solids) was measured using a free induction decay analysis (FID) after a single 90°

pulse. The decay envelopes were fitted to mono-exponential behaviour with the following equation:

$$I = A \exp(-t/t_{2\text{-FID}}) \quad (1)$$

where I represents protons' signal intensity, $t_{2\text{-FID}}$ corresponds to the relaxation time of protons in the polymeric chains of the sample and of tightly bound water, and A is a constant. Since no 180° refocus pulse was used in the experiments, the spin–spin relaxation time constants are apparent relaxation time constants, i.e. $t_{2\text{-FID}*}$. However for solid samples (like ours), we can consider that the intrinsic $t_{2\text{-FID}}$ is very close to the $t_{2\text{-FID}*}$, as reported previously by Fullerton and Cameron (1988). Therefore, $t_{2\text{-FID}}$ was used for convenience.

The t_2 associated with the slow relaxing protons (related to the populations of water molecules displaying less interaction with solids) was measured using the Hahn spin echo pulse sequence (90°-τ-180°) with an interpulse (τ) range of 0.001–2 ms. This method limits the effect of field inhomogeneity and allows the measuring of relatively slowly relaxing water protons. This range allowed the registering of the complete decay of the signal. The decay envelopes were fitted to bi-exponential behaviour, with the following equation:

$$I = A_1 \exp(-t/t_{2\text{-Hahn-1}}) + A_2 \exp(-t/t_{2\text{-Hahn-2}}) \quad (2)$$

where I represents the NMR signal intensity at time t. The relaxation time $t_{2\text{-Hahn-1}}$ corresponds to the protons in the less mobile water fraction. A_1 is proportional to the number of protons in the $t_{2\text{-Hahn-1}}$ state. The relaxation time $t_{2\text{-Hahn-2}}$ corresponds to the more mobile water fraction. A_2 is proportional to the number of protons in the $t_{2\text{-Hahn-2}}$ state.

All determinations were performed in duplicate.

2.7. Degree of Maillard reaction

The degree of Maillard reaction was determined by reflectance measurements of the colour attribute luminosity (L^*) with a white background of reflectance. A handheld tristimulus reflectance spectrocolorimeter with an integrating sphere (Minolta CM-508-d, Minolta Corp., Ramsey, NJ) was employed. Colour functions were calculated for illuminant D65 at 2° standard observer and in the CIELab uniform colour space. The colour function ΔL^* ($L_0^* - L^*$) was found to be an adequate parameter, to evaluate the non-enzymatic browning reactions in opaque samples (Buera & Resnik, 1989), being L_0^* and L^* the sample colour attribute before and after heat treatment, respectively. The colour function L^* was calculated as follows:

$$L^* = 116(Y/Y_n)^{1/3} - 16 \quad (3)$$

Where Y is the Y tristimulus value of the sample and Y_n the Y value for illuminant D65.

Six replicates were analysed for each storage time, and an average value was reported.

3. Results

Fig. 1 shows the non-enzymatic browning (NEB) rate (calculated as zero-order kinetic coefficient) for potato discs along the water content scale at 70 °C. The NEB rate shows a maximum value at a water content of 26 g/100 g of solids ($a_w = 0.84$), above which the rate markedly decreased. In potato powder samples the maximum rate of browning at 70 °C occurred close to a water content of 15 g/100 g of solids ($a_w = 0.75$) (Acevedo, Schebor, & Buera, 2006); this difference might be accounted for by the sample structure, which has a specific impact on the reaction kinetics, as was recently reported by Acevedo et al. (2006).

The browning rate, as a function of (T–T_g), the difference between the storage temperature and the glass transition temperature (T_g) for potato discs stored at 70 °C during 48 h is shown in Fig. 2. Non-enzymatic browning could be detected in the glassy state at $a_w = 0.11$ and 0.22, but the browning rates were higher in the supercooled state, reaching a maximum value (at $a_w = 0.84$), well above the glass transition temperature (T–$T_g = 40$ °C).

Fig. 3a shows the a_w values at 23 °C versus water content and the glass transition temperature values (T_g),
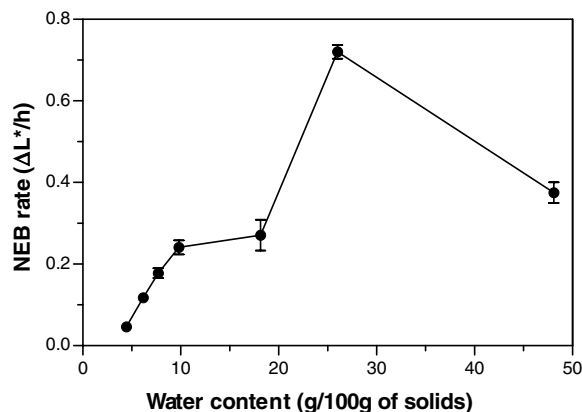
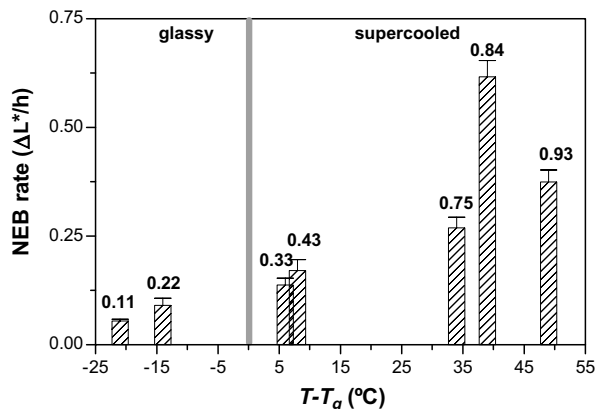Fig. 1. NEB rate at 70 °C in potato discs at different water content values.

Fig. 2. NEB rate versus (T–T_g) for potato discs at different a_w values.
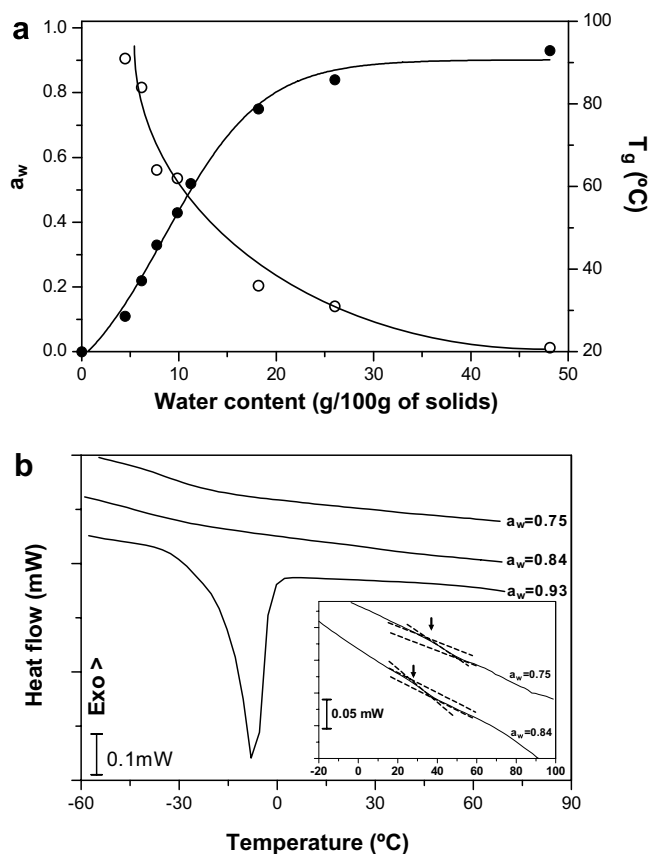
Fig. 3. Water activity (a_w) values at 23 °C (filled symbols) and glass transition temperatures (open symbols) for freeze-dried potato powders versus water content (a). Thermograms obtained by DSC for freeze-dried potato powders. The endothermic peak corresponds to the melting of water (frozen water). The inset shows the glass transitions (b).

obtained by DSC as a function of water content. The water sorption data were fitted with the GAB model (Van den Berg & Bruin, 1981) giving a "monolayer" water content (m_0) of 6 g/100 g of solids which corresponds to an a_w value close to 0.21. The m_0 value is in agreement with previously reported values for potato slices at similar temperature (Kaymak-Ertekin & Gedik, 2004; McLaughlin & Magee, 1998; McMinn & Magee, 2003; Wang & Brennan, 1991). Fig. 3a also shows the typical drop in T_g as the water content increased. The glass transition temperature values were higher than those previously reported (Acevedo et al., 2006; Karmas et al., 1992). The different variety and origin of the vegetable may have an influence on the physical properties and susceptibility to water plasticisation. When samples were frozen to −100 °C and then heated for the DSC scans, frozen water was detected in the thermograms as an endothermal event at $a_w = 0.93$, but not below this a_w value (Fig. 3b).

According to Timmermman and Chirife (1991), three different stages can be identified in the water sorption isotherm: the first stage corresponds to water contents up to the so called "monolayer" value; a second stage in which the state of water is different from that of the first stage

and of bulk water; and a third stage corresponding to high water activities, in which the systems show a water sorption larger than that predicted by the GAB model. The third stage can be identified by means of a linearised form of the GAB equation, which shows a linear trend up to certain a_w value, after which the points deviate downwards, showing the onset of the third stage. The GAB equation can be linearised in the following way:

$$\frac{a_w}{m(1 - ka_w)} = \frac{1}{Ckm_0} + \left[\frac{(C-1)}{Cm_0}\right]a_w \qquad (4)$$

were m is the water content in g/g of solids at a given a_w, C is the characteristic energy constant of the BET equation, and k is the characteristic constant of the GAB equation.

The linearised GAB equation has been applied to the experimental points of the potato powder sorption isotherm, in which points corresponding to the samples prepared in the high a_w region were included for a better observation (Fig. 4). A transition can be observed between the linear behaviour and the deviated points, located at $a_w = 0.84$, indicating a change in the physical state of adsorbed water above $a_w = 0.84$. The water molecules at this stage would be more liquid-like than in the preceding layers, coinciding with the appearance of frozen water, as detected by DSC (Fig. 3b), which can be related to a decrease in browning rate (Fig. 1). Adamson (1963) associated the steep increase of water adsorption occurring at high a_w, to capillary condensation.

The effect of water on chemical reactions, via a_w or by plasticising amorphous systems, has been discussed before (Bell, 1995). Since the inhibitory effect of water seems to be a decisive factor in the drop of the reaction rate from a given point, it can be hypothesised that water mobility may have a direct impact on NEB reaction kinetics, determining the position of the maximum rate in the a_w scale. Proton spin–spin or transverse relaxation times (t_2) were analysed by H^1 NMR, with the purpose of elucidating the relationship between browning rate, water–solids interaction and water mobility. Fig. 5 shows the t_2 relaxation times determined by FID after a single 90° pulse, as a function of temperature. This fast decaying component,
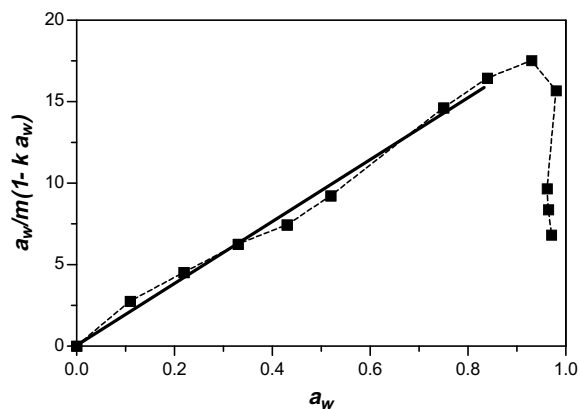

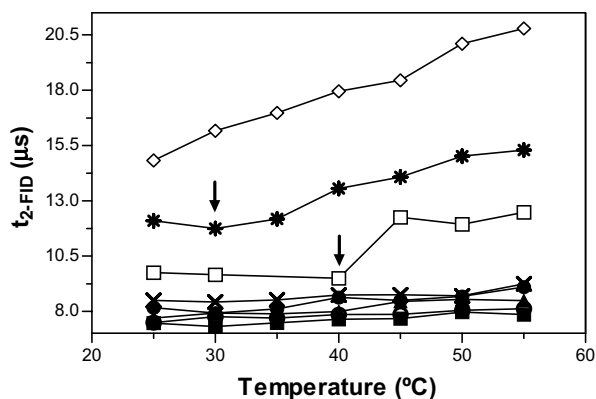Fig. 4. Linear GAB plot for potato powder at 23 °C.

Fig. 5. Spin–spin relaxation time ($t_{2\text{-FID}}$) obtained from a single 90° pulse by ^{1}H NMR for potato powder, as a function of temperature. Samples were equilibrated at different a_w: 0.11 (■), 0.22 (○), 0.33 (▲), 0.43 (●); 0.52 (×); 0.75 (□); 0.84 (✳) and 0.93 (◇).

($t_{2\text{-FID}}$) was attributed to protons from solid polysaccharides and from water molecules that are strongly interacting with the solid matrix by hydrogen bonding (Kalichevsky et al., 1992; Ruan et al., 1999, Rugraff, Desbois, & Le Botlan, 1996). Tang, Godward, and Hills (2000), analysed potato starch samples using a single 90° pulse and suggested that $t_{2\text{-FID}}$ was primarily dependent on motions in amylose and amylopectin molecules. Between 0.11 and 0.52 water activities, $t_{2\text{-FID}}$ values slightly increased, as a_w and temperature increased. The potato powders equilibrated at $a_w = 0.75$, 0.84 and 0.93 presented much higher $t_{2\text{-FID}}$ values than those obtained at lower a_w. Also, above $a_w = 0.52$ a marked effect of temperature on $t_{2\text{-FID}}$ increase could be observed (Fig. 5). The increase of $t_{2\text{-FID}}$ with a_w can be attributed to the plasticising effect of water, which provides greater mobility to the solid's protons. Chatakanonda, Dickinson, and Chinachoti (2003); and Choi and Kerr (2003) studied the molecular mobility in potato and wheat starch, respectively by NMR and also found that t_2 increased as the water activity increased (a_w range from 0 to 0.97).

The break observed in the $t_{2\text{-FID}}$ versus temperature curves at a_w 0.75 and 0.84 (Fig. 5) could be related to the glass transition phenomenon. It has been previously reported that glass transition temperatures obtained by NMR can be some degrees lower than those measured by DSC. (Kalichevsky & Blanshard, 1992; Kalichevsky et al., 1992; Kou et al., 2000; Ruan et al., 1999). NMR analyses short range mobility (molecular motions of individual components), whereas DSC measurements report on the overall mobility of the system (polymer motions at a macroscopic level). An increase in $t_{2\text{-FID}}$ with temperature at $T > T_g$ has been previously reported for maltodextrin (Ruan et al., 1999), amylopectins and amylopectin-sugar mixtures (Kalichevisky, Blanshard, & Tokarczuk, 1993, Kalichevsky et al., 1992) and corn starch (Kou et al., 2000). A change in $t_{2\text{-FID}}$ with temperature can be associated with the thermal motion of molecules

(Ruan et al., 1999). Above the glass transition temperature, however, the motion is intensified due to the increased molecular mobility of the matrix. Therefore, after passing the glass transition temperature, the mobility of protons connected with the polymeric molecules increases sharply with the temperature, as can be observed by a steeper slope on the $t_{2\text{-FID}}$ versus temperature curves at a_w values of 0.75, 0.84 and 0.93 (Fig. 5).

The analysis of the Hahn spin-echo data of the protons associated with water and solids present in the potato powder samples at different a_w showed two t_2 components. A short component $t_{2\text{-Hahn-1}}$ in the order of 30–40 μs was present at all the analysed a_w. This faster decaying component corresponds to protons of solid polysaccharides and of water strongly interacting with solids, as the $t_{2\text{-FID}}$ measured by a single 90° pulse, (note that the relaxation times are different from those obtained by FID after a single pulse, due to the different technique employed). Above $a_w = 0.22$ a long $t_{2\text{-Hahn-2}}$ component in the range of 400–950 μs was also observed, whose value increased with the increase in water content (Fig. 6). The intensities of the signals corresponding to the different proton populations offer a relative estimation of the amount of water protons that contribute to a certain t_2. Fig. 6 also shows the intensity of the signal (A_2) corresponding to the $t_{2\text{-Hahn-2}}$ component, along with the corresponding relaxation time values. $t_{2\text{-Hahn-2}}$ and A_2 increased with increasing water content. A_2 increase could be related to the increase in the amount of water protons that contribute to the slowly relaxing component. Above a water content of 26 g/100 g of solids ($a_w = 0.84$) $t_{2\text{-Hahn-2}}$ and A_2 values tended to reach a plateau, which coincides with the presence of more mobile water (frozen water, as detected by DSC) (Fig. 3b). Also, the onset of the third water sorption stage corresponds to the appearance of a plateau in the $t_{2\text{-Hahn-2}}$ values in the water content scale.

It is interesting to note that at low water contents up to the GAB "monolayer" value (6.0 g/100 g of solids,
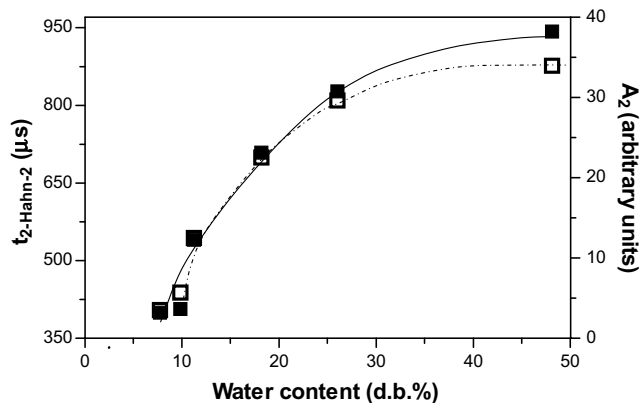

Fig. 6. Spin–spin relaxation time ($t_{2\text{-Hahn-2}}$) and intensity of the signal (A_2) obtained by spin echo Hahn sequence for potato powder as a function of water content. The filled squares correspond to the relaxation times ($t_{2\text{-Hahn-2}}$) and the open squares to the amplitude (A_2) values.

$a_w = 0.21$), only one relaxation time was detected $t_{2\text{-Hahn-1}}$ at 30–40 μs, which corresponds to protons of the solid components and of water molecules tightly interacting with them. Upon addition of water layers beyond m_0, another relaxation time could be detected, $t_{2\text{-Hahn-2}}$, at a_w values higher than 0.21. Bulk water could only be detected at and above $a_w = 0.93$ by the presence of frozen water, as analysed by DSC (Fig. 3b).

4. Discussion

The results of this work allow the establishment of a relationship between the rate of NEB and the degree of interactions between water and solid molecules, and with the physical state of the food matrix.

When increasing a_w from anhydrous conditions, the relaxation times $t_{2\text{-Hahn-2}}$ (and also the proportion of protons that contribute to this t_2 component) increase (Fig. 6). At low water content levels the increasing molecular mobility contributes to the acceleration of the NEB reaction (Fig. 1). Upon the appearance of frozen water (Fig. 3b) and highly mobile water (determined by the third sorption stage and $t_{2\text{-Hahn-2}}$ value) the behaviour markedly changed. At this point the NEB rate decreases because the water molecules can act, inhibiting the reaction and/or diluting the reactants.

The $t_{2\text{-FID}}$ values displayed a marked increase around the glass transition temperature (close to the values determined by DSC), and then NMR proved to be an effective tool for the study of glass transition in potato powders.

Although the influence of water on NEB kinetics has been investigated from several aspects (water activity, water plasticisation), the analysis of the water sorption data using the linearised GAB equation allowed the identification of the point at which the reaction rate decreases (onset of the third stage). The complementary analysis of ^{1}H NMR relaxations allows the evaluation of each of those stages.

Acknowledgement

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