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Oscillatory Water Sorption Test for Determining Water Uptake Behavior in Bread Crust

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In this work, water sorption kinetics of bread crust are described using an oscillatory sorption test in combination with a Langmuir type equation. Both kinetic and thermodynamic information could be obtained at the same time. An advantage of applying a Langmuir type equation for a quantitative description of the water uptake kinetics is that no prior knowledge is necessary with respect to shape and surface area of the sample. It was shown that adsorption and desorption of water to the bread crust particle surface is much faster than the experimental time used (15 min at minimum). From this, we may conclude that diffusion of water into the solid matrix is the rate-limiting step in the water sorption process. The method also allows one to calculate a Gibbs free energy. The method is suitable for use up to relative humidities of 60%.

KEYWORDS: Bread; crust; kinetics

INTRODUCTION

The crispy/crunchy characteristics of crusts are closely related to the fracture behavior of the solid matrix and the morphology of the crust. The solid matrix should break in a brittle way while sound is emitted. This character is lost at a higher water activity (*1*, *2*). For example, for bread crust, this is at a water activity above approximately 0.6 (*3*). It is especially difficult to keep a food crispy when the product has a moist interior. Water then migrates from the interior to the crust causing hydration of the crust components. This results in an increase of the mobility of the macromolecules, which causes a brittle to ductile transition of the amorphous regions of the crust (mainly proteins and carbohydrates) that were initially in the brittle state (*4*). Roughly at the same time, a loss of the crispy behavior occurs (*5*, *6*). This makes the product less desirable for the consumer because of the loss of perceived freshness. To improve crispy behavior, more information is required about the mechanisms underlying the deterioration of crispiness. Because it is clear that water causes the loss of crispiness, it is of interest to investigate the state of water in a food product, the kinetics of water uptake, and the mechanism of water binding in a food product.

General water uptake (equilibrium conditions) is usually described by using a sorption isotherm. Several models are fitted to these curves to describe water uptake (*7*). However, with respect to storage stability, it is important not only to know the total uptake of water at a certain environmental relative humidity (RH) (as determined by thermodynamics) but also to know the kinetics of water uptake. This is because the faster the water uptake, the faster the loss of crispiness. Often researchers use Fick's law to describe water sorption kinetics (*8*, *9*). Fick's first law describes water diffusion related to Brownian motions. The diffusion coefficient depends on local water concentration (*10*). Others used empirical models like the Weibull model or a mathematical model that accounts for both polymer relaxation and stochastic diffusion to describe water uptake kinetics of dry foods (*11*−*14*). The Weibull model can be used to determine the process mechanism of water uptake. Cunha et al. (*13*) did this to describe water uptake processes controlled by internal diffusion, external resistance to mass transfer, and relaxation phenomena. A disadvantage of this model is the lack of a theoretical basis (*11*).

Roman-Gutierrez et al. (*8*, *15*) studied the rate of water uptake of a hard and a soft wheat flour and of different flour components. Diffusion coefficients of water in starch or wheat flour systems were determined. Roman-Gutierrez et al. (*15*) used Fick's law to interpret sorption rates of the flour components (water uptake vs time). They did not observe a difference in initial sorption rates for the selected wheat components, except for the water-insoluble pentosans. These adsorbed water faster than all other components.

Del Nobile et al. (*14*) used an oscillatory sorption test for determining the water transport properties of chitosan-based films. In this experiment, they used cycles of oscillating water pressures. The water pressure levels around which the water pressure oscillated was for every cycle set at a higher level as well. They proposed an anomalous diffusion model and a nonideal Fickian model to fit the experimental data; in the latter, they did not take relaxation phenomena into account. The

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Table 1. Characteristics of Soissons Wheat Flour (dm), Results from Primo-Martin et al. (*3*)

parameter	value	parameter	value
water absorption (%)[a]	56.5	starch (%)	77
moisture (%)	14.1	damaged starch (%)	6.0
ash (%)	0.58	energy input (J)[b]	290×10^{-4}
protein (%)	10.9	falling number	333

[a] Farinograph (Brabender). [b] Alveograph (Chopin).

anomalous diffusion model accounts for both stochastic diffusion and polymer matrix relaxation, whereas the nonideal Fickian model neglects the polymer matrix relaxation phenomenon (*16*). Both proposed models fitted well to stepwise water sorption data, but only the anomalous diffusion model fitted well to the oscillatory sorption data. These results suggest that when the water sorption kinetics are controlled by polymer relaxation, an oscillatory sorption test should be used instead of stepwise sorption tests. The use of an oscillatory sorption test will allow a better determination of the relationship between the water diffusion coefficient and the local water concentration (*14*).

A disadvantage of using Fick's law for describing the diffusion of water into a bread crust particle is the requirement to make an assumption regarding the particle surface to volume ratio. This is mostly done by assuming a spherical shape of the particle, which is not the case for bread crust particles. Besides that, Fick's law results in a diffusion constant of water, which is an average of the contributions from the adsorption on the surface of the particles and the diffusion into the particle and assuming no matrix relaxation. When results obtained by applying Fick's law are interpreted as diffusion inside a bread particle, instant adsorption of the water at the surface of the material is assumed. Currently, it is unclear whether this assumption is correct.

In this article, a combination of an oscillatory sorption test and the use of a Langmuir type equation (*17*) is proposed to allow a quantitative analysis of water uptake behavior without prior knowledge of shape and surface area of the sample. By varying the oscillation time, it should in principle be possible to differentiate between water adsorption/desorption from the surface and diffusion of water into the particle.

In the oscillatory sorption experiment described in this paper, the air RH oscillates between two different values. Water uptake and release during the time span of the oscillation period involved are measured with a microbalance. In contrast to the method applied by del Nobile et al. (*14*), oscillations in RH are applied until a steady state has been reached. Water sorption kinetics can be investigated as a function of particle size, oscillation time, the A_w range studied, and product properties. How the weight changes in reaction to a change in air RH depends on the rate of transport to the surface, on the rate of adsorption and desorption of water at the surface of the sample, and on the rate of diffusion of the water into the sample. The water sorption kinetics are described using a very simple model based on an equation equal to the equation derived by Langmuir (*17*). Besides that, in this article, the use of our model for the calculation of an imaginary surface area of the sample will be discussed.

MATERIALS AND METHODS

Materials. Bread crusts baked of a soft wheat flour (Soissons) were used. The flour was purchased from Meneba (Meneba Meel BV, Rotterdam, The Netherlands). The composition of the flour is shown in **Table 1**.

Methods. *Part-Baked Breads.* 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 (*18*), yeast (50 g), salt (70 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 it was mixed, 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 during 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 of steam injection and convection heating during 5 min at 235 °C. After bake off, the breads were allowed to cool down during 0.5 h at ambient temperature (fresh bread). Next, the crust (2 mm thickness) was separated from the crumb with a slicing machine (250 TC, Manconi&C, Sumirago-Varese, Italy). The crust samples were milled in a coffee grinder for 10 s at a time with a maximum of three times (to prevent heating of the sample) until a fine powder was obtained. The powder was sieved with different sieves (63 μm, 0.25 mm, and 0.5 mm), and the different sieve fractions (<63 μm, 63 μm to 0.25 mm, and 0.25−0.5 mm, called S, M, and L, respectively) were freeze-dried. The largest sieve fraction (>0.5 mm) was discarded. Samples were kept at room temperature in closed tubes until use.

Oscillatory Sorption Experiments. The oscillatory sorption experiments were performed using a VTI-SGA 100 symmetric vapor sorption analyzer (VTI Corp., Hialeah, FL). This is a continuous vapor flow sorption instrument for obtaining water and organic vapor 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 0.5 mm) were performed at 25 °C. Every experiment was started with a drying step at 50 °C during 120 min (this resulted in a water content at the start of each experiment of approximately 2.5% for all samples). The oscillation experiment was performed by applying block wise oscillations of the environmental RH between 60 and 80% RH, 50 and 70% RH, 40 and 60% RH, and 20 and 40% RH, respectively. The rising and falling times of each block were 4.5 min (**Figure 1**). The isotherm was determined by changing the RH 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. The measurements were stopped when the oscillation of the sample weight became steady. Two different oscillation times were used (28 and 48 min).

Differential Scanning Calorimetry (DSC). Crust and crumb samples (around 15 mg) were weighed, and distilled water was added to a 3:1 ratio of water to the sample in stainless steel pans (TA Instruments Inc., United States). DSC measurements were performed with a Perkin-Elmer DSC 7 calorimeter (Perkin-Elmer Corp., United States). Indium was used for calibration of the system. The samples were heated from 10 to 130 °C at 10 °C/ min. An empty stainless steel pan was used as a reference during the DSC measurement. The enthalpy was expressed in J/g of sample (*19*). Relative crystallinity (RC) was calculated as:

$$\mathrm{RC} = \frac{\Delta H_\mathrm{s}}{\Delta H_\mathrm{f}} \times 100 \qquad (1)$$

where ΔH_s represents the melting enthalpy (J/g) of starch crystallites in the sample and ΔH_f represents the enthalpy (J/g) of starch gelatinization in the flour.

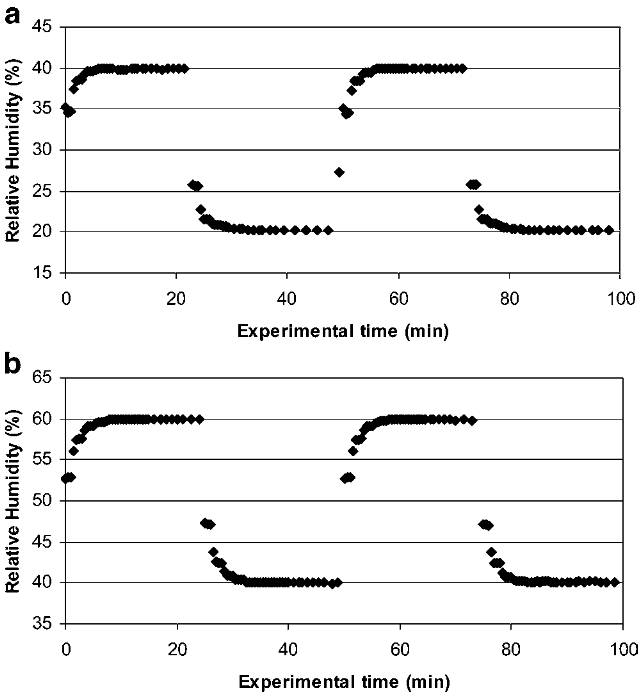

Figure 1. Change in applied RH as a function of time for two RH combinations in the VTI-SGA-100 analyzer (**a**) 20 and 40% RH and (**b**) 40 and 60% RH, respectively.

Protein Analysis. The protein content was determined according to the Dumas method using a NA2100 Nitrogen and Protein Analyzer (CE Instruments). Methionine was used as a standard (*20*).

Total Starch. The total starch content was measured using a total starch assay kit from Megazyme (α-amylase/amyloglucosidase method) (Megazyme International Ireland, Wicklow, Ireland).

Theory. *Analysis by Using a Simple One Exponential Equation.* Weight change [$\Delta m(t)$] was defined as follows:

$$\Delta m(t) = \frac{M(t) - M(0)}{M(0)} \text{ (g water/g dry weight)} \tag{2}$$

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

For the analysis of the uptake of water by bread crust, this process is assumed to be expressed by:

$$\mathrm{H_2O(gas)} \underset{k_{\mathrm{des}}}{\overset{k_{\mathrm{ads}}}{\rightleftharpoons}} \mathrm{H_2O(adsorbed)} \tag{3}$$

Then, the oscillation experiment can be described by an equation equal to the Langmuir equation (*21*).

When using this equation, we assume that all sorption sites are equal and that the adsorption energy is independent of the degree of coverage of the surface. With these assumptions, we can express the change in weight in time $\mathrm{d}\Delta m(t)/\mathrm{d}t$ as (*21*):

$$\frac{\mathrm{d}\Delta m(t)}{\mathrm{d}t} = -k_{\mathrm{des}}\Delta m(t) + k_{\mathrm{ads}}P[\Delta m_{\max} - \Delta m(t)] \tag{4}$$

where k_{ads} is the apparent rate constant for adsorption ($\mathrm{s}^{-1}\ \mathrm{Pa}^{-1}$), k_{des} is the apparent rate constant for desorption (s^{-1}), P is the water vapor pressure (Pa), t is time, and $\Delta m_{\max}$ is the maximum weight increase. The latter parameter has only a physical meaning when the properties of the adsorbent do not change as a function of the amount of water adsorbed. In many practical cases, above a certain degree of water uptake, the material will begin to swell, introducing a time dependence in $\Delta m_{\max}$, which will in theory eventually lead to an infinite value for $\Delta m_{\max}$, because the system has become a solution. Moreover, a change in adsorbate properties due to swelling may affect the adsorption energy and with that k_{des} and k_{ads}.

The rate of the change of surface coverage due to adsorption is proportional to P and the amount of available surface area (i.e., number of sorption sites) [$\Delta m_{\max} - \Delta m(t)$]. Equation 4 can be solved as follows:

$$\mathrm{d}t = \frac{\mathrm{d}\Delta m(t)}{-(k_{\mathrm{des}} + k_{\mathrm{ads}}P)\Delta m(t) + \Delta m_{\max}k_{\mathrm{ads}}P} \tag{5}$$

Integration of eq 1.5 gives

$$t = \frac{-1}{(k_{\mathrm{des}} + k_{\mathrm{ads}}P)} \ln \frac{-(k_{\mathrm{des}} + k_{\mathrm{ads}}P)\Delta m(t) + \Delta m_{\max}k_{\mathrm{ads}}P}{c} \tag{6}$$

$$e^{-(k_{\mathrm{des}}+k_{\mathrm{ads}}P)t} = \frac{-(k_{\mathrm{des}} + k_{\mathrm{ads}}P)\Delta m(t) + \Delta m_{\max}k_{\mathrm{ads}}P}{c} \tag{7}$$

where c is an integration constant. This gives the next expression for $\Delta m(t)$:

$$\Delta m(t) = \frac{\Delta m_{\max}k_{\mathrm{ads}}P}{k_{\mathrm{des}} + k_{\mathrm{ads}}P} - \frac{c}{k_{\mathrm{des}} + k_{\mathrm{ads}}P}\, e^{-(k_{\mathrm{des}}+k_{\mathrm{ads}}P)t} \tag{8}$$

when t is 0 then:

$$\Delta m(0)' = \frac{\Delta m_{\max}k_{\mathrm{ads}}P}{k_{\mathrm{des}} + k_{\mathrm{ads}}P} - \frac{c}{k_{\mathrm{des}} + k_{\mathrm{ads}}P} \tag{9}$$

$$c = -\Delta m(0)' \times (k_{\mathrm{des}} + k_{\mathrm{ads}}P) + \Delta m_{\max}k_{\mathrm{ads}}P \tag{10}$$

This leads to:

$$\Delta m(t) = \left[\Delta m(0)' - \frac{\Delta m_{\max}k_{\mathrm{ads}}P}{k_{\mathrm{des}} + k_{\mathrm{ads}}P}\right]e^{-(k_{\mathrm{des}}+k_{\mathrm{ads}}P)t} + \frac{\Delta m_{\max}k_{\mathrm{ads}}P}{k_{\mathrm{des}} + k_{\mathrm{ads}}P} \tag{11}$$

where $\Delta m(0)'$ is the weight change at the start of the part of the experiment considered. If the experiment is started from the dry state, $\Delta m(0)'$ is 0, and when considering the water uptake kinetics for one oscillation step, $\Delta m(0)'$ is equal to $\Delta m(t)$ at the start of the oscillation step. The fit results of the last five oscillation steps (when the oscillations were visually steady) were averaged to obtain a value for the adsorption/desorption of water in a single oscillation step. To avoid the need for a third adjustable parameter, we assume that the thermodynamics of the upward and downward water sorption process are equal. Then, we assume that the equilibrium constant

$$K = \frac{k_{\mathrm{ads}}}{k_{\mathrm{des}}} \tag{12}$$

and $\Delta m_{\max}$ are identical for both upward and downward branches of the oscillating data curves of $\Delta m(t)$. Note that K has the units Pa^{-1}. Consequently, fits of

$$\Delta m(t) = [\Delta m(0)' - a_0]e^{-t\times a_1} + a_0 \tag{13}$$

to upward and down branches were carried out with a_0 and a_1 as adjustable parameters. From

$$\frac{a_{0\mathrm{h}}}{a_{0\mathrm{l}}} = \frac{P_{\mathrm{h}}}{P_{\mathrm{l}}}\,\frac{1 + P_{\mathrm{l}}K}{1 + P_{\mathrm{h}}K} \tag{14}$$

(P_{h} and P_{l} are the water vapor pressure values, and $a_{0\mathrm{h}}$ and $a_{0\mathrm{l}}$ are the fitted equilibrium weight change levels for the upward and downward oscillation branches, respectively) and

$$a_{0,i} = \frac{\Delta m_{\max} K P_i}{1 + K P_i} \tag{15}$$

and

$$a_{1,i} = k_{\mathrm{des},i} + P_i k_{\mathrm{ads},i} \tag{16}$$

K, $\Delta m_{\max}$, $k_{\mathrm{des},i}$, and $k_{\mathrm{ads},i}$ can be calculated. The subscript i equals "h" or "l" and refers to the upward and downward branches of the oscillating curve.

From the obtained equilibrium constant K and the water vapor pressure P_i, the Gibbs free energy (ΔG) of the adsorption of 1 mol of water can be calculated as follows (*21*):

$$\Delta G = -RT \ln K P_i \tag{17}$$

where R is the gas constant (8.314 J/mol K) and T is the temperature (298 K).

RESULTS

Reaction Constants. Figure 2a shows an example of an oscillatory sorption experiment for two different RHs. The experiment can be divided into two parts; the first part in which a steady state is not yet reached and in which a large amount of water is taken up and a second part in which a steady oscillating state (five repetitive oscillation steps are the same within one experiment) is reached. In this study, we will focus on the second part, the steady oscillating state situation. **Figure 2a** shows that the overall water uptake is less and proceeds at a lower rate at a lower air RH as expected. The model was fitted to the separate oscillation steps in the second part of the experiment. **Figure 3** shows the single-exponential fit (eq 13) of the results obtained for Soissons bread crust with an oscillation time of 48 min for an upward oscillation step. Fits of the downward oscillations were similar (data not shown). From this graph can be concluded that a single-exponential model fits the experimental data with an accuracy of $R^2 \cong 0.99$. Fitting of the single-exponential model resulted in two kinetic parameters, k_{ads} and k_{des}. The values for these two parameters are shown in **Figure 4a**,**b**, respectively, for both the upward and the downward oscillation branches. k_{ads} should not change with water content when the affinity for water does not change with water content. However, as can be seen in **Figure 4a**, k_{ads} is lower for a higher air RH range for both the upward and the downward RH process. k_{des} is higher at a higher air RH oscillation range (**Figure 4b**). Both k_{ads} and k_{des} for the upward RH process are lower than for the downward RH process. At lower air RH (20−40%), this effect is clearer than at the higher air RHs (**Figure 5** shows the ratio for $k_{\mathrm{des,upward}}/k_{\mathrm{des,downward}}$, data for k_{ads} not shown). This could indicate that the material changes relatively stronger over the considered lower RH range. This complies with the fact that at lower RH the isotherm also shows the largest hysteresis effect (**Figure 2b**). Apparently, already hysteresis occurs at small changes in water content. Therefore, the assumption that there are no differences between the parameters of the upward and downward oscillation branch (K and $\Delta m_{\max}$ are equal for upward and downward branch) cannot be maintained.

Gibbs Free Energy. The Gibbs free energy change due to water adsorption (dG) can give information on the direction of the reaction of water uptake or loss. The Gibbs free energy of the adsorption/desorption process was calculated from the ratio of $k_{\mathrm{ads}} \times P/k_{\mathrm{des}}$. **Figure 6** shows the results for Soissons bread crust with an oscillation time of 48 min. The Gibbs free energy goes to zero and reaches a positive value with increasing water content. An increasing Gibbs free energy with increasing RH indicates a weaker drive for water to adsorb onto crust with a higher water activity. A Gibbs free energy of zero suggests the absence of a preference for water molecules to be either in the vapor state or in the adsorbed state.

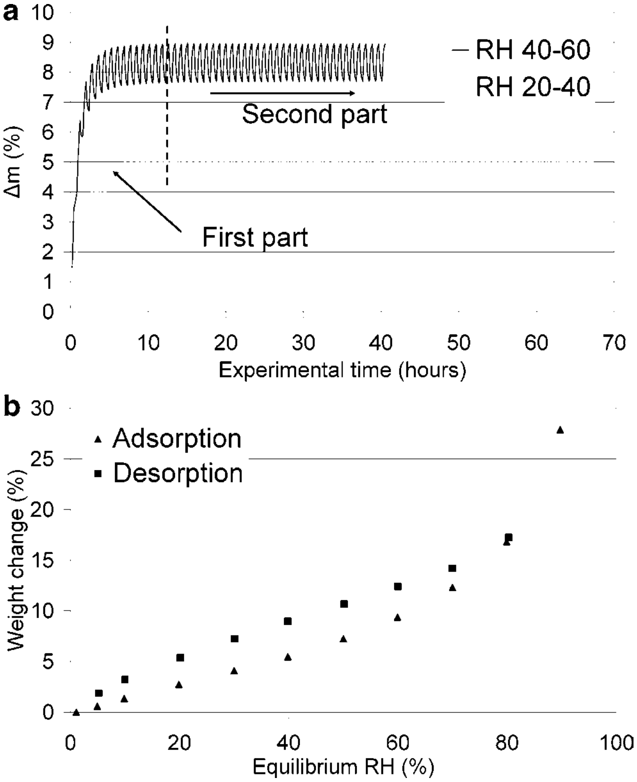

Figure 2. Oscillatory sorption experiments for bread crust particles (size large) of Soissons flour at two different RHs (40–60 and 50–70%) (**a**) and water sorption isotherm of Soissons bread crust large-sized particles (**b**).

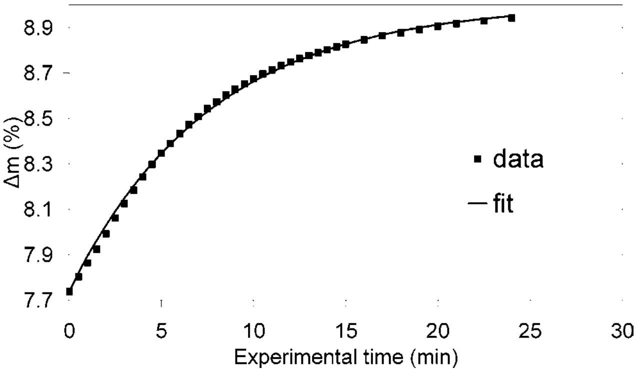

Figure 3. Fit of the single-exponential type equation (eq 1.13) for large Soissons bread crust particles with a RH oscillating between 40 and 60%.

Effect of Size. Figure 5 also shows that the difference between the upward and the downward process is not influenced by the size of the particle. In other words, the activation energies for adsorption and desorption do not depend on the particle size. The other determined parameters are influenced by size. **Figure 6** shows the effect of particle size on dG. dG was found to depend on the size of the particles at lower RH. In a lower air RH range, dG becomes more negative with increasing sample size. **Figure 7** shows that $\Delta m_{\max}$ increases with decreasing sample size. This indicates an increase in active "surface area" per unit mass for smaller particles. With an increasing air RH, $\Delta m_{\max}$ also increases. This also indicates an increase in the number of sorption sites. **Figure 8a**,**b** shows $k_{\mathrm{ads}} \times P$ and k_{des} for Soissons bread crust of different size classes of crust particles

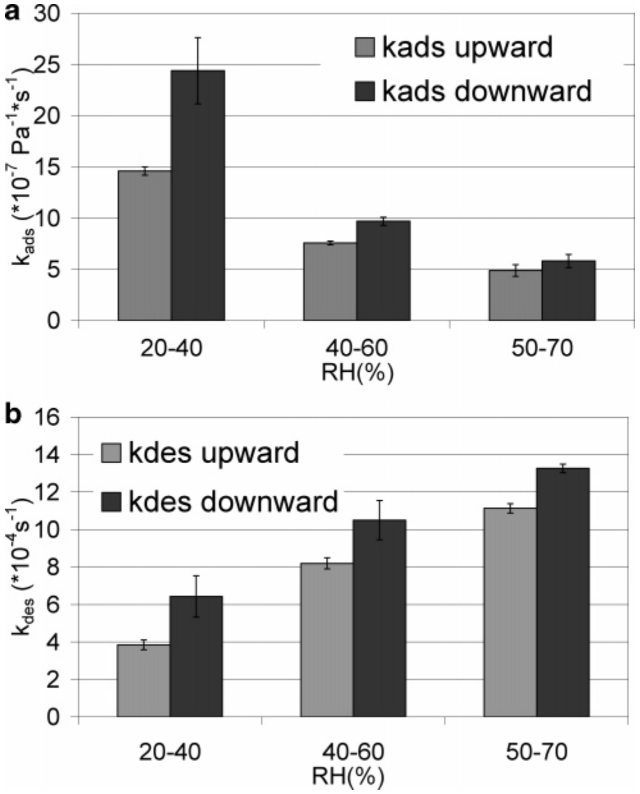

Figure 4. k_{ads} (**a**) and k_{des} (**b**) as a function of air RH for the absorption and desorption process for a large-sized particle.

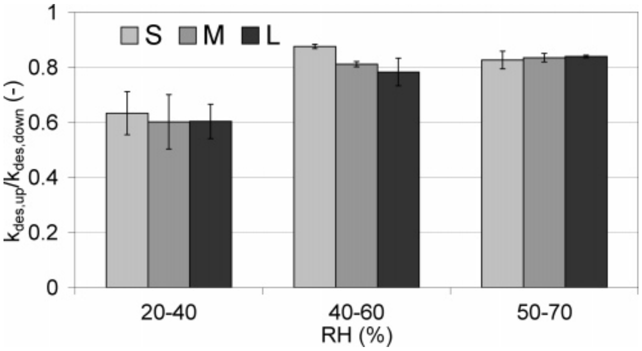

Figure 5. Hysteresis in k_{des} as a function of size (indicated) and air RH between the upward and the downward branch of the RH oscillation.

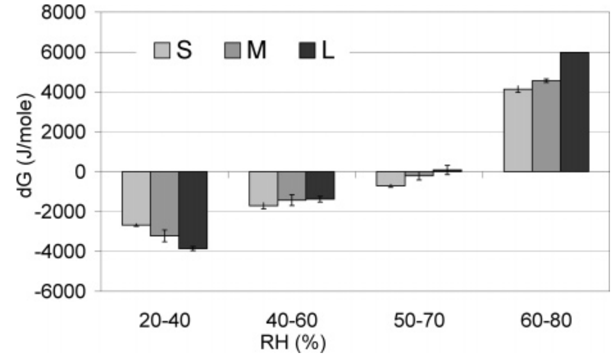

Figure 6. dG for Soissons bread crust with different particle sizes and for three different RH oscillation ranges.

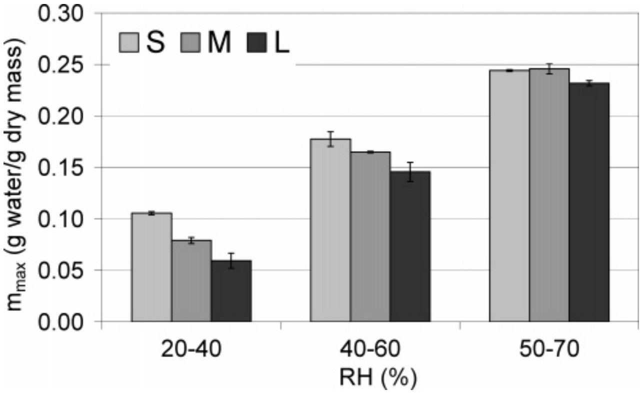

Figure 7. Imaginary maximum water uptake for Soissons bread crust with different particle sizes and for three different RH oscillation ranges.

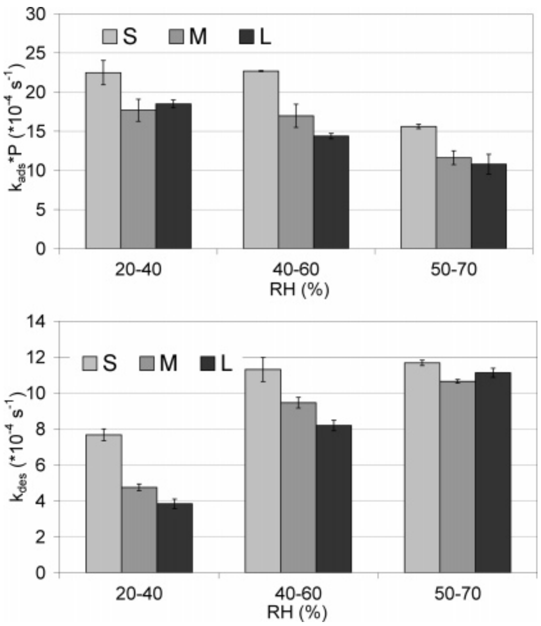

Figure 8. k_{ads}*P for Soissons bread crust of different size and for different RH ranges (**a**) and k_{des} for Soissons bread crust of different size and for different RH ranges (**b**).

for the upward branch. $k_{ads} \times P$ and k_{des} both decrease with increasing particle size. The diffusion distance of water into the particles will be longer for larger-sized particles (average diameter of 0.19 mm as measured with a stereomicroscope) than for smaller-sized particles (approximate average diameter of 0.01 mm); therefore, the water uptake process will go slower for larger particles.

Effect of Oscillation Time. No significant difference was found between oscillation times of 28 and 48 min for any of the parameters (data not shown). That means that all processes that determine the kinetics and average level of water uptake have a characteristic time that is either well below 28 min or is much longer than 48 min. This conclusion is supported by the small size of the hysteresis found when comparing weight change curves at increasing and decreasing RHs (i.e., the upward and downward branches of the oscillations).

DISCUSSION

Our results show that it is possible to obtain new information (Δm_{max}, k_{ads}, and k_{des}) from the combination of an oscillatory sorption test under steady-state conditions and an analysis based on a single-exponential model. The advantage of this method as compared to the generally used Fick's law is that no information is required about geometry and size of the used sample because this information is included in one of the fit parameters of the model. This method allows in principle differentiation between diffusion of water into the matrix and adsorption and transport of water to the surface although we did not see the latter in our experiments.

No influence was found of the oscillation time between 28 and 48 min on parameters considered. Because the product also shows hysteresis, most likely, we may conclude that adsorption and desorption processes at the surface and transport of water to the surface are much faster than the oscillation rates used. This means that diffusion of water into the matrix is the rate-limiting step in the water uptake process. This also confirms one of the assumptions that is made when using Fick's law to describe the diffusion process, instant adsorption of the water to the surface of the product. The use of shorter oscillation times could be of interest, but with our equipment, unfortunately, this is not possible. The Langmuir parameters and Fickian diffusion can be linked together through k_{des}. Desorption is always activated because the particles have to be lifted from the bottom of a potential well (*21*). A higher k_{des} therefore indicates a smaller activation energy for water to jump from one place to another. Diffusion can be thought of as water molecules jumping from one place to another. The jumping distance is determined by the size of the voids/free volume in the system. For example, a glassy system has more voids than a crystal, so faster diffusion (*22*). k_{des} increases with increasing RH in our bread crust particles, thus also suggesting faster diffusion of the water.

Both the adsorption and the desorption rate tend to decrease with increasing particle size. Besides the difference in surface to volume ratio, the smaller particles have a higher water content in the steady state (results not shown), likely due to a higher percentage of the material structurally affected by the penetration of water. Material into which water has penetrated has a higher ability to retain water and a higher water diffusivity. The latter could result in a higher k_{des} and k_{ads} for smaller particles.

Δm_{max} of a smaller-sized sample is larger; the surface area to volume ratio of a smaller sample is also larger, and as above-described, this could increase the amount of water penetrating the sample and thus increase Δm_{max}. Through the parameter Δm_{max}, it is therefore possible to get an indication of the size of the active surface area per unit mass of the sample. The size effect on Δm_{max} is only a factor 2 whereas the average diameter differs by a much larger factor (approximately 10). An earlier study by image analysis (R. H. Tromp, unpublished data) showed that the two-dimensional projections of larger-sized toasted rusk roll crumb particles have a larger perimeter per surface area as compared to smaller particles. In other words, the surface of larger particles is rougher than the surface of smaller particles. This would imply a relatively larger surface area for the larger particles than expected based on their diameter and the assumption of a smooth surface. Such an effect can explain the smaller difference between the Δm_{max} for the different sizes. The dependence of Δm_{max} on RH and particle size indicates that this parameter may be used as a tool to characterize the active sorption sites of particles from different bread sources. It is probably a relevant parameter to describe the difference in the rate of aging due to a change in humidity of bread crust with different ingredients. At higher water contents, the differences between the Δm_{max} for the differently sized particles become smaller. This is probably caused by the fact that at a RH above 60% the assumption that all sorption sites are equal does not hold anymore.

The fact that d*G* is not the same for all sizes indicates that a change in the chemical composition of the sample may have occurred during sieving, although no difference in protein content, starch content, or amount of gelatinized starch (100-RC) was found (**Table 2**). The DSC thermograms of the bread crust particles showed a peak at around 70 °C for all sizes, which is similar to results found before (*23*). There could be a difference in nonstarch polysaccharide content (likely a lower content of nonstarch polysaccharide in the small-sized sample), which could cause a difference in dG. According to Roman-Gutierrez et al. (*24*), pentosans have a relatively high equilibrium water content as compared to other wheat components. To clarify this point, further research needs to be done.

Table 2. DSC Results and Protein Content for Different-Sized Fractions of Soissons Bread Crust Particles

size	relative crystallinity (%)	SD	protein (% dm)	SD	total starch (% dm)	SD
large	23	3.1	10.9		74	1
medium	21	1.0	10.9	0.2	73	1
small	18	2.5	11.0	0.1	ND	

k_{ads} and k_{des} of Soissons bread crust differ for different air RHs (for both the upward and the downward branch) even within one oscillation experiment (**Figure 4a**,**b**). This suggests that the material changes when the water content of the material changes. Because of the water uptake, the material probably swells. This is also indicated by the increase in Δm_{max} with the applied RH range, which indicates an increased number of sorption sites. The variation of k_{ads} and k_{des} with RH could mean that the type or number of sorption sites changes (for example, from highly reactive polar sites on the macromolecule at low RH to binding sites with higher activation energies at higher relative humidities). The change in Gibbs free energy also confirms that a change in the material with a change in RH has occurred.

The hysteresis effect as shown between the upward and the downward branch is not compatible with the absence of an influence of oscillation time on the considered parameters. The latter indicates that at all times the system is in equilibrium, whereas a hysteresis indicates a nonequilibrium. Further research is necessary to clarify this point. Taking smaller ranges of air RH could probably improve the experiment. These findings also indicate that the diffusion is likely not purely Fickian. More likely, the diffusion mechanism lies somewhere between Fickian diffusion (case 1 diffusion) and case 2 diffusion, which also involves matrix relaxation. Case 2 diffusion occurs when the characteristic relaxation processes of the polymer are slower than that of the diffusion process and the diffusion is completely controlled by the polymer relaxation rate. This relaxation of the polymer causes a change in the effective local diffusion coefficient of the diffusing molecules. This behavior is characterized by the presence of a sharp penetrant concentration profile that propagates into the polymer with a constant velocity (*25*). The hysteresis effect also indicates a change in the material. Then, according to Del Nobile et al. (*14*), indeed, an oscillatory sorption test should be used.

It should be noted that the ratio between the $k_{des,upward}$ and the $k_{des,downward}$ is equal for all sizes but changes with RH. This indicates that this parameter may be used as a material property. This ratio is lower at a lower water content (RH 20−40), suggesting a difference in activation energy for the binding of water between the upward and the downward branch. This indicates a more ordered state of the sample as compared to the samples at higher RHs. With a larger part of the material in an ordered state, this hysteresis effect will be larger and the ratio between $k_{des,upward}$ and $k_{des,downward}$ will be further away from 1. This ratio being 1 would mean that the material is behaving as a dilute solution. d*G* was calculated for the bread crust samples at an oscillation time of 48 min (**Figure 6**). This table shows that the Gibbs free energy increases with increasing water content. The Gibbs free energy becomes zero somewhere in the water activity range of 0.5−0.7. This indicates a (generally broad) transition from a more adsorption dominated process to a more dilution dominated process. This water activity range is also the range at which the crispiness of the bread crust is lost (*3*). A positive value, as found at the highest RH, would mean a "negative" adsorption of water or an increase of the pressure of water vapor when it is exposed to a crust of a water activity of around 0.7. As this is unrealistic, it should be concluded that the single-exponential−adsorption approach fails in the high RH regime (RH > 60%) or that there is a change in the process that provides the energy for water adsorption. Most likely, the ordered state of the bread crust at lower relative humidities finally dissolves. The point at which dG equals zero in this respect can be used as a rough indication to determine at which RH the ordered state has disappeared.

As became clear from the results and as can be expected, the conditions that are assumed when using the one exponential approach were not or only approximately met during the process of water uptake by bread crust. However, our approach does provide a framework within which this complicated process can be discussed.

The combination of the single-exponential model approach and an oscillatory sorption tests allowed us to calculate kinetic and thermodynamic parameters at the same time under steady-state or quasi-equilibrium conditions.

The test shows that adsorption and desorption of water to the bread crust particle surface take most likely place on a time scale of the order of minutes. From this, we may conclude that diffusion of water into the solid matrix is the rate-limiting step in the water sorption process. Besides that, a method is developed that enables us to describe water sorption kinetics irrespective of the particle geometry but with the possibility to obtain new information (k_{abs}, k_{des}) about the water sorption process. These rate parameters change with changing size of the particles and with changing water content of the sample and thus may help to understand the water sorption process and can give information on water uptake kinetics and on activation energies, necessary for the water to adsorb to or desorb from the particle. The parameter $k_{\mathrm{des,upward}}/k_{\mathrm{des,downward}}$ can be used to describe material properties since it was shown to be independent of particle size. The use of a simple one-exponential model could be especially convenient for porous products, because it is difficult to determine the surface area of these samples. In this way, it might be possible to compare different ingredient formulations with each other without knowing the exact particle sizes or porosities. The often-used Fick's law to describe the water sorption process, for example, does require this information on surface area. It also appears possible to determine changes in the active sorption area (Δm_{max}) with changing particle size and water content. To validate the method better, it will be necessary to evaluate more different materials. The results for the Gibbs free energy show that our approach cannot be used at a RH above 60% for bread crust particles.

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