Water Uptake Mechanism in Crispy Bread Crust

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Crispness is an important quality characteristic of dry solid food products such as crispy rolls. Its
retention is directly related to the kinetics of water uptake by the crust. In this study, a method for the
evaluation of the water sorption kinetics in bread crust is proposed. Two different sorption experiments
were used: an oscillatory sorption test and a sorption test in which the air relative humidity (RH) was
increased stepwise. These two experiments had different time scales, which made it possible to get
a better understanding of the mechanisms involved. Results show that the adsorption and desorption
dynamics of the oscillatory sorption test could be described by a single exponential in time. The
water uptake rate (k) was one of the fitting parameters. A maximum in the water uptake rate was
found for a RH value between 50 and 70%. The rate parameters of the experiment where RH was
increased stepwise were around a factor 10 lower than those derived from oscillatory sorption
experiments. This is an important factor when designing experiments for the determination of water
uptake rates. In addition, also a parameter describing the time dependence of the rate parameters
of the oscillatory sorption experiment was calculated (C), again by fitting a single exponential to the
rate parameters. C was in the same range as the rate parameter of the isotherm experiment. This
indicates that different (relaxation) processes are acting at the same time in the bread crust during
water uptake.

INTRODUCTION

Maintaining the sensory characteristics of crispy and crunchy
foods during their shelf life can be very difficult if not impossible
when the product is not in an equilibrium situation. This is the
case when a crispy product is stored in a humid environment or
when the crispy product is a composite food that also has a moist
part, for example, bread with a dry and crispy crust and a moist
and soft crumb. Then moisture migration will take place from the
environment or moist core to the dry and crispy parts. This results
in a loss of sensorial crispness of the product (*1–3*). Since the
amount of water present in the crust is an important factor in
determining its crispness, the rate of loss of crispness will be related
to the kinetics of water uptake by the crispy parts of the product.

When a dry solid polymer material like protein or starch is
brought into contact with water, the water diffuses into the
polymer and, in the case of an energetically favorable interaction
between the water and the polymer, the polymer matrix swells.
Diffusion involves migration of the water molecules into pre-

existing or dynamically formed spaces between polymer chains.
This first stage follows Fickian diffusion (*4*), for example, in
the case of organic vapor sorption (vinyl chloride, acetone, and
methanol) into glassy polymer powders (poly(vinylchloride)).
Fickian diffusion in polymers is an ideal case of penetrant
transport, corresponding to free diffusion of penetrant without
interference of polymer chain rearrangement, i.e. structural
relaxation (*5*). The second stage in penetrant sorption is the
swelling of the matrix due to polymeric relaxations. These
provide a redistribution of the free-volume elements, which
ultimately results in a time-dependent increase of free-volume
to accommodate additional penetrant (anomalous penetrant
transport). It is believed that for an initially glassy polymer
matrix system both concentration gradient controlled migration
(stochastic or Fickian diffusion) and relaxation or swelling
controlled migration (Case II diffusion) contribute to the rate
and extent of penetrant sorption (*4, 6, 7*). However, many
variations exist (*5*).

Water uptake rates for food systems are often calculated with
the use of Fick's law (*8, 9*). Despond et al. (*7*) found that water
transport in chitosan films is governed by a Fickian process for
partial pressures lower than 0.4 and that in that range of partial
pressures, the diffusion coefficient is concentration dependent.
At a higher water activity, the rate of diffusion becomes quite
similar to the rate of relaxation, leading to anomalous diffusion

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6440 *J. Agric. Food Chem.,* Vol. 56, No. 15, 2008

van Nieuwenhuijzen et al.

(which means somewhere in between Fickian and Case II diffusion). Del Nobile et al. (*10*) concluded for chitosan films that in the range of a_w 0.2−0.6 the characteristic time of stochastic diffusion was smaller than the characteristic time associated with polymer matrix relaxation. Therefore, polymer matrix relaxation was assumed to be the limiting step controlling water-sorption kinetics in chitosan films. Fickian diffusion was found by Hopkinson et al. (*11*) for water vapor sorption into amylose pellets. For food materials, no reports on pure Case II behavior (diffusion is very fast compared to the rate of relaxation of the solid material) were found in literature when considering vapor sorption. For bread crust, no water uptake mechanism has been suggested at all.

Besides Fickian diffusion and relaxation of the polymers, other processes may play a role in the sorption process. Valiullin et al. (*12*) studied the sorption hysteresis in Vycor porous glass, which is a glass of SiO_2 prepared according to Hood and Nordberg (*13*). The observed hysteresis suggests that for a certain range of vapor pressures, the amount of a molecular species adsorbed by the porous host at a specific RH is higher during desorption than during adsorption, indicating a failure of the system to equilibrate over the time span studied. This phenomenon is often found in food systems as well (*14*). Valiullin et al. (*12*) found for Vycor silica glass at low water vapor pressure (outside the hysteresis region) that the gas diffuses into the pore structure, forming adsorbed layers on the pore walls. The relaxation process is here essentially diffusive in character. As the water pressure increases (into the hysteresis region), the adsorbed layers finally grow together and a droplet of water may be formed in the pores. This process is called capillary condensation. This will reduce the surface area exposed to the water vapor/air mixture. The dynamics slow down dramatically and, at long times, are dominated by activated rearrangement of the water within the host material.

Wolf et al. (*15*) classified the variations in hysteresis loops in foods into three general groups, namely, high-sugar/high-pectin (e.g., apple), high-protein (e.g., pork), and high-starch systems (e.g., rice). Starch gives the largest hysteresis loop of the three groups. Several theories have been suggested to explain the hysteresis in porous solid foods. Most were based on the above-mentioned capillary condensation phenomena (*16*). For starch-type products also activation of (additional) sorption sites due to the history of high water content was suggested as a possible explanation (*15, 17*).

In previous work (*18*), we used the combination of an oscillatory sorption test and a Langmuir-type approach to describe water uptake. By varying the oscillation times, we found that the characteristic time for water adsorption on the surface of the bread crust is smaller than approximately 15 min. From this, it was concluded that the transport of water into the material is the rate limiting step in the water uptake process. The objective of the current article is to obtain a more profound understanding of the mechanism of water uptake in bread crust at different water contents. An understanding of the mechanism will make it possible to develop crispy products that maintain their crispness for a longer time. Besides that it is necessary to have a good model that is representative of water uptake in bread crust in order to be able to compare the water uptake kinetics of different variations of crispy products (e.g., due to ingredient variation).

MATERIALS AND METHODS

Materials. Model bread crusts were prepared from two air-classified fractions of a wheat flour (a protein rich and a starch rich fraction).

Table 1. Composition of the Flours That Were Used to Make the Bread Crusts

component	starch rich flour	protein rich flour	Soissons
starch (% dm)	82	69	79
protein (% dm)	9.5	17.3	12.9
damaged starch (% dm)	6.2	10.3	4.9
fat (% dm)	0.6	1.8	1.2
moisture (%)	9.6	9.2	14.8
insoluble nonstarch polysaccharides (%)	0.1	0.03	1.5
soluble nonstarch polysaccharides (%)	0.47	1.01	0.42

Rusk rolls were prepared with Soissons wheat flour. The flours were purchased from Meneba (Meneba Meel BV, Rotterdam, The Netherlands). The composition of the flours is shown in **Table 1**. Native wheat starch (Excelsior) was purchased from Avebe (Veendam, The Netherlands).

Methods. *Preparation of Model Bread Crust.* Dough was prepared by mixing in a faringograph mixer (Brabender, Duisburg, Germany) using a 50 g mixing bowl. The formulation included flour (50 g), NaCl (1 g), and dry yeast (0.85 g). For the protein-rich dough and the starch-rich dough 40 and 31.5 mL water, respectively (based on Farinograph water absorption, ICC 115/1, 1991) (*19*), on the basis of flour was used to prepare the dough. The temperature of the added water was 22 °C, and the starting temperature of the mixing bowl and flour was 22.5 and 23 °C, respectively. The dough was mixed at a speed of 100 rpm until the dough temperature reached 26 °C, which corresponded to the maximum in the torque-time curve. After mixing, the dough was separated into three pieces and proofed at 30 °C and 90% RH for 15 min in a climate chamber (Wekk 0028, Weiss Enet, Tiel, The Netherlands). Next, the dough pieces were flattened by hand, rounded, and again proofed at 30 °C for 15 min. The dough was then sheeted between Teflon paper using a pasta machine (Titania, Imperia, Sant'Ambrogio di Torino, Italy) in order to get a flat piece of dough. Sheeting was repeated until a sample thickness of 2 mm was obtained (from position 1 to 4 of the pasta machine). Test pieces were cut from the dough sheet with the help of a stainless steel 6 cm diameter ring. Next, the dough was proofed for 70 min at 30 °C and 90% RH. Finally, the dough sheet was placed on a punctured stainless steel plate. This supports the dough during baking and allows moisture loss from the bottom of the sample.

The dough samples were baked in a HR83 halogen heater (Mettler Toledo, Tiel, The Netherlands). The temperature program was selected to simulate baking conditions. First, the dough was baked at 130 °C for 4 min (including 1 min to reach 130 °C). Next, the temperature was increased to 160 °C for 4 min (including 40 s to increase the temperature to 160 °C) and finally to 185 °C for 50 s (including 20 s to increase the temperature). Model crusts of different batches were used for the duplicate measurement.

Preparation of Rusk Roll Crust. Part-baked rusk rolls (8 cm diameter, 4 cm height) were prepared at the TNO baking laboratory (TNO Quality of Life, Zeist, The Netherlands). Wheat flour (3000 g), water (1695 mL), based on farinograph water absorption (*19*), yeast (50 g), salt (60 g), and ascorbic acid (20 ppm) were mixed in a high speed mixer (Kemper SP 15, Kemper, The Netherlands) as explained below. First, all ingredients (temperature 5 °C) except water were dry mixed for 1 min at low speed. Next water (10 °C) was added, and everything was mixed at low speed for 2 min. Finally, the dough was kneaded at high speed until a dough temperature of 26 °C was reached. After mixing, the dough was allowed to rest for 15 min. Next, the dough was divided and rounded. Proofing was performed at 30 °C and 80% RH until a fixed volume of the dough sample (500 mL SJA) was reached. The breads were part-baked at 215 °C for 12 min in a Rototherm RE oven (Haton, The Netherlands). The part-baked breads were allowed to cool down for 30 min and frozen at −30 °C and stored at −18 °C until use.

Breads were baked off in a Bakermat Mastermind oven (Leventi, Gilze, The Netherlands). The bake off conditions were as follows: preheating of the oven at 250 °C, followed by 5 s steam injection, and convection heating for 5 min at 235 °C.

Water Uptake Mechanism

J. Agric. Food Chem., Vol. 56, No. 15, 2008   **6441**

After the bake off, the breads were allowed to cool down for 0.5 h at ambient temperature. Next, the crust (2 mm thickness) was separated from the crumb with a slicing machine (250 TC, Manconi&C, Sumirago-Varese, Italy). Bread crusts of 2 different breads were used for the duplicate measurements.

Sample Preparation. Bread crust samples were milled in an analytical grinder (type A10, IKA Labortechnik, Staufen, Germany) for 10 s at a time with a maximum of 3 times (to prevent heating of the sample) until a fine powder was obtained. The powder was sieved using different sieves (63 μm, 0.25 mm, and 0.5 mm). The different sieving fractions (<63 μm, 63 μm-0.25 mm, and 0.25 mm-0.5 mm, called S, M and L, respectively) were freeze-dried. The largest sieve fraction (>0.5 mm) was discarded. From the model crust samples, only the large particle size samples were used. Samples were kept at room temperature in closed tubes until use.

Oscillatory Sorption Experiments. Oscillatory sorption experiments were performed using a VTI-SGA 100 symmetric vapor sorption analyzer (VTI Corporation, Hialeah, Florida USA). This is a continuous vapor flow sorption instrument for obtaining water and organic vapor sorption isotherms. The instrument is equipped with a dew point analyzer and a Cahn microbalance. All tests on crust samples (5–7 mg with an approximate thickness of the powder bed of 1 mm) were performed at 25 °C. Samples were stored over P_2O_5 for at least 3 days before starting the experiment, resulting in an initial water content of approximately 1.5%. Every experiment was started with a drying step in the VTI at 50 °C for 120 min. Oscillatory sorption experiments were performed by applying block wise oscillations of the environmental RH between 40 and 50% RH, 50 and 60% RH, 60 and 70% RH, and between 70 and 80% RH, respectively, for the model crust samples. For the Soissons bread crust, steps of 20% RH were taken (20–40, 40–60, 50–70, and 60–80%). These results were obtained during an earlier study, and therefore, the step size was different (*18*). The rising and falling times of each block were 4.5 min. The measurements were stopped when the oscillations of the sample weight became steady. Oscillation times of 23 min were used.

Stepwise Sorption Isotherm Experiments. The isotherm was determined following the same procedure and equipment as described above, but the RH was increased with 10% every 570 min or when the isotherm was stable (less than 0.0001% weight change in 10 min). The weight change of the sample (caused by the change in environmental RH) was measured in time. An example of an oscillatory sorption experiment and a stepwise sorption experiment is given in **Figure 1**.

Starch Content. *Total Starch.* The total starch content was measured using a total starch assay kit from Megazyme (the *R*-amylase/ amyloglucosidase method) (Megazyme International Ireland, Wicklow, Ireland). Experiments were carried out in duplicate.

Damaged Starch. The damaged starch content was measured using a damaged starch assay kit from Megazyme (the α-amylase method) Megazyme International Ireland, Wicklow, Ireland). Experiments were carried out in duplicate.

Protein Content. Protein content was determined according to the Dumas method (*20*) using an NA2100 Nitrogen and Protein Analyzer (CE Instruments). Methionine was used as a standard. Experiments were carried out in duplicate.

Pentosan Content. *Insoluble Pentosans.* Flour (50 g) is dispersed in water (450 mL), and 50 mL of 12% SDS and 0.5 g dithiotreitol (DTT) were added. The solution was stirred for 3 h. After stirring, the solution was poured over a sieve (45 μm), and the residue was thoroughly washed with water. The contents of the sieve were collected and freeze-dried and weighed. The protein content was determined with the Dumas method. Experiments were carried out in duplicate.

Soluble Pentosans. Forty grams of flour was added to a solution of 36 g Trichloro-acetic acid (TCA) in 164 g of water (18% (w/w)). The solution was stirred overnight at 4 °C and then centrifuged at 10,000 rpm in a Sorvall centrifuge for 30 min. Cold (4 °C) ethanol was added to the supernatant until a concentration of 70% (v/v). The solution was left overnight to sediment the insoluble parts, and the supernatant was centrifuged again at 2,000 rpm. The residue was washed 2 times with cold 70% (v/v) ethanol to remove the TCA. Then, the residue was dissolved in 40 mL of 100 mM citric acid buffer at pH 4.6. Fourteen units amyloglucosidase was added, and the solution was incubated at
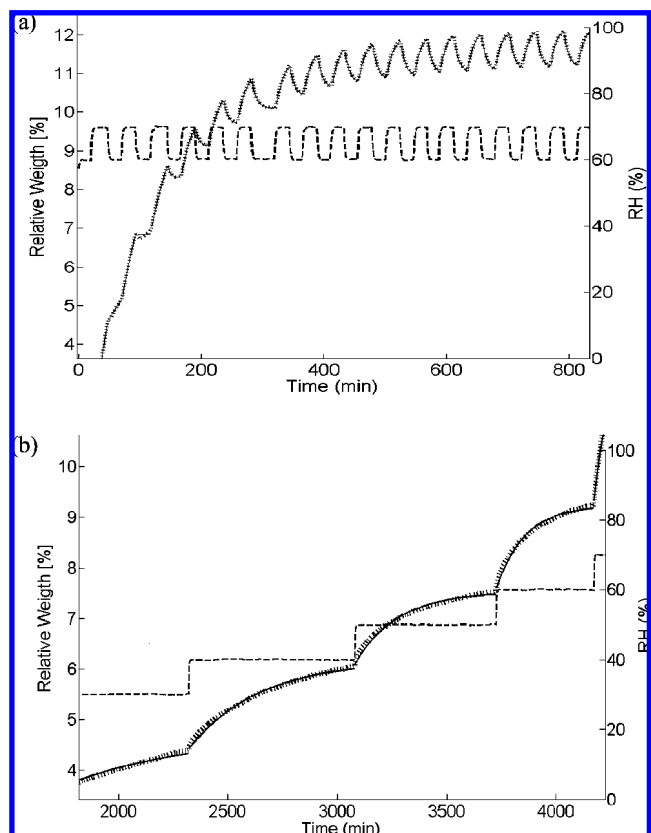

Figure 1. Relative change in weight as a function of time for a protein rich model crust during an oscillatory sorption experiment when oscillating the RH between 50 and 60% (**a**) and the same for part of an isotherm experiment when increasing the RH in steps of 10% (**b**). (---) indicates the RH, (···) experimental data, and (—) the fitted curve.

40 °C overnight to digest the remaining starch. The solution was cooked for 5 min, cooled down, and centrifuged until a clear solution was obtained. The solution was dialyzed against distilled water (3 × 5 L). The solution was freeze-dried, and the weight was determined. Experiments were carried out in duplicate.

Fat Content. The fat content was measured with Soxtec (Avanti 2050). Hexane was used as extraction fluid. The samples (around 10 g) were immersed in the fluid for 30 min and rinsed with hexane for 2 h. Experiments were carried out in duplicate.

RESULTS AND DISCUSSION

Two different methods to investigate water uptake kinetics were compared: an oscillatory sorption test and a sorption test in which the air RH was increased stepwise. In this way, the effect of experimental time could be studied. In the oscillatory sorption test, water uptake and loss in model bread crusts were followed while the relative humidity (RH) of the surrounding air oscillates stepwise between two set values. The water uptake process was studied by fitting the changes in weight with a single exponential. In addition, the effect of different RH oscillation ranges was investigated in order to better understand the relationship with the sensorial loss of crispness. Oscillatory sorption data were compared with data from nonoscillatory, long-term water uptake sorption isotherms to evaluate the effect of the experimental set up. Model bread crusts prepared from two fractions of an air-classified flour (a protein-rich and a starch-rich fraction) and a bread flour were studied to check the use of the developed methods for investigating the effect of ingredient composition on water uptake kinetics.

Figure 1a shows an example of an oscillatory sorption experiment with the RH stepwise oscillating between 60 and

70%. The experiment can be divided into two parts: the first part in which a steady state in the oscillation of the sample weight is not yet reached and in which a large amount of water is taken up and a second part in which a steadily oscillating state is reached. The percentage relative weight ($\Delta m(t)$) was defined as follows:

$$\Delta m(t) = \frac{100 \times [M(t) - M(0)]}{M(0)}(\%) \qquad (1.1)$$

where $M(t)$ and $M(0)$ are the weight at time t and the initial weight after the drying step of the sample, respectively.

Figure 1b shows part (between RH 30% and 60%) of the result of an alternative, nonoscillatory way for measuring water sorption kinetics in which the RH was increased with steps of 10% RH until 90% RH was reached. The experimental time per step (3.5–10 h depending on how fast an apparent steady state was reached) was longer than in the oscillatory sorption experiment (around 23 min per step).

Analysis of Sorption Rates. The kinetics of water sorption were studied at a temperature of 25 °C at different relative humidities (RH). A single exponential function was found to be the best simple fit for the water uptake data.

$$M(t) = [M(0) - M(\infty)]e^{-kt} + M(\infty) \qquad (1.2)$$

$M(t)$ is the mass of the sample at time t, $M(0)$ is the initial sample weight, and $M(\infty)$ is the sample weight at apparent equilibrium. Both $M(\infty)$ and k are adjustable parameters. A double exponential improved the fit for the experiment with stepwise increasing RH, but the two resulting k-values only differed a factor of two from each other. To prevent overinterpretation of the data, a single exponential fit was chosen.

Often, Fick's law is used for this type of analysis; however, a very well defined surface area or diffusion distance is required. Since the geometry of a bread crust particle is difficult to define, only a rate parameter k was calculated by fitting eq 1.2 to the experimental data. The geometry of the particles in this case will also influence k. In **Figure 1a** and **b**, the fit results are shown. The quality of fit, expressed by R^2 is better for the oscillatory sorption experiments ($R^2 \sim 0.99$) than for the sorption experiments with stepwise increasing RH ($R^2 \sim 0.98$).

Figure 2 shows the fit results of rate parameter k for the upward and downward branches of an oscillatory sorption experiment with the RH oscillating between 40 and 50% (**a**) and between 70 and 80% (**b**). The fit results of $M(\infty)$ values for the adsorption branch were close to the measured $M(\infty)$ values in a stepwise water sorption experiment at equal RH. The $M(\infty)$ values that were obtained for water activities smaller than 0.6 for the desorption branch were lower than those measured for the stepwise isotherm experiment. This is likely due to the fact that the maximum water activity that these samples reached was lower than 0.9 (results not shown). An a_w of around 0.9 would correspond to the maximum effect of hydration, which did not occur in the oscillatory sorption experiments at lower RH. The k-values for the adsorption steps at the start of the oscillatory sorption experiment (**Figure 2a** and **b**) are very low. This is most likely due to the dryness of the material, which therefore has a very small free volume available for water. As a consequence, the rate of transport of water through the material will also be slow. With increasing water content, water will hydrate the polymers, and the material will swell, thus creating more space for water to move through. This will result in an increase of the k_{osc}-value until a steady state in the material is reached, and the average water content is constant. The average steady state k_{osc}-value also increases
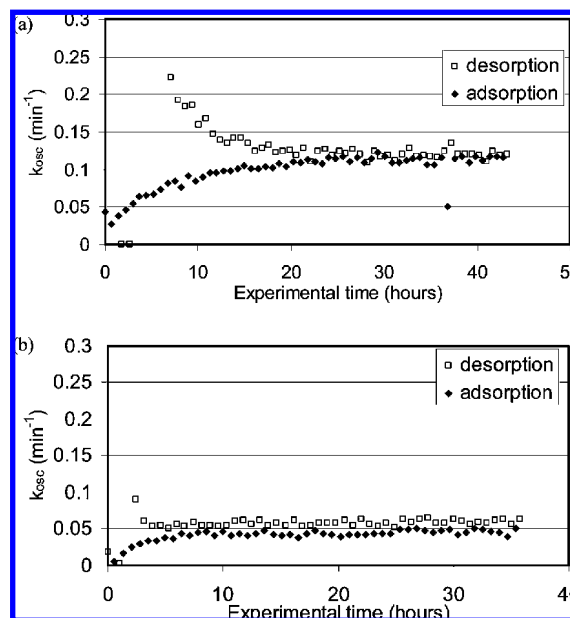

Figure 2. Rate parameter k_{osc} for the separate oscillation steps of 23 min each as a function of the total experimental time for an oscillatory sorption experiment. Results for the adsorption and desorption steps for a protein rich model crust with RH oscillating between 40 and 50% (**a**) and RH oscillating between 70 and 80% (**b**).

with increasing water content or RH for the lower RH combinations (up to 60% RH), probably as a result of the process described above. The k_{osc}-value of the desorption branch for the first 1–3 steps was close to 0. This has to do with the fact that for the first steps also during the desorption step water is adsorbed because even at this desorption step, the driving force for water to move into the sample is high enough (in other words, the sample is dry enough; see also **Figure 1a**). The shape of the curve apparently is not well fitted by a single exponential for those first steps. For the next 4–5 steps, the rate parameter likely is higher than that of the adsorption step because a steady state is reached quickly. This is due to the fact that water does not only move out of the sample but also toward the center (that was initially dry) of the sample upon desorption. In this way, an equilibrium is reached in a faster manner.

For the RH oscillations between 40 and 50% (**Figure 2a**), the k-values for the upward and downward branches become similar when the system reaches a steady state situation. At higher RH (**Figure 2b**), the k-values from the upward branch have a little lower steady state value than the k-values from the downward branch of the oscillatory sorption experiment. The ratio of $k_{osc,\,up}/k_{osc,\,down}$ varied between 0.96 ± 0.009 for the 40–50% RH combination and 0.85 ± 0.11 for the 70–80% RH combination for the PR model crusts. All ratio's were significantly below 1. For the SR model crust, this ratio was significantly lower than 1 only at the higher RH combinations (60–70 and 70–80%). This difference in upward and downward k-values must correspond to a difference in the shapes of the upward and downward branches. Such a difference in shape is not unexpected considering the fact that in a stepwise sorption experiment with this material hysteresis is observed. The material may have changed during water uptake and will therefore behave differences upon moisture loss. It could also be that the difference in upward and downward k_{osc}-values is due to the difference in initial water content. This difference is much larger at higher RH. According to Bruin and Luyben (*21*), the diffusion coefficient (D) of water increases with increasing water content from 10^{-15} m^2/s at low water content (<5% water)
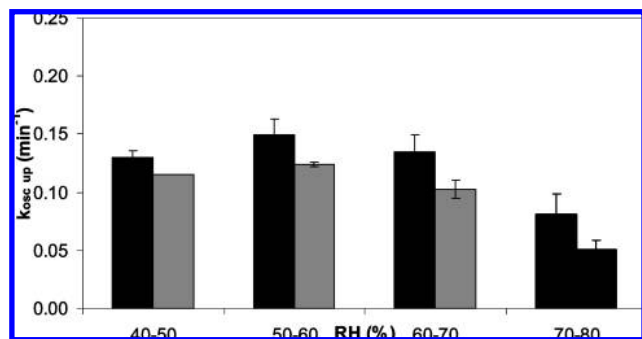
Figure 3. Average rate parameter k_{osc} for starch rich (black columns) and protein rich (gray columns) model crusts oscillating between different RHs for the adsorption branch. Average of k_{osc} for the last five adsorption steps in the steady state situation.

to 10^{-10} m^2/s at 50% water content. The k-value as calculated here is proportionate to the diffusion coefficient divided by the squared diffusion distance, assuming that the effective surface area for diffusion does not change. (The calculation of D by Fick's law is also based on a single exponential (*22*).) This means that the transport of the water out of the sample at the start of a downward branch will be faster than the transport of water into the sample at the start of an upward branch. This is because the initial water content is higher for the desorption part than for the adsorption part.

Figure 3 shows the k_{osc}-values for adsorption (average of the last 5 oscillation steps in the steady state situation) for particles of a protein-rich and starch-rich model crust. A maximum in the rate parameter k_{osc} was found for a RH value between 50 and 70%. At even higher water activities, a smaller rate parameter k_{osc} was found. This is probably due to the swelling of the material with increased water content, which results in a reduced effective surface area and possibly even caking of the particles. **Figure 3** also shows that the protein-rich model crust has smaller k-values than the starch-rich model crust. The reason for this is not yet fully understood.

For Soissons rusk roll crusts, experiments were performed in the same way as for the protein-rich and starch-rich model crusts. However, for the Soissons rusk roll crust the RH was oscillated over ranges of 20% RH difference (20−40; 40−60; 50−70; and 60−80). Also for the Soissons rusk roll crusts, a single exponential could be fitted to the oscillatory sorption experiments. **Figure 4a**, **b**, and **c** show the development of the k_{osc}-values from the start of the experiment until a steady state was reached. At high RH, the rate parameter k_{osc} of the adsorption branch is lower than the k_{osc} of the desorption branch, even when an apparent steady state is reached. At very low RH (20−40%), the trend is the opposite: the k_{osc}-value of the adsorption branch is higher than the k-value of the desorption branch. As mentioned before, a difference between adsorption and desorption rates at an apparent dynamic equilibrium might be the result of an interplay between hysteresis (changes in the sample during each oscillation step) and nonsingle-exponential behavior.

The effect of particle size on the k_{osc}-values of Soissons bread crust at steady state is shown in **Figure 5**. A smaller particle size gives a higher k-value. This is expected since the smaller particles have a relatively larger surface area, and consequently, the sample will reach a steady state in less time. The k-values for the larger particle size of the Soissons bread crust are similar to the values for the model crusts.

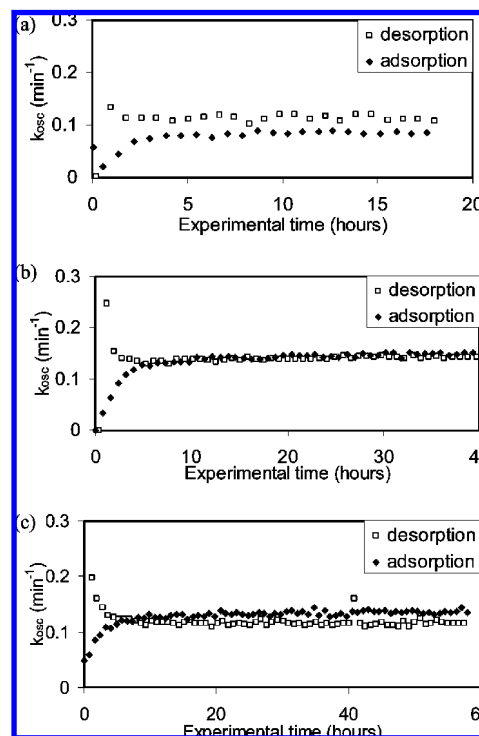**Comparison of Sorption Rates Measured by Oscillatory Sorption and Standard Step Sorption Experiments.** The

Figure 4. Evaluation of the rate parameter k_{osc} for adsorption and desorption steps of 23 min in an oscillatory sorption experiment as a function of the total experimental time. Results for a Soissons rusk roll crust with RH oscillating between 60 and 80% (**a**); 40 and 60% (**b**); and 20 and 40% (**c**).
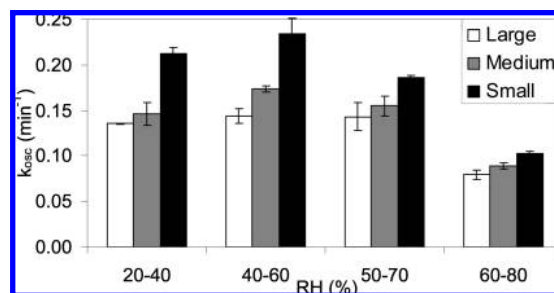

Figure 5. Effect of particle size on the average k_{osc} of the adsorption step in the steady state situation (average of the last 5 oscillation steps). Results for a Soissons rusk roll crust in an oscillatory sorption experiment. The RH was oscillated between different values. Large = 0.25−0.5 mm, medium = 0.063−0.25 mm, and small = <63 μm.

water uptake curves obtained during the determination of a sorption isotherm by stepwise increasing RH (**Figure 1b**) were analyzed in the same way as the oscillatory sorption curves (by fitting an exponential function). In the sorption experiments with a stepwise increase of RH, water uptake was followed for 600 min for each step, whereas one step in an oscillatory sorption experiment took only 23 min. However, in an oscillatory sorption experiment, it could take 600 min or more before a steady oscillating state was reached. The isotherm experiments gave rate values (k_{step}) that are around a factor of 10 lower than those obtained with the oscillatory sorption experiments (k_{osc}) (**Figure 6**). The maximum in the rate parameter calculated from an isotherm experiment is found at higher RH than for an oscillatory sorption experiment. These differences may be due to the fact that the fit is not perfect ($R^2 < 1.00$). In the oscillatory sorption experiment, the duration of an oscillation was 23 min. Therefore, the first 23 min of each step in the sorption experiment with a stepwise increasing RH were considered
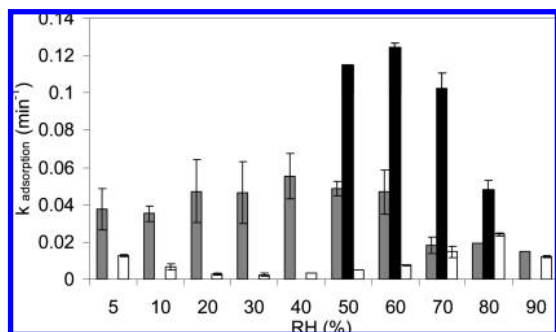
6444 *J. Agric. Food Chem.,* Vol. 56, No. 15, 2008

van Nieuwenhuijzen et al.

Figure 6. Rate parameter of both isotherm data (k_{step}) and oscillatory sorption data (k_{osc}) calculated from the adsorption branch for the protein rich model crust. White, k_{step}; black, k_{osc}; gray, k_{step} where only the first 23 min of the data per step were used for the fit.
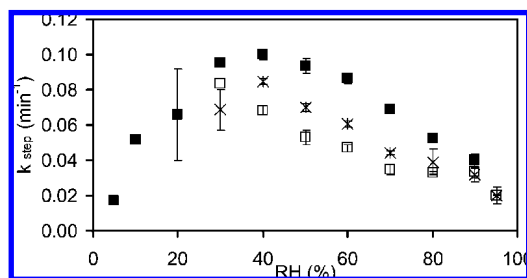

Figure 7. Effect of the experimental time per step on the k_{step} rate parameter for a sorption experiment with stepwise increase of RH for native wheat starch. Results for experimental times per step of 300 min (□), 60 min (■), and 300 min where only the first 60 min were used for the fit (×).

separately. From this early part of the sorption curve, still smaller k-values than those of the oscillatory sorption experiments are obtained (**Figure 6**), although the experimental time considered was the same. This suggests that oscillating the water content in the sample changes the response of the sample to a changing RH.

Different results with changing experimental times were also found in a separate experiment in which the effect of the time per step in an experiment with a stepwise increase in RH was considered for native wheat starch. The resulting rate parameters k_{step} for adsorption are shown in **Figure 7**. The experimental times were 60 and 300 min per step. Also from the experiment with 300 min steps, a k_{step} was calculated from the weight change during the first 60 min of each step. The results show that the adsorption rate during the first 60 min of a 300 min step is not the same as the sorption rate during a 60 min step, nor the same as those of a fit of the total 300 min. This suggests that at longer experimental times more relaxation processes take place. However, deviations between the fit and the experimental data could play a role. The equilibrium values were the same for both experiments (results not shown). This means that when designing experiments to study the kinetics of water uptake the equilibration time should always be chosen carefully in accordance with the research question, taking the relevant time scales into account.

The maximum in the values of k_{step} and k_{osc} occurs at different values of RH. The oscillatory sorption experiment displays a maximum at a lower RH than the step experiment. The maximum in the k_{step} obtained from the first 23 min of the isotherm experiment is different again and shifts to a lower RH value (approximately 40%) compared to the k_{step} of the full experiment (**Figure 6**). This suggests that the maximum in the k-value depends on both the time scale of the experiment and
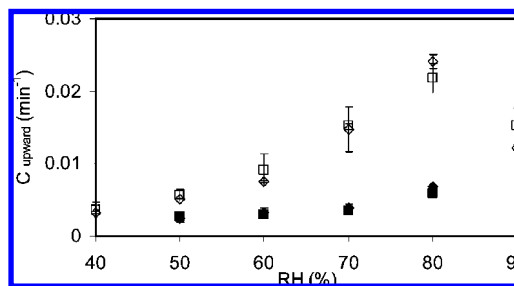

Figure 8. Rate parameter C of the oscillatory sorption experiment for PR (♦) and SR (■) model crusts compared with the rate parameters k_{step} of the isotherm experiment for PR (◊) and SR (□) model crusts (for further explanation, see the text).

the state of the sample. Different k-values and different positions of the maxima are expected because different processes will likely take place; water adsorbs to the surface of the particles and then migrates into the particle. Water that migrates into the dry matrix will probably do that at a different rate as compared to water migrating into the already hydrated matrix. Therefore, different experimental setups having different experimental times lead to the description of these different processes. Besides that a variation in the relaxation times between the different molecules of the solid matrix may also result in different k-values. This is the subject of a follow up article, describing a multilayer water uptake model in which the different water uptake processes are taken into account (*23*).

Dependence of Rate Parameter k on Experimental Time. From **Figure 2a** and **b**, we calculated the time dependence of the rate parameter k_{osc} by fitting a single exponential function to these results:

$$k_{osc}(t) = k_{osc}(\infty) - [k_{osc}(\infty) - k_{osc}(0)]e^{-Ct} \qquad (1.4)$$

where $k_{osc}(0)$, $k_{osc}(t)$, and $k_{osc}(\infty)$ are the values of k_{osc} at times 0, t, and at steady state, respectively, and C is an overall rate parameter, which describes how fast the sorption rate changes with time. The results for C are shown in **Figure 8** for model crust of protein-rich and starch-rich flour. C increases with increasing water content, which indicates that at higher water content equilibrium is reached sooner. The characteristic time ($1/C$) of the experiment changes from 400 min at low RH (40−50% RH) to 150 min at higher RH (70−80% RH). Compared to k_{step}, also included in **Figure 8**, C is smaller, but both rate parameters are of the same order of magnitude. It should be noted that no difference in C or in k_{step} was observed between the protein-rich and starch-rich model crust. The difference in water uptake rates probably only manifests itself at specific time scales, or the relatively long experimental times used to calculate C and k_{step} make the method less precise.

For Soissons rusk roll crust, the results for C and k_{step} are shown in **Figure 9a** and **b**. The fit ($R^2 \sim 0.95$) was not as good as that for the starch-rich and protein-rich model crusts ($R^2 \sim 0.98$). This is not well understood yet. A minimum in C is found around 60% RH for small sized particles of Soissons rusk roll crust (**Figure 9a**). This is not expected but might have to do with the fit, which was not as good as the fit for the model crusts. For medium and large sized particles, C was more or less constant for all RHs. As for the model crusts and also for the Soissons rusk roll crust, the C value is about equal to k_{step} at lower RH, while at higher RH, k_{step} is higher than C (**Figure 9b**). This could be due to caking or reduction of the surface area during the oscillatory sorption experiment. The sample is
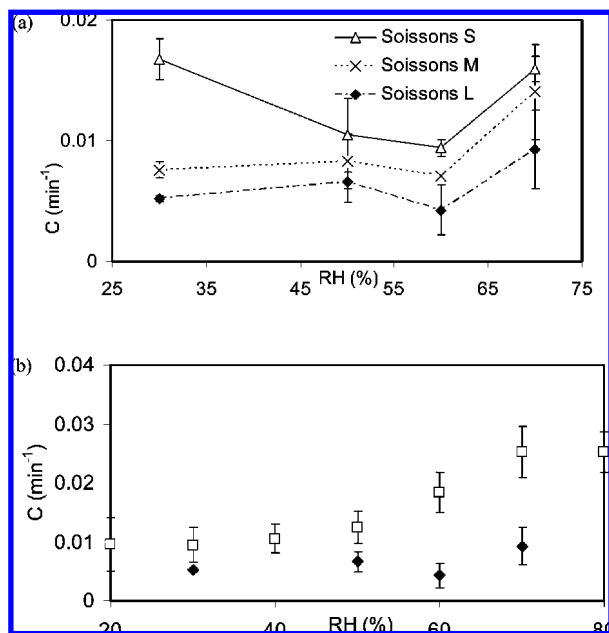
Water Uptake Mechanism

J. Agric. Food Chem., Vol. 56, No. 15, 2008 **6445**

Figure 9. Effect of particle size on the rate parameter (C) for Soissons rusk roll crust at different RH combinations, S = <63 μm, M = 0.063−0.25 mm, L = 0.25−0.5 mm (**a**), and comparison of the rate parameter C for Soissons rusk roll crust (♦) with the rate parameter k_{step} of the isotherm experiment (□) for a large particle size (0.25−0.5 mm) (**b**).

constantly at a high RH during the oscillatory sorption experiment, while for the isotherm experiments the high RHs involve only part of the total time. Additionally, the time considered to calculate C varies between 20 and 60 h, which is longer than the experimental time per step in a stepwise sorption experiment.

This slower process with a characteristic time of 150−400 min is found in both the oscillatory sorption experiment and the isotherm experiment. This suggests that k_{step} found in the isotherm experiment and C found for the oscillatory sorption experiment stem from a mechanism that manifests itself in both experiments. The sample in an oscillatory sorption experiment senses an average water content. This will be the water from which a part will penetrate further into the sample with the slow C-value that is similar to k_{step}. No exact agreement may be expected since C is calculated for a process starting from a dry state and k_{step} for an increase of RH by 10%. Our working hypothesis is that this could be a relaxation process, which is also responsible for the loss of crispness since the time scales on which crispness is lost are in the same range (*24*).

Maximum of *k*-Values and Relationship with Glass Transition. A transition point is found in sensorial crispness as well as in water mobility (as measured by nuclear magnetic resonance) at a water activity of around 0.58 (*25*). However, the glass transition of bread crust at room temperature as measured with DSC and PTA is around water activities of 0.85 and 0.80, respectively (*25*). Aguerre and Suarez (*26*) found a maximum in the diffusion coefficient for sorghum and corn at a water content of around 0.10 kg water per kg dry solid at 40 °C, but they did not give an explanation for this observation. That maximum shifted to lower water content with increasing temperatures, which could point at a relationship with glass transition. The maximum in the *k*-values we found is at about a water activity of 0.6 (∼0.11 kg water/kg dry matter) for the oscillatory sorption experiment and at 0.8 (∼0.16 kg water/kg dry matter) for the sorption experiment with stepwise increasing RH. It appears, therefore, that the transition point in the mobility of water with increasing water content as measured with NMR

(*26*) is found at roughly the same a_w as the maximum in the rate parameter k_{osc} as measured with an oscillatory sorption experiment and that the transition point as measured with the PTA and DSC is found at roughly the same a_w as the maximum in the rate parameter k_{step}.

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