12 Water Sorption and Transport in Dry, Crispy Bread Crust

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Abstract

Water-sorption and dynamic properties of bread crust have been studied in gravimetric sorption experiments. Water uptake and loss were measured while relative humidity (RH) was stepwise increased or decreased (isotherm experiment) or varied between two adjusted values (oscillatory experiment). Experimental results were compared with the Fickian diffusion model and empirical models like the exponential and power-law model. The sorption curves that resulted from the isotherm experiments were best described by the Fickian diffusion model for low RH and by the exponential model for high RH. Transport rates depended on moisture content and showed a maximum around RH = 70%. Adsorption and desorption curves from oscillatory experiments were best described by the exponential model. From comparison of the experimental sorption curves and the power-law model for short times it followed for all bread crust that the diffusion coefficient n is close to 1. Normally, this is associated with so-called case II diffusion and water transport that are limited by relaxation of the solid material. However, additional observations suggest that this may not be a valid explanation and that a gradual instead of stepwise change in RH and/or a kinetic barrier for water transfer to the solid matrix may explain the observed exponential behavior.

Introduction

One of the most important factors on which consumers base their appreciation of dry cellular solid-food products is crispness (e.g., see Szczesniak 1971; Roudaut and others 2002; Luyten and others 2004). A dry, crispy product that is in contact with a more humid environment takes up water, and the crispy character is quickly lost when the water activity (a_w) becomes higher than about 0.5 (Labuza and Hyman 1998; Luyten and others 2004; Payne and Labuza 2005). To control crispness and increase the shelf life of composite products that consist of a dry and crispy part and a more humid and soft part, fundamental knowledge about water-sorption dynamics and its dependence on ingredients and morphology is needed. However, water sorption in these products is complex and governed by various phenomena like migration of water vapor through mesoscopic open pores and microscopic capillaries, sorption and migration of water through the solid matrix, swelling and/or relaxation of the matrix, and hysteresis.

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Most models that describe sorption dynamics in polymeric porous systems are based on diffusion (for a review, see Masaro and Zhu 1999). Two extreme cases can be distinguished in the literature: (a) *Fickian diffusion*, where the transport of a penetrant like water is controlled by its concentration gradient, and the dynamics can be described by Fick's law; and (b) *case II diffusion*, where transport is controlled by the relaxation of the solid material. When sorption dynamics are controlled by both processes and the corresponding rates are similar, this is called *anomalous diffusion*. A way to distinguish between the sorption mechanisms is by analyzing the uptake behavior for short times. Then, Fickian diffusion behaves like $t^{0.5}$, case II like t^1, and anomalous diffusion like t^n with $0.5 < n < 1$.

Various studies have been published about the sorption behavior in biopolymeric systems. Fickian diffusion including a water concentration–dependent diffusion coefficient was used to describe sorption dynamics of sponge cake (Guillard and others 2003), dry biscuit (Guillard and others 2004), and waxy maize starch (Enrione and others 2007). A single exponential was used to describe the sorption kinetics of wheat flours (Roman-Gutierrez and others 2002). For chitosan films, diffusion seems Fickian for $a_w < 0.4$ and anomalous for $a_w > 0.4$ (Despond and others 2001). Del Nobile and coworkers developed a model where Fickian diffusion, including a concentration-dependent diffusivity, and polymer relaxation were combined to describe sorption dynamics of spaghetti and films of nylon, chitosan, alginate, casein, and zein (Del Nobile and others 1997, 2000, 2003a, 2003b, 2004; Buonocore and others 2005). These studies gained much insight, but fundamental generic knowledge that enables crispness to be controlled is still lacking. Furthermore, no studies have been published about the sorption dynamics of crispy bread crust. Therefore, to obtain more insight into the water-sorption mechanisms and dynamics of bread crust, we conducted a detailed study. Gravimetric stepwise oscillatory and isotherm sorption experiments on model bread crusts were performed and compared with different sorption models like Fickian diffusion, the exponential model, and the power-law model.

Materials and Methods

Sorption experiments were performed on model bread crusts and crusts of a rusk roll. Model bread crusts were obtained by baking thin sheets of dough (diameter, 60 mm; and thickness, 2 mm) in a halogen heater. Dough was prepared from a protein-rich and starch-rich wind-sifted fraction of wheat flour. Rusk roll crusts were removed from rolls prepared from wheat flour and baked in an oven. Crust samples were milled and sieved afterward in three different fractions with sizes smaller than 63 μm, between 63 and 250 μm, and between 250 and 500 μm (called small, medium, and large, respectively). Gravimetric sorption experiments were performed on about 6 mg of these fractions by using a VTI-SGA 100 symmetric vapor-sorption analyzer (VTI, Hialeah, FL, USA) at a temperature T of 25°C. Samples were dried above phosphorus pentoxide for at least 3 days. Before sorption experiments started, a drying step was performed for 2 h at 50°C. Starch, protein, pentosan, and fat contents were also determined. A detailed description of the sample preparation and experimental methods,

as well as the results of the ingredient analysis, can be found elsewhere (van Nieuwenhuijzen and others 2007, 2008).

Models

For Fickian diffusion, the weight change as a function of time t for a spherical particle having radius r_s, initially having a homogeneous water concentration C_0, a constant surface concentration C_s, and a diffusion coefficient D independent of concentration C is given by Crank (1975).

$$m - m_0 = (m_\infty - m_0)\left(1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-D n^2\pi^2 t/r_s^2\right)\right) \tag{12.1}$$

with $m = m_t$ and $m_i = M_0 + \int C_i dr$ (for i = t, 0, ∞) and M_0 as the mass of the dry particle. This equation is fitted against experimental sorption curves, with D/r_s^2 and m_∞ as fit parameters. For all analysis, the first minute of the experimental sorption curve was excluded from the fit because during this time the system needs to settle after a sudden change in relative humidity (RH) and environmental conditions are uncertain. Furthermore, it is assumed that diffusion through the vapor phase is not limiting because the water diffusion coefficient in air is more than 5 orders of magnitude larger than that of the solid matrix.

Sorption dynamics are also compared with single exponential behavior, where the weight change as function of time is described by

$$m - m_0 = (m_\infty - m_0)(1 - \exp(-kt)) \tag{12.2}$$

with k the transport rate. Here k and m_∞ are fit parameters. Exponential behavior may be used to describe the relaxation dynamics of the polymeric matrix (Berens and Hopfenberg 1978).

For short times, sorption dynamics may also be described by the empirical power-law relation

$$m - m_0 = at^n \tag{12.3}$$

where the "a" is a constant and the n is the diffusion exponent. In the short time limit, the diffusion exponent n is evaluated from the sorption curves plotted on a log-log scale and is equal to the derivative of the first linear part in that plot. When $n = 0.5$, $n = 1$, or $0.5 < n < 1$, the sorption mechanism is said to be Fickian, case II, or anomalous, respectively. Calculations were performed using Matlab (MathWorks, Natick, MA, USA).

Results and Discussion

Figure 12.1a shows a typical example of the relative change in weight of bread crust (in this case, a starch-rich model crust, large fraction) together with the RH as
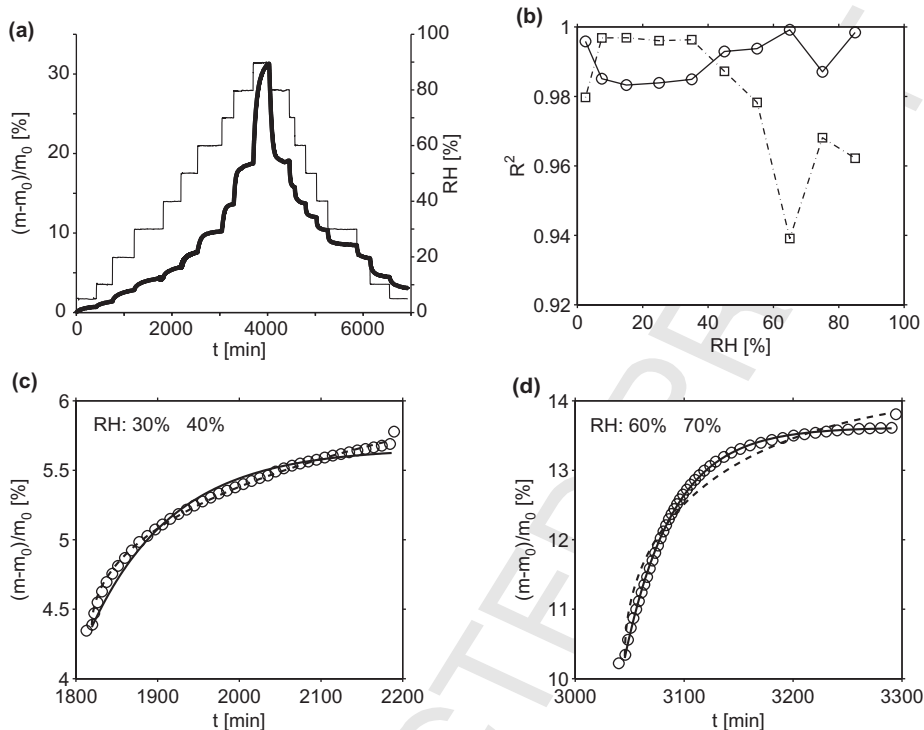
Figure 12.1. **(a)** Measured relative change in weight $(m - m_0)/m_0$ (*thick line*, left axis) of a starch-rich model crust and the adjusted external relative humidity (RH) (*thin line*, right axis) as a function of time t during an isotherm experiment. **(b)** R^2 of the best fit between the measured $(m - m_0)/m_0$ and the diffusion model (Equation 12.1, *open squares*) and single exponential (Equation 12.2, *open circles*) as a function of RH. **(c)** Enlargement of an adsorption curve (*open circles*) and the best fit of the diffusion model (Equation 12.1, *dashed line*) and single exponential model (Equation 12.2, *continuous line*) as a function of t. The external RH changed from 30% to 40%. **(d)** Similar, but RH changed from 60% to 70%.

a function of t. The sorption curves for each step were analyzed and fitted against the sorption models described earlier. Equilibrium values $(m_\infty - m_0)/m_0$ yield the isotherm. For all bread crusts, isotherms showed hysteresis and were best described by the Guggenheim-Anderson-de Boer (GAB) equation. This corresponds well with what has been observed for most food systems (Basu and others 2006). The diffusion exponent n (Equation 12.3) turned out to be close to 1, suggesting the sorption mechanism to be case II and controlled by the relaxation rate of the polymeric matrix.

Figure 12.1c and d show examples of adsorption curves for two RH steps. Also, the best fits of the diffusion model (Equation 12.1) and the exponential model (Equation 12.2) are shown. Comparison between experimental and simulated sorption curves

shows that water sorption in the low-moisture regime is better described by the Fickian diffusion equation, whereas in the high moisture regime it may better be described by an exponential. This is also illustrated in Figure 12.1b, where the R^2 of the fits is plotted for the adsorption curves as a function of RH. It is seen that the transition point is around RH = 40%. This is similar to results found for chitosan films (Despond and others 2001) and waxy maize systems (Enrione and others 2007), although in those cases based on evaluation of the diffusion exponent n.

For the desorption curves, similar behavior is found, only the change in going from more exponential to diffusive behavior is around RH = 60% (results not shown).

Figure 12.2 (left) shows the sorption rates k obtained from the fits by using a single exponential as a function of RH. Also, diffusion coefficients D are shown (right) obtained from the fits by using the Fickian diffusion model and assuming a particle radius $r_s = 190\,\mu$m. The figure shows that water-adsorption rates increase with RH up to a value of about 70% and decrease at higher RH. Similar behavior is observed for the other bread crust samples (results not shown) and has also been observed for other food systems (Guillard and others 2003, 2004; Enrione and others 2007). The increase in transport rate may be associated with an increase in free volume due to the plasticizing effect of water. The decrease at high humidities may be attributed to capillary condensation and/or, more likely, to collapse and caking of the polymeric structure due to a transition from the glassy state to the rubbery state. For the bread crusts, this transition occurs at room temperature at about RH = 80% (van Nieuwenhuijzen and others 2008). Collapse might result in a reduction of the effective area exposed to the solvent and therefore a decrease in sorption rate.
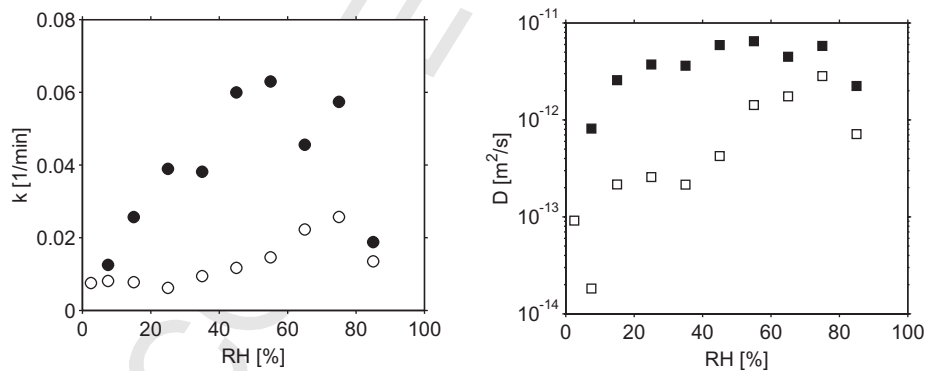

Figure 12.2. **(Left)** Adsorption rates (*open circles*) and desorption rates (*solid circles*) k obtained from the best fits between the relative change of weight of a starch-rich model crust during the isotherm experiment shown in Figure 12.1A and the single exponential model (Equation 12.2) as a function of relative humidity (RH). **(Right)** Effective diffusion coefficients D during adsorption (*open squares*) and desorption (*solid squares*) obtained from the best fits of the Fickian diffusion model (Equation 12.1) assuming $r_s = 190\,\mu$m.
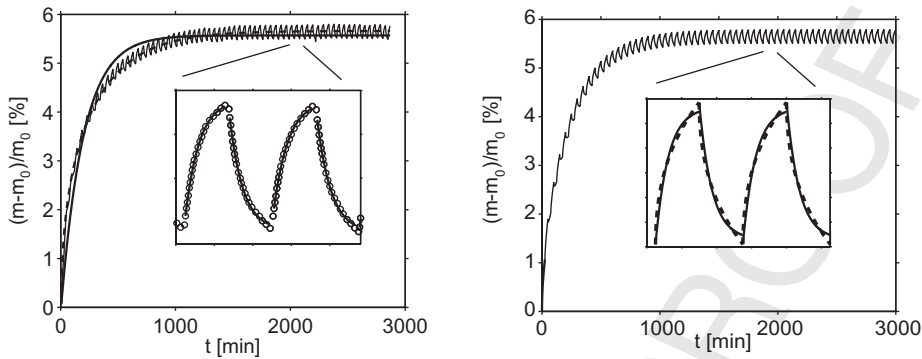
Figure 12.3. **(Left)** Measured relative change in weight $(m - m_0)/m_0$ (*thin line*) of a starch-rich model crust because of an oscillatory stepwise change in adjusted relative humidity from 40% to 50% and the best fit of the diffusion model (Equation 12.1, *dashed line*) and single exponential model (Equation 12.2, *continuous line*) as a function of time *t*. *Inset:* Examples of experimental sorption curves (*open circles*) and best fits of the single exponential model. **(Right)** Simulated moisture uptake obtained by numerically solving the diffusion equation ($D = 10^{-12} \, m^2/s$, $r_s = 190 \, \mu m$) and an oscillatory stepwise change of surface concentration C_s between 4.4% and 6.1%. *Inset:* Calculated sorption curves (*dashed line*) and best fit of the single exponential model (*continuous line*).

For all RHs, desorption rates are found to be higher than adsorption rates. An explanation is that water-diffusion rates are higher than matrix relaxation rates so that during desorption, when the matrix is already swollen, the water transport is not limited by the matrix relaxation. However, then Fickian diffusion with $n \approx 0.5$ is expected for the desorption steps, which is contrary to what is found in our study. It is also observed that the maximum desorption rate is at a lower RH than that of adsorption. This might be due to the hysteresis that shifts the glass-rubber transition to a lower RH.

Figure 12.3 (left) shows a typical example of an oscillatory sorption experiment on bread crust. Here the relative moisture uptake is shown as a function of time for a starch-rich model crust (large fraction). The initially dry sample was exposed to an RH stepwise varying between 40% and 50% with an oscillation time of 25 min. It is seen that the moisture uptake seems to be a sum of a smooth curve that increases from zero to an equilibrium value and an oscillating one with the same frequency as the changes in RH. The figure also shows the best fits of the overall curve with the diffusion model (Equation 12.1) and the exponential model (Equation 12.2). The diffusion model turned out to describe the overall sorption curve best for low RH (oscillating between 40%–50% and 50%–60%) and the exponential model for higher RH (oscillating between 60%–70% and 70%–80%). This trend is similar to that found for the isotherm measurements. The fitted rate values are about a factor of 2 smaller than the rates found for the isotherm measurements because of the strong positive relation

between transport rates and moisture content. This causes an effective lower transport rate for the oscillatory experiments because the time-averaged moisture content of the crust particles during adsorption is lower compared to that during the isotherm measurements. The fitted equilibrium values correspond well to the adsorption branch of the isotherm.

The inset in the left pane of Figure 12.3 shows the relative moisture uptake during an adsorption step and the best fit of the exponential model (Equation 12.2). All oscillatory experiments on bread crusts show that the diffusion exponent n is about 1 for all adsorption and desorption curves. Furthermore, all single sorption curves could be very well described by a single exponential ($R^2 > 0.98$) and did not show the characteristic Fickian behavior with $n = 0.5$. This might be because during an oscillatory experiment the system is never in equilibrium and the moisture content at t_0, when RH switches, is not homogeneously distributed. Thus, Equation 12.1 is not valid for describing the sorption curves of the oscillatory experiments. To check whether the exponential behavior is caused by the system not being in equilibrium when RH switches, we solved the diffusion equation numerically for a spherical particle with radius $r_s = 190 \mu m$, initially dry ($m_{t=0} = m_0$), and a stepwise oscillating surface concentration C_S between 4.4% and 6.1% with an oscillation time of 25 min. Figure 12.3 (right) shows the results for a constant $D = 10^{-12} m^2/s$. At first sight, there is a good correspondence between experimental and simulated water uptake. However, the simulated sorption curves for each oscillating step show the typical Fickian $n \approx 0.5$ behavior, and bad correspondence is observed with a single exponential function, as can be seen in the inset in the figure. Calculations using a moisture-dependent diffusion coefficient taken from the isotherm measurements (Figure 12.2) show similar results and cannot explain the experimentally observed exponential behavior. Table 12.1 summarizes results of the comparisons between experiments, simulations, and model fitting.

Figure 12.4 shows the mean sorption rates of starch-rich model crust during oscillatory sorption experiments in the stationary regime as a function of RH. Sorption rates k_{osc} are obtained from best fits between experimental sorption curves and the single exponential model (Equation 12.2) for each oscillation step. The oscillatory

Table 12.1. Summary of fitted diffusional coefficient (*n*) and goodness of fits of the diffusion (D model) and exponential model (E model), for low and high relative humidity (RH), isotherm and oscillatory experiments, as well as isotherm and oscillatory simulation of Fickian diffusion in a sphere

RH	Experimental				Simulation			
	Isotherm		Oscillation		Isotherm		Oscillation	
	Low	High	Low	High	Low	High	Low	High
D model	+	−	−	−	++	++	++	++
E model	−	+	+	+	−	−	−	−
n	~1	~1	~1	~1	~0.5	~0.5	~0.5	~0.5

++, +, and − correspond to $R^2 \approx 1$, ≈0.99, and <0.98, respectively.
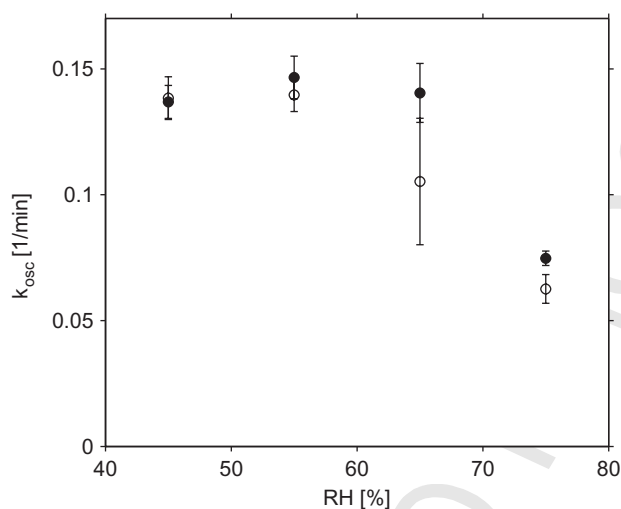
Figure 12.4. Adsorption rates (*open circles*) and desorption rates (*solid circles*) k_{osc} of a starch-rich model crust during oscillatory sorption experiments. Mean values and indicated standard deviations are calculated from 20 fitted values after the stationary state has been reached. RH, relative humidity.

sorption rates are about a factor 10 larger than those obtained from the isotherm experiments. This is because, during oscillating RH, the moisture concentration varies only in an outer part of the particle while the inner part stays more or less constant at the time-averaged value. This can be seen effectively as a reduction in the particle radius, which results in an increase in the sorption rate. Sorption rates of an oscillatory sorption experiment are positively related to the oscillation frequency. The observation that the maximum in the sorption rates is shifted toward lower RH with respect to that found in the isotherm experiments is not fully understood yet but may be related to differences in the relaxation state of the solid matrix. During the oscillatory experiments, the participating part of the matrix will probably be more relaxed than during isotherm adsorption experiments. It is therefore expected that, during oscillatory sorption experiments, water migration will not be limited by the polymer matrix relaxation. This would imply a Fickian behavior instead of the experimentally observed exponential one.

From the aforementioned observations, no definite conclusion about the sorption mechanism of food systems can be drawn. Certain observations even seem contradictory. For example, for the bread crusts, $n \approx 1$ for all humilities is found, suggesting water transport limited by matrix relaxation processes. For a system in the glassy state (low RH), this might be expected. However, this is contrary to the Fickian $n \approx 0.5$ behavior found for chitosan and waxy maize for $a_w < 0.4$. It is also expected that, for the stationary regime in an oscillatory experiment, the water transport rate is not limited by the relaxation rate, contrary to the exponential ($n = 1$) behavior that is

found. The same holds for desorption from the rubbery state. However, the association of Fickian behavior with $n = 0.5$ is based on the assumption that the particle surface is continuously in equilibrium with the surrounding air. It might, however, very well be that this assumption is invalid and that a sorption barrier or external resistance for water transfer exists between the air and solid matrix. This is also observed for water sorption in biscuits (Guillard and others 2004) and can account for the observed exponential behavior (Meinders and van Vliet 2009). This is also supported by the more surface-sensitive oscillatory experiments that show exponential behavior for all sorption curves. Crust particles are also not spherical and monodispersely distributed but are cellular porous systems with irregular shapes and sizes, which also might have considerable effects on the estimation of the diffusion constant n (Peppas and Brannon-Peppas 1994). Furthermore, n is determined from sorption curves at small t after a stepwise change in RH, at which experimental environmental conditions may be uncertain.

Conclusion

Water-sorption curves of isotherm experiments, where the RH was stepwise increased or decreased, could be best described by the Fickian diffusion model for low RH and by the exponential model for higher RH. Transport rates depend strongly on moisture content and show a maximum around RH = 70%. For all RHs, desorption rates are found to be higher than adsorption rates. Moisture-uptake curves from oscillatory experiments are a sum of (a) a smooth curve increasing from zero to an equilibrium value and (b) alternating adsorption and desorption curves oscillating with the same frequency as RH. The smooth curve shows similar behavior to those measured during isotherm measurements. The oscillatory adsorption and desorption curves could be best described by the exponential model. All sorption curves behave for small times as t^1, which is normally associated to so-called case II diffusion. This suggests that water transport is limited by relaxation of the solid material. However, this association may be invalid, and more information concerning the time dependency of moisture profiles in the solid material, matrix relaxation rates, available free volumes, and morphology is needed to reach a firm conclusion about the sorption mechanism of cellular solid-food systems.

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