Determination of the Bulk Moisture Diffusion Coefficient for Corn Starch Using an Automated Water Sorption Instrument

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The bulk moisture diffusion coefficient (D_b) is an important physical parameter of food ingredients and systems. However, the traditional method of measuring D_b using saturated salt solutions is very time-consuming and cumbersome. New automated water sorption instruments, which can be used to conveniently and precisely control both relative humidity and temperature, provide a faster, more robust method for collecting the data needed for determining D_b. Thus, the objectives of this study were to (1) investigate the use of the DVS instrument for collecting the data needed for determining the adsorption (D_{ba}) and desorption (D_{bd}) bulk moisture diffusion coefficients for dent corn starch as a function of relative humidity and (2) determine the effect of temperature on D_{ba} for dent corn starch at a constant relative humidity. Kinetic water sorption profiles of dent corn starch were obtained at eight relative humidity values ranging from 10 to 80% at 10% intervals at 25 °C and at five temperatures, 15, 20, 25, 30, and 35 °C, at 50% relative humidity using a DVS instrument. D_b was calculated from the kinetic water sorption profiles using the full solution of Fick's second law for the thin slab model, as well as the slope method, a simplification of the full model. The D_{ba} of dent corn starch at 25 °C reached a maximum at intermediate relative humidity values, after which D_{ba} decreased due to a change in the moisture diffusion mechanism from vapor to liquid diffusion. The D_{bd} of dent corn starch at 25 °C remained nearly constant as a function of relative humidity. The D_{ba} for dent corn starch increased as temperature increased from 15 to 35 °C, with an activation energy of 38.85 ± 0.433 kJ/mol.

KEYWORDS: Moisture diffusion coefficient; corn starch; dynamic vapor sorption; relative humidity

INTRODUCTION

One of the most important physical phenomena occurring in foods during processing and storage is water transfer. This could be the diffusion of water inside the food or moisture transfer between the food and the surrounding environment, during processing as well as storage. Thus, the moisture diffusion coefficient is an important physical parameter of food materials, useful for determining the rate of water transfer and modeling

of various food-processing operations, such as estimation of drying times in the falling rate period (*1*).

There are two basic types of diffusion. The first is random and uncoordinated molecule motion, often referred to as Brownian motion or self-diffusion. The self-diffusion coefficient of water at the molecular level is commonly measured using pulsed field gradient nuclear magnetic resonance (NMR) spectroscopy and imaging (MRI) (*2–5*). The second type of diffusion, and the one of focus in this paper, is directional and concerted molecule motion attributed to the presence of a driving force (e.g., differences in chemical potential), often referred to as flow or bulk diffusion.

Determination of the bulk moisture diffusion coefficient (D_b) of water in food materials is commonly obtained from kinetic data from three processes: drying, sorption, and permeation (*6*). The first two processes are applicable to various food shapes, whereas permeation (or permeability) is mainly applicable to films (*7*). Obtaining D_b from drying data (i.e., moisture loss

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Table 1. Comparison between the Saturated Salt Solution Method and the DVS Instrument for Collecting Data for Determining the Bulk Moisture Diffusion Coefficient

exptl feature	saturated salt solution method	DVS instrument
av sample size	1–2 g	5–100 mg
expt time	weeks to months	days
expt design	less flexible; discrete relative humidity values dependent on salts selected and exptl temperature	more flexible relative humidity and temperature control; can obtain absorption and desorption data on the same sample in a short time
air flow	static to slow movement with use of a fan or stir bar inside the chamber	dynamic; air continuously flows past the sample
data collection	wt measurements disturb the environmental relative humidity; fewer, discrete data points	wt measurements do not disturb environmental relative humidity; numerous, nearly continuous data points (e.g., 30–60 s intervals)
labor	more labor intensive (periodic weighing of samples for weeks to months)	less labor intensive (instrument weights sample)
cost	low	high

over time at elevated temperatures) is the most commonly investigated process (*1, 6, 8–10*).

A lesser utilized process for obtaining D_b, and the one investigated in this paper, is the sorption process [i.e., gain (adsorption) or loss (desorption) of water over time via equilibration of test material to various relative humidity values at constant temperature]. Lomauro and others (*11*), using Petri dishes containing saturated salt solutions to control relative humidity, measured the D_b of dry and semimoist foods, such as flour, shredded wheat, dry milk, and raisin cookies, and some freeze-dried products at 25 ± 1 °C. The sorption data were obtained by weighing these samples with initial weights of 1.0–1.3 g at 1-week intervals until equilibrium was reached. Most of the food samples reached equilibrium within 1 month on the basis of the criterion of no more than a 0.5% dry basis moisture content difference over three successive readings taken at 1-week intervals. Similarly, Steckel and others (*12*) used relative humidity rooms to study moisture diffusion properties of various wood-flour materials at 65 and 85% relative humidity (RH) at 20 °C. Adsorption data collection at 85% RH lasted 130 days. In general, equilibrating samples to relative humidity values using saturated salt solutions or relative humidity rooms requires long data collection times and cumbersome and time-consuming weight measurements.

New automated water sorption instruments, which can be used to conveniently and precisely control both relative humidity and temperature, provide a faster, more robust method for determining D_b compared to the traditional saturated salt solution technique. Commercially available automatic water sorption instruments include, the Dynamic Vapor Sorption (DVS) instrument from Surface Measurement Systems Ltd., the IGA*sorp* from Hiden Analytical, the SGA-100 Symmetric Gravimetric Analyzer from VTI Corp., the Cisorp Water Sorption Analyzer from C. I. Electronics Ltd., the Q5000SA from TA Instruments, and the AquaSorp from Decagon Devices. Compared to the saturated salt solution method, these instruments offer many advantages. A comparison between the saturated salt solution method and the DVS instrument is given in **Table 1**.

Only a few researchers have utilized these new automated water sorption instruments for obtaining the sorption data needed for calculating D_b. Roman-Gutierrez and others (*13*) used the DVS instrument to collect adsorption data used to determine the moisture diffusion coefficient of wheat flour samples placed on a DVS flat video pan. (Pan type information was obtained from the corresponding author via e-mail.) They used the full polydisperse sphere model derived from Fick's second law to determine D_b. Burnett and others (*14*) used the DVS instrument to collect adsorption data used to determine the moisture

diffusion coefficient of proton exchange membranes contained in a DVS mesh pan. They used the simplified thin slab model (for short times) derived from Fick's second law to determine D_b. Roca and others (*15*) investigated the impact of porosity and fat content of sponge cakes (pan type used not specified) on water vapor diffusion using the DVS. They used a numerical solution of Fick's second law to determine D_b. Enrione and others (*16*) studied the water vapor sorption and diffusion characteristics of thermomechanically extruded waxy maize starch and glycerol samples (pan type used not specified). They used a simplified spherical diffusion model (for short times) derived from Fick's second law to determine D_b.

These studies used different mathematical models to calculate D_b. Selection of the appropriate mathematical model for calculating the bulk moisture diffusion coefficients is dependent upon the type and geometry of the sample, the type of DVS pan used, and the diffusion mechanism (case I or case II diffusion), which is influenced by the experimental conditions, most importantly, relative humidity and temperature. More research is needed to explore the determination of the bulk moisture diffusion coefficient using these new automatic water sorption instruments.

Thus, the objectives of this study were to (1) investigate the use of the DVS instrument for collecting the data needed for determining the adsorption (D_{ba}) and desorption (D_{bd}) bulk moisture diffusion coefficients for dent corn starch as a function of relative humidity and (2) determine the effect of temperature on D_{ba} for dent corn starch at a constant relative humidity. As part of objective 1, this study examined using the full solution of Fick's second law for the thin slab model, as well as the slope method, a simplification of the full model.

MATERIALS AND METHODS

Sample. Dent corn starch (lot SF2M3244A) was provided by Tate & Lyle (Decatur, IL). Native dent corn starch, such as that used in this study, exists as semicrystalline granules and is composed of approximately 25% amylose and 75% amylopectin (*17*). Native dent corn starch granules range in size from approximately 2 to 34 μm (*18*). Approximately 70% of the mass of the starch granule is regarded as amorphous and 30% as crystalline in nature (*19*). The amorphous regions contain essentially linear amylose and branching points of amylopectin, whereas the crystalline regions consist primarily of amylopectin (*19*).

The "as is" moisture content of the dent corn starch was 0.088 ± 0.0002 g of water/g of sample, determined by placing triplicate samples in a vacuum oven at 60 °C at 30 in Hg for 24 h. The "as is" water activity value of the dent corn starch at 25 °C was 0.370 ± 0.001, determined in triplicate using the AquaLab Series 3TE Water Activity Meter (Decagon Devices, Pullman, WA).

Kinetic Water Sorption Profiles. Kinetic water sorption profiles of dent corn starch were obtained at eight relative humidity values ranging from 10 to 80% at 10% intervals at 25 °C and at five temperatures, 15, 20, 25, 30, and 35 °C, at 50% RH using a DVS 2000 instrument (Surface Measurements Systems, London, U.K.). The precision (calculated as the standard deviation) of the DVS relative humidity and temperature control for the sample chamber was found to be similar for all relative humidity values and for all temperatures investigated and, on average, was <±0.5% RH and <±0.1 °C, respectively.

The DVS sorption automatic operation (SAO) method was used to set both the desired percent relative humidity steps and the equilibrium criterion. First, each sample was equilibrated to 0% RH using an equilibrium criterion of a change in mass over time (called d_m/d_t) of no greater than 0.0005% for 5 consecutive minutes. After this equilibrium criterion was reached at 0% RH, the relative humidity was increased automatically to the target value and equilibrated using the same d_m/d_t criterion (0.0005% for 5 consecutive minutes); then the relative humidity was decreased to 0% RH using a d_m/d_t criterion of 0.01% for 5 consecutive minutes. Sample mass data and sample and reference chamber relative humidity and temperature data were automatically collected every 60 s. A new sample was used for each relative humidity and temperature experimental run. A 60.0 ± 10 mg native dent corn starch sample was placed in a DVS quartz round-bottom sample pan (13 mm in diameter). The starch sample was evenly distributed and lightly compressed in the DVS pan by tapping the bottom of the DVS, a few times, on the laboratory bench surface, forming a thin layer of native dent corn starch with an average thickness across the pan of 2.3 ± 0.1 mm. Total gas flow was parallel to the sample surface and was set at 500 cm³/min for all experiments. Duplicate runs were done for each treatment.

Determination of the Bulk Moisture Diffusion Coefficient. The bulk moisture diffusion coefficient can be determined from Fick's second law using the water content gradient as the potential for mass transfer through a unit area of a section (20)

$$F = -D\frac{\partial C}{\partial x} \qquad (1)$$

where F is the mass flow of water per unit area (kg/s × 1/m²), D is the diffusion coefficient (m²/s), C is the water concentration (kg/m³), and x is the distance (m) in the flow direction. The moisture diffusion coefficient can be obtained by solving Fick's second law for the applicable experimental conditions.

Even though the native dent corn starch examined in this study is composed of individual spherical particles (granules), when placed together en masse on the DVS pan, they formed a thin slab with moisture diffusion occurring via the top exposed planar surface. It is important to note that spherical diffusion should be used if the starch granules were distributed more or less individually on the DVS pan and the resultant moisture diffusion was radial. For the experimental conditions studied here, the moisture diffusion coefficient can be calculated by numerically solving Fick's second law for one-dimensional, isothermal penetrate (water) diffusion into (adsorption) or out of (desorption) a thin slab of hydrophilic polymer (starch). Additional assumptions include that (1) D is constant for a given sorption experiment, (2) swelling (or shrinkage) during adsorption (or desorption) is negligible, and (3) the native dent corn starch sample is homogeneous. Equation 1 for the thin slab model may be written as (20)
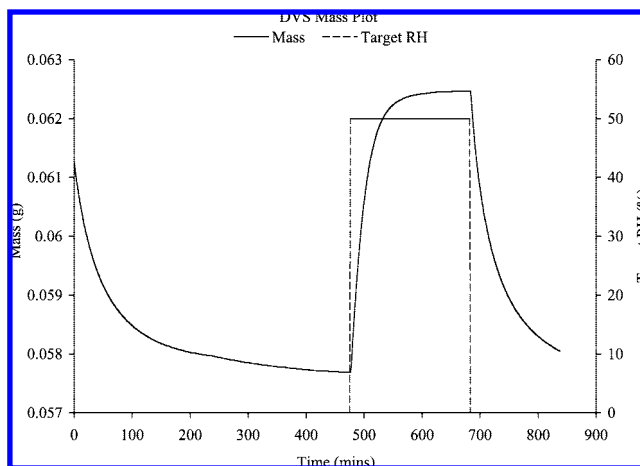
$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (2)$$

The appropriate initial and boundary conditions for the thin slab model used in this study were

initial condition: at $t = 0$, $C = C_0$ for $0 < x < l$

boundary condition: at $t > 0$, $C = C_1$ for $x = l$ and $\partial C/\partial x = 0$ for $x = 0$

where t is time, l is the sample thickness, C is the water concentration,

Figure 1. Example kinetic water sorption profile for dent corn starch. The "as is" dent corn starch sample was first equilibrated to 0% RH (initial sample equilibration to a moisture content close to zero), then equilibrated to 50% RH (adsorption step), and then equilibrated back to 0% RH (desorption step) again, with all steps being carried out at 25 °C.

C_0 is the initial uniform water concentration, and C_1 is the constant water concentration at the surface. The initial and boundary conditions specified above correspond to typical conditions found in gravimetric sorption experiments, where the sample is contained in a sample holder and water sorption is occurring via the top surface (one side) of the sample.

The solution to Fick's second law in the form of a trigonometric series for the above specified conditions is (20)

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}\exp\left[\frac{-D(2n+1)^2\pi^2 t}{4l^2}\right] \qquad (3)$$

where M_t is defined as the mass of water uptake at time t, M_∞ is the mass of water uptake as time approaches infinity (note that moisture contents can also be used for M_t and M_∞), and n are integers. Equation 3 is referred to in this paper as the full-fit method for the infinite thin slab model.

When $M_t/M_\infty < 0.60$, eq 3 can be simplified to (20, 21)

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{\pi l^2}\right)^{1/2} \qquad (4)$$

Equation 4 in this paper is referred as the slope method for the infinite thin slab model. Equations 3 and 4 were used to calculate the adsorption bulk moisture diffusion coefficient (D_{ba}).

Similarly, to calculate the desorption bulk moisture diffusion coefficient (D_{bd}), eqs 3 and 4 were modified to yield eqs 5 and 6, respectively, so the moisture loss during desorption can be expressed similarly to the moisture gain during the adsorption process

$$\frac{X_t - X_e}{X_0 - X_e} = \sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}\exp\left[\frac{-D(2n+1)\pi^2 t}{4l^2}\right] \qquad (5)$$

$$\frac{X_t - X_e}{X_0 - X_e} = 1 - 2\left(\frac{Dt}{\pi l^2}\right)^{1/2} \qquad (6)$$

where X_0, X_t, and X_e are the sample moisture contents at time 0, time t, and equilibrium, respectively.

Sample D_b Calculations. To illustrate the bulk adsorption (D_{ba}) and desorption (D_{bd}) moisture diffusion coefficient calculation procedure using eqs 3 and 4 and 5 and 6, respectively, example calculations are given below using one of the kinetic water sorption profiles for dent corn starch at 50% RH (**Figure 1**). The "as is" dent corn starch sample was first equilibrated to 0% RH (initial sample equilibration to a moisture content near zero), then equilibrated to 50% RH (adsorption

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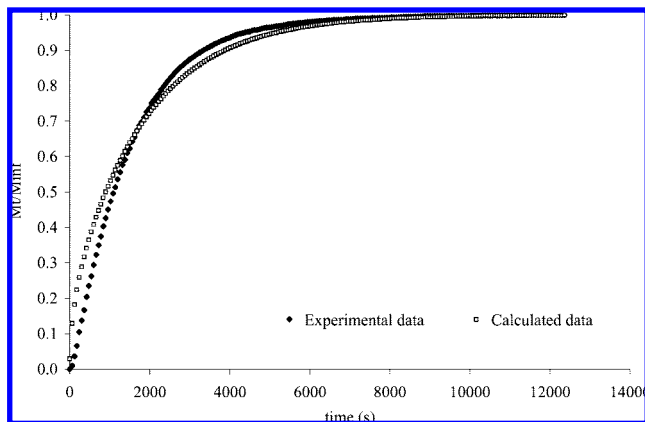
Figure 2. M_t/M_∞ values plotted as a function of time in seconds for dent corn starch adsorption of moisture from 0 to 50% RH at 25 °C.
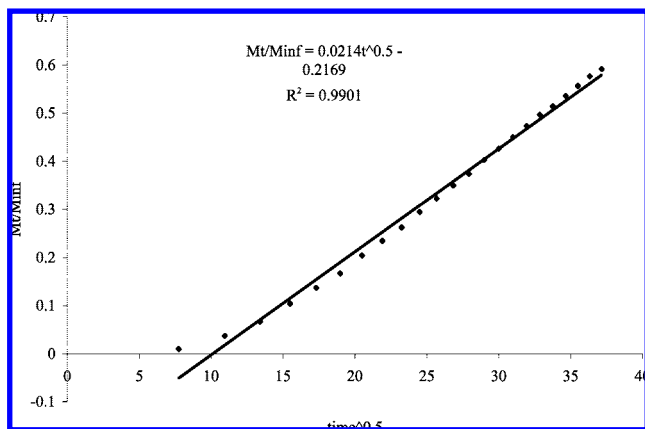
Figure 3. M_t/M_∞ values < 0.60 plotted as a function of the square root of time, with time in seconds, for dent corn starch adsorption of moisture from 0 to 50% RH at 25 °C.

Figure 4. $(X_t - X_e)/(X_0 - X_e)$ values plotted as a function of time in seconds for dent corn starch desorption of moisture from 0 to 50% RH at 25 °C.

Figure 5. $(X_t - X_e)/(X_0 - X_e)$ values < 1.0 and > 0.40 plotted as function of the square root of time, with time in seconds, for dent corn starch desorption of moisture from 0 to 50% RH at 25 °C.

step), and then equilibrated back to 0% RH (desorption step), with all steps being carried out at 25 °C.

As shown in **Figure 1**, once the sample was exposed to 50% RH, the sample mass began increasing due to moisture sorption. The beginning of sorption (time = t_0 and mass of water uptake = 0) was assigned when the relative humidity of the sample chamber initially switched from 0% RH to the target relative humidity (in this case 50% RH). On average, it took approximately 2 min for the system to reach 97.5% of the target relative humidity. For the example shown in **Figure 1** t_0 began at 476 min (marked as adsorption time = 0 s), the initial mass of the sample (weight of the dry starch) was 0.0577 g (with 0 g of water uptake and 0 moisture content), and the final equilibrium mass of the sample was 0.0625 g [and was reached at 682 min ($\sim t_\infty$) when d_m/d_t was <0.0005% for 5 min] with M_∞ equal to 0.0048 g of water uptake (or 0.0832 g of water/g of dry starch).

Calculations for D_{ba} Using the Full-Fit Method (Equation 3). D_{ba} was calculated by minimizing the sum of squares error (SSE) between the experimental (**Figure 2**) and the predicted (calculated using eq 3) moisture content values using the solver function in Microsoft Excel. For the example, $D_{ba} = 11.56 \times 10^{-10}$ m²/s.

Calculations for D_{ba} Using the Slope Method (Equation 4). Experimental values of M_t/M_∞ < 0.6 were plotted as a function of the square root of time in seconds and are shown in **Figure 3**, along with the linear fit and resultant equation. Substituting the value of the slope from **Figure 3** into eq 4 and solving for D yields $D_{ba} = (0.0214)^2 \pi l^2/4$; therefore, $D_{ba} = 19.03 \times 10^{-10}$ m²/s with $l = 0.0023$ m.

Calculations for D_{bd} Using the Full-Fit Method (Equation 5). Because the equilibrium criterion, d_m/d_t, for the desorption step was larger than the d_m/d_t for the adsorption step, the desorption step equilibrium was not fully reached. To compensate for this difference, the equilibrium sample mass of the desorption step was assigned to be the same as the initial sample mass of the adsorption step (after the
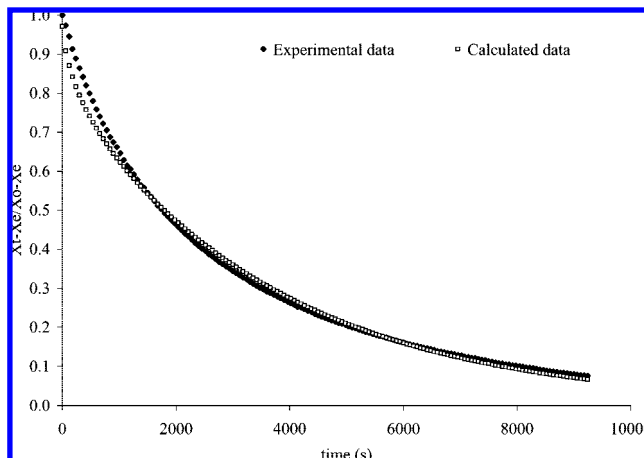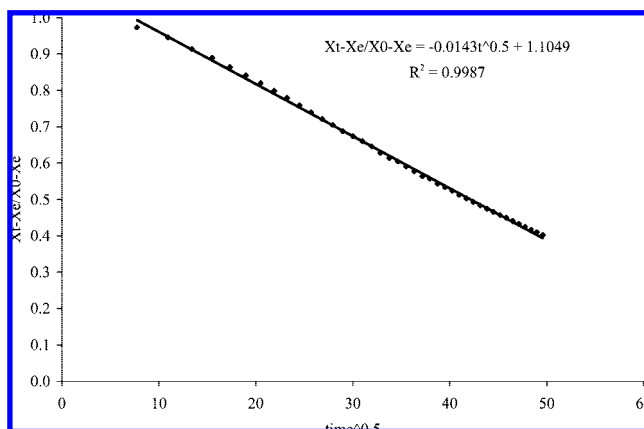
initial equilibration to 0% RH step). For the example case, the final equilibrium mass of the sample was assigned to be the same as the initial mass of the adsorption step, 0.0577 g (0 moisture content), whereas the initial sample mass of the desorption step was 0.0624 g (or 0.0815 g of water/g of dry starch). The initial mass of the desorption step was assigned when the relative humidity of the sample chamber initially switched from 50 to 0% RH; this value is just slightly less than the final mass of the adsorption step given previously (0.0625 g). The initial moisture content, X_0, and the final equilibrium moisture content, X_e, were calculated on the basis of the assigned initial and final sample mass values given above, whereas the moisture content values at the various times t, X_t, were calculated using the data from the kinetic water sorption profiles. D_{bd} was calculated by minimizing the sum of squares error (SSE) between the experimental (**Figure 4**) and the predicted (calculated using eq 5) moisture content values using the solver function in Microsoft Excel. For the example, $D_{bd} = 5.80 \times 10^{-10}$ m²/s.

Calculations for D_{bd} Using the Slope Method (Equation 6). Experimental values of $(X_t - X_e)/(X_0 - X_e)$ of <1.0 and >0.40, which corresponds to M_t/M_∞ values < 0.60, were plotted as a function of the square root of time in seconds and are shown in **Figure 5**, along with the linear fit and resultant equation. Substituting the value of the slope from **Figure 5** into eq 6 and solving for D yields $D_{bd} = (-0.0143)^2 \pi l^2/4$; therefore, $D_{bd} = 8.50 \times 10^{-10}$ m²/s, with $l = 0.0023$ m.

Statistical Analysis. Diffusion data were analyzed using SAS v. 9.1.3 proc GLM. The Tukey multiple-comparison test was employed to distinguish the following: (1) whether D_{ba} and D_{bd} were dependent on relative humidity; (2) if there was a significant difference between D_{ba} and D_{bd} using the full-fit method and using the slope method; and

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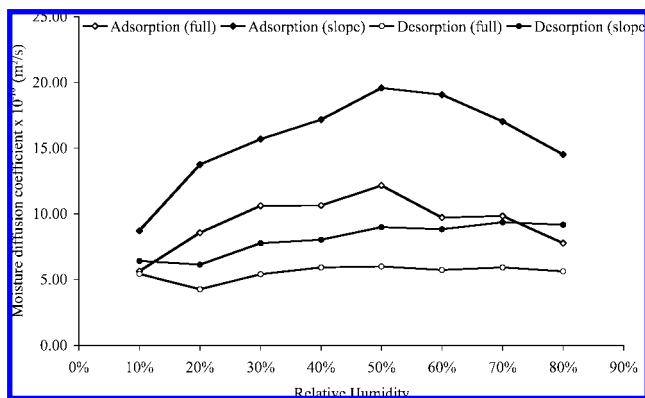
Figure 6. Adsorption (D_{ba}) and desorption (D_{bd}) bulk moisture diffusion coefficients of dent corn starch plotted as a function of relative humidity at 25 °C.

(3) if there was a significant difference between the full-fit method and the slope method within D_{ba} and within D_{bd}. The average standard deviations for the D_{ba} slope and D_{ba} full-fit values for the adsorption relative humidity study at 25 °C were $\pm 1.63 \times 10^{-10}$ and $\pm 0.856 \times 10^{-10}$ m²/s, respectively. The average standard deviations for the D_{bd} slope and D_{bd} full-fit values for the desorption relative humidity study at 25 °C were $\pm 1.11 \times 10^{-10}$ and $\pm 0.971 \times 10^{-10}$ m²/s, respectively. The average standard deviation for the D_{ba} slope values for the adsorption temperature study at 50% RH was $\pm 0.713 \times 10^{-10}$ m²/s.

RESULTS AND DISCUSSION

Analysis of the Full-Fit and Slope Methods for both Adsorption and Desorption Data. The absorption (D_{ba}) and desorption (D_{bd}) bulk moisture diffusion coefficients of dent corn starch at relative humidity values from 10 to 80% at 25 °C were calculated using both the full-fit method (eqs 3 and 5) and the slope method (eqs 4 and 6) using the adsorption and desorption data, respectively. The resultant D_{ba} and D_{bd} values are plotted as a function of relative humidity in **Figure 6** (note the effect of relative humidity on these D_b values is discussed in a subsequent section). The R^2 values obtained for the slope method, for both adsorption and desorption data, were all >0.990, ranging from 0.998 to 0.990, which indicates that the thin slab model was a good fit to the data. In addition, the high R^2 values obtained indicate that the type of diffusion observed was Fickian diffusion. In the case of Fickian diffusion, also called case I diffusion, the water mobility is much lower than the segmental relaxation rate. In contrast, in the case of non-Fickian diffusion, also called case II diffusion, the water mobility is much higher than the segmental relaxation rate (*21*). For starch, case II diffusion is expected to occur near its glass transition temperature (T_g) (*2, 21*). The water activity corresponding to $T_g = 20$ °C for pregelatinized corn starch was reported as 0.936 a_w (or 93.6% RH) by Kou and others (*22*), which is larger than the highest relative humidity studied here, 80% RH, further indicating that case I diffusion was a good model selection for all relative humidity values investigated in this study.

The root-mean-square [rms; equal to the square root of (SSE/n)] was used to describe how well the full-fit thin slab mathematical model described the experimentally obtained data. The rms values obtained for the full-fit method, for both adsorption and desorption data, ranged between 0.013 and 0.068 for all relative humidity values, which indicates that the thin slab model was a good fit to the data and thus a reasonable model selection.

Even though both the full-fit and slope models exhibited a good fit to the data, it is still important to consider possible sources contributing to the discrepancy between the models and the experimental data. The discrepancy between the models and the experimental data in **Figures 2**−**5** may be attributed, in part, to the effect of variable boundary conditions on the water transport behavior, as discussed by Peppas and Brannon-Peppas (*21*). The mathematical model used in this study is based on the assumption that the surface concentration, C_0, is instantaneously increased to the constant penetrant concentration, C_1, at the start of the experiment. However, as mentioned above, the relative humidity in the DVS increased rapidly, but not instantaneously (on average, it took approximately 2 min to achieve 97.5% of the target relative humidity). Peppas and Brannon-Peppas (*21*) investigated this boundary problem by considering a system in which the water concentration was initially zero and the water concentration at the surface approached an equilibrium concentration exponentially, which they say represents "the conditions encountered in a dynamic sorption experiment where the penetrant diffuses from a liquid reservoir through an inert gas to reach the surface of the sample," which describes how the DVS instrument used in this study works. The calculated uptake curves, shown in Peppas and Brannon-Peppas (*21*), for which the surface concentration rose at a finite rate, exhibited points of inflection, similar to those observable in **Figures 3** and **5** (where the initial sorption time points are very visible). Additional lack of fit may be attributed to some smaller violations of the infinite thin slab model assumptions that occurred in the DVS experiments. These violations are (1) the actual geometry of the samples contained in the round-bottom DVS pans was not an ideal infinite thin slab and (2) samples contained in the round-bottom DVS pans did not have a uniform thickness across the entire length of the pan, so the average thicknesses was used in all of the diffusion calculations. Another factor to consider when the moisture diffusion coefficient of starch is measured is the nature of the surface of the sample. If the starch sample surface is not sufficiently compressed, the starch granules in the top layers may experience radial diffusion of water, whereas the inner sample layers will experience thin slab diffusion of water. In an attempt to avoid this sample geometry complication, the starch samples in this study were evenly distributed and slightly compressed by tapping the DVS pan containing the sample on the laboratory bench before they were loaded into the DVS instrument.

The bulk moisture diffusion coefficient calculated by the slope method ranged from approximately 1.5 to 2.1 times larger than the moisture diffusion coefficient calculated by the full-fit method for adsorption diffusion and from 1.3 to 1.6 times larger for desorption diffusion, which can be observed by taking the ratio of the D_{ba} slope method to D_{ba} full-fit method values plotted in **Figure 6**. The slope method calculates the average diffusion coefficient for the first 60% of the moisture adsorption or desorption step, which normally occurs over the first 10% of the experimental time frame during which the driving force [the difference between the increasing (adsorption) or decreasing (desorption) sample RH and the constant environmental RH] remains large. [For the 50% RH adsorption example shown in **Figure 3** the slope method was applied to the first 11.2% of the experimental time frame ($M_t/M_\infty < 0.60$). On the other hand, the 50% RH desorption example (**Figure 5**) was applied to the first 19.9% of the experimental time frame.] In contrast, the full-fit method calculates the average diffusion coefficient over the entire adsorption or desorption step that occurs over the entire experimental time frame during which the driving force continuously decreases. Due to its ease of use, the slope method

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is more widely employed than the full-fit method. When we make use of the diffusion coefficients calculated from the slope method, it is important to keep in mind that the results reflect only the diffusion coefficient for the first 60% of the moisture adsorption or desorption step.

The average adsorption bulk moisture diffusion coefficients of dent corn starch in this study calculated from the slope method ranged from a low of 8.72×10^{-10} m^2/s at 10% RH to a high of 19.58×10^{-10} m^2/s at 50% RH at 25 °C. Two moisture adsorption diffusion studies on materials similar to the dent corn starch studied here were found in the literature. Lomauro and others (*11*) used saturated salt solutions for adsorbing wheat flour samples from their "as is" state to 75% RH. They reported an effective diffusion coefficient for wheat flour to be 3.2×10^{-11} m^2/s (16.9 g of water/100 g of solids) at 25 °C, which is somewhat lower than the diffusion coefficients obtained in this study for dent corn starch. Roman-Gutierrez and others (*13*) used the DVS for adsorbing starch and wheat flour samples from 60 to 70% RH. They reported water diffusion coefficients for starch to be 0.67×10^{-15} m^2/s and for soft wheat flour to be 4.97×10^{-15} and hard wheat flour to be 2.19×10^{-15} m^2/s at 25 °C. These diffusion coefficients are much lower than the average D_{ba} of dent corn starch at 70% RH obtained in this study, which was 9.84×10^{-10} m^2/s for the full-fit method and 17.04×10^{-10} m^2/s for the slope method at 25 °C. This difference can be attributed to two factors: (1) percent relative humidity step size used and (2) model type used. Roman-Gutierrez and others (*13*) used a smaller adsorption percent relative humidity step size (from 60 to 70% RH), compared to that used in this study (from 0 to 70% RH), which equates to a smaller driving force and thus to smaller diffusion coefficients. In addition, Roman-Gutierrez and others (*13*) used a flat-bottom video pan but a polydisperse sphere diffusion model for calculating the diffusion coefficients. Roman-Gutierrez and others (*13*) themselves mentioned that the diffusion coefficients they reported were relatively low compared to literature values. They attributed their low diffusion coefficient values to the relatively large sample weight used (10−20 mg). With these large sample sizes it was not possible to form a true monolayer distribution of particles on the sample holder, and thus vapor transport probably did not occur via individual particles (spherical diffusion model), but inside a more or less porous particle bed (thin slab or planar model).

In addition, both moisture diffusion (via drying data) and self-diffusion of water coefficients for starch were found in the literature and included here for comparison purposes, even though the process (drying data) and type of diffusion (self-diffusion) were not the same as that measured in this study. Karathanos and others (*7*) estimated the moisture diffusion coefficient of hydrated Amioca, a high-amylopectin starch powder, from drying data to range from 20×10^{-10} m^2/s at 0.05 g of water/g of solids to 10×10^{-10} m^2/s at 0.95 g of water/g of solids with a maximum diffusion coefficient of 38×10^{-10} m^2/s at 0.10 g of water/g of solids for drying at 80 °C, and to range from 36×10^{-10} m^2/s at 0.05 g of water/g of solids to 18×10^{-10} m^2/s at 0.95 g of water/g of solids with a maximum diffusion coefficient of 70×10^{-10} m^2/s at 0.15 g of water/g of solids for drying at 100 °C. Hopkinson and others (*2*) reported the self-diffusion coefficient of water in corn starch amylose at a moisture content of 0.1 g of water/g of solid to be approximately 2.5×10^{-10} m^2/s using stray field NMR at 20 °C, and Fukuoka and others (*4*) estimated the self-diffusion coefficient of water in wheat starch to be nearly linear, starting with a value of 3×10^{-10} m^2/s at 0.48 g of water/g pf sample
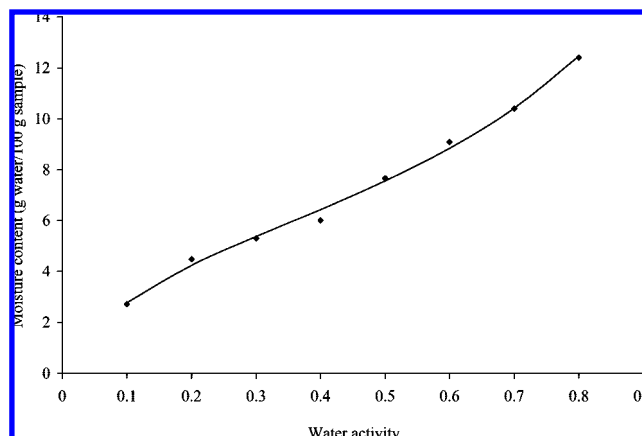
Figure 7. Adsorption isotherm for dent corn starch at 25 °C fit to the GAB isotherm equation with parameters $m_0 = 5.62$, $c_1 = 10.82$, and $k = 0.72$.

and ending with a value of 8×10^{-10} m^2/s at 0.78 g of water/g of sample at 20 °C using pulsed field gradient NMR. These diffusion coefficients are similar in magnitude to the bulk moisture diffusion coefficients of dent corn starch reported in this study, even though the process and type of diffusion measured were different.

Effect of Relative Humidity on the Adsorption and Desorption Bulk Moisture Diffusion Coefficients. As introduced previously, the D_{ba} and D_{bd} of dent corn starch as a function of relative humidity at 25 °C are given in **Figure 6**. The equilibrium moisture contents (EMC) of dent corn starch at each tested relative humidity were also obtained for each adsorption kinetic water sorption profile. The obtained equilibrium moisture contents were plotted as a function of relative humidity to yield the adsorption isotherm of dent corn starch at 25 °C (**Figure 7**). The dent corn starch adsorption isotherm was fit to the GAB equation, with the GAB curve fit and parameters presented in **Figure 7**. In **Figure 6** a maximum D_{ba} was observed at 50% RH, where the equilibrium moisture content was 7.66 g of water/100 g of sample (or 8.30 g of water/100 g of solid) (from **Figure 7**). The location of the maximum D_{ba} in the intermediate moisture region was found to be in agreement with other studies. Karathanos and others (*7*), using drying data, found that the water diffusivity in corn starch gels was reported to be at a maximum value at intermediate moisture content values and was significantly smaller at lower and higher moisture contents. Hanson and others (*23*), using the sorption kinetics technique, found that the diffusivity of water in individual corn starch granules reached a maximum near a moisture content of 13 g of water/100 g of sample (or 15 g of water/100 g of solid). The maximum adsorption bulk moisture diffusion coefficient at intermediate moisture contents is believed to be due to a change in the mechanism of diffusion from vapor diffusion at low relative humidity values to liquid diffusion at high relative humidity values.

The average D_{bd} of dent corn starch at various relative humidity values at 25 °C calculated from the slope method fell into a rather narrow range from 6.14×10^{-10} to 9.36×10^{-10} m^2/s, which is smaller than the range for the average D_{ba} values (slope method), which was from 8.72×10^{-10} to 19.58×10^{-10} m^2/s. Lomauro and others (*11*) also reported a smaller effective desorption diffusion coefficient of 0.39×10^{-11} m^2/s (6.28 g of water/100 g of solid) for desorbing wheat flour from the "as is" state to 0.11 a_w compared to the value for adsorbing from the "as is" state to 0.75 a_w of 3.2×10^{-11} m^2/s, at 25 °C. This finding of D_{bd} being lower than the comparable D_{ba} for dent

Table 2. Results of *F* Test for Percent Relative Humidity Dependence of D_{ba} and D_{bd} with $p = 0.05$

mode and (method)	DF	sum of squares	mean square	F value	Pr > F	conclusion
adsorption (full)	7	2.2130E−20	3.1616E-21	1.88	0.1058	% RH independent
adsorption (slope)	7	6.3157E−20	9.0224E-21	5.37	0.0004	% RH dependent
desorption (full)	7	4.9978E−21	7.1396E-22	0.42	0.8795	% RH independent
desorption (slope)	7	1.3482E−21	1.9260E-22	1.15	0.3605	% RH independent

Table 3. Results of the Tukey Multiple-Comparison Test among the Adsorption Full Method, Adsorption Slope Method, Desorption Full Method, and Desorption Slope Method

| mode and (method)	adsorption (full)	adsorption (slope)	desorption (full)	desorption (slope)
adsorption (full)		*p* < 0.0001 (different)	*p* < 0.0001 (different)	
adsorption (slope)	*p* < 0.0001 (different)			*p* < 0.0001 (different)
desorption (full)	*p* < 0.0001 (different)			*p* = 0.0003 (different)
desorption (slope)		*p* < 0.0001 (different)	*p* = 0.0003 (different)	

corn starch indicates that the mechanisms of moisture adsorption and desorption may be different. This difference in adsorption and desorption diffusion coefficients is reminiscent of the difference between adsorption and desorption isotherms, termed sorption hysteresis, where the equilibrium moisture content is higher for the desorption isotherm compared to the adsorption isotherm at the same relative humidity (or water activity). Several theories described by Kapsalis (*24*), such as the inkbottle neck theory and the domain theory, are often used to explain hysteresis. These theories may also give insight to help explain the difference between D_{ba} and D_{bd}. However, it is important to note that diffusion coefficients are calculated from kinetic data, whereas hysteresis is observed during isotherm measurements, which are based on equilibrium thermodynamics. However, as discussed in Schmidt (*25*), the hysteresis phenomenon itself constitutes a violation of thermodynamic equilibrium, an assumption underlying the water activity concept. Additionally, **Figure 6** indicates that relative humidity has no significant impact on D_{bd} slope and full-fit methods and the D_{ba} full-fit method, but did affect the D_{ba} slope method (see statistical analysis below). A similar lack of dependence of D_{bd} on relative humidity was reported by Spieles and others (*10*) for freeze-dried hydroxyethyl starch. It is possible that the factors that affect the desorption of starch at low moisture contents are the same as those that affect the falling rate region during dehydration. According to Fellows (*26*), moisture transfer in the falling rate region is not affected by external factors, such as the relative humidity gradient or temperature, but is determined by the internal properties of the sample itself.

Statistical analysis of the data presented in **Figure 6** was performed to determine (1) whether D_{ba} and D_{bd} were dependent on relative humidity (**Table 2**), (2) if there was a significant difference between D_{ba} and D_{bd} using the full-fit method and using the slope method (**Table 3**), and (3) if there was a significant difference between the full-fit method and the slope method (**Table 3**) within D_{ba} and within D_{bd}. The statistical results showed that D_{ba} for the slope method was dependent on relative humidity, whereas D_{ba} for the full-fit method and D_{bd} for the slope and full-fit methods were not, although D_{ba} for the full-fit method was nearly significant for a *p* value of 0.10. The statistical results also showed that there was a significant difference between D_{ba} and D_{bd} using the full-fit method and using the slope method and that there was a significant difference between the full-fit method and slope method within D_{ba} and within D_{bd}.

Effect of Temperature on the Adsorption Bulk Moisture Diffusion Coefficient. The effect of temperature on the adsorption bulk moisture diffusion coefficient of dent corn starch at

50% RH is shown in **Figure 8**. The equilibrium moisture contents of dent corn starch at each tested temperature at 50% RH were also obtained for each adsorption kinetic water sorption profile. These equilibrium moisture contents were plotted against temperatures for dent corn starch at 50% RH (**Figure 9**). **Figure 8** shows that the moisture diffusion coefficient increased as temperature increased. This could be due to two factors related to temperature. First, when temperature increases, the water mobility increases due to more available energy, resulting in an increase in the moisture diffusion coefficient. Second, the amount of moisture absorbed increases when temperature increases, as shown in **Figure 9**. However, when the temperature
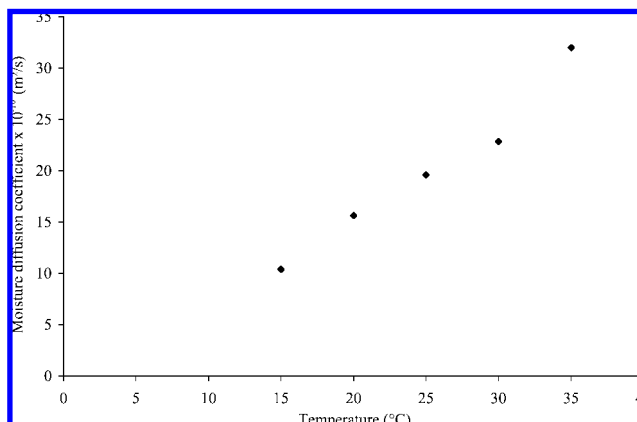
Figure 8. Effect of temperature on the adsorption bulk moisture diffusion coefficient (D_{ba}) for dent corn starch from 0 to 50% RH (slope method) at 15, 20, 25, 30, and 35 °C.
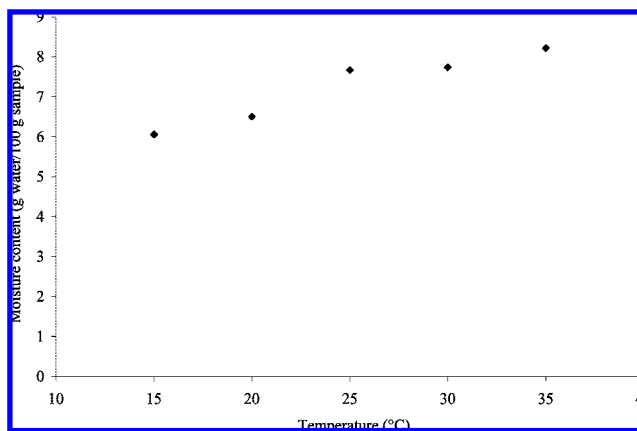
Figure 9. Adsorption equilibrium moisture contents for dent corn starch at 50% RH plotted as a function of temperature.

DVS-Determined Bulk Moisture Diffusion Coefficient

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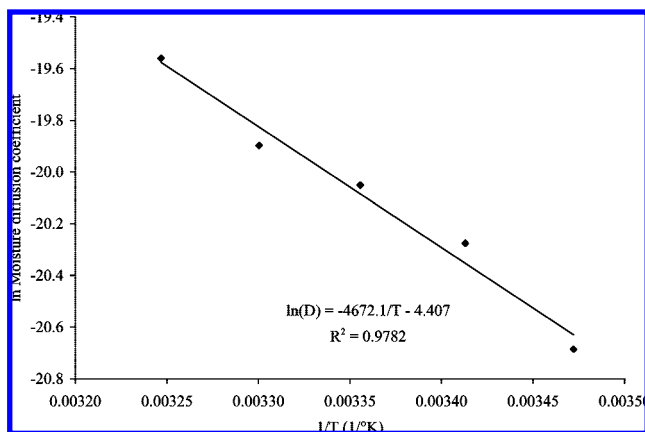
Figure 10. Natural log (ln) of the adsorption bulk moisture diffusion coefficient (slope method) for dent corn starch plotted as a function of the inverse of temperature. The line and equation given in the graph are the fit to the natural log version of eq 8.

approaches the glass transition temperature of dent corn starch, according to Peppas and Brannon-Peppas (*21*), the diffusion behavior will transition from Fickian diffusion (case I) to non-Fickian diffusion (case II). Peppas and Sinclair (*27*) developed a semiempirical equation for analyzing the transport mechanism in glassy polymers

$$\frac{M_t}{M_\infty} = k t^n \tag{7}$$

where *k* is a constant incorporating characteristics of the macromolecule network system and penetrant and *n* is the diffusional exponent, which is indicative of the transport mechanism. For the thin slab model, $n = 0.5$ for case I transport and 1.0 for case II transport. However, as discussed in Peppas and Brannon-Peppas (*21*), the equation cannot be used to describe sorption behavior correctly if the instantaneous boundary condition is violated, which is believed to be a limitation encountered in dynamic sorption experiments, as discussed previously. Thus, the equation could not be used here as another means of determining the nature of the transport mechanism.

The observed temperature dependence of the moisture diffusion coefficient follows the Arrhenius-type equation

$$D = D_0 \exp\left[\frac{-E_D}{RT}\right] \tag{8}$$

where D_0 is the diffusion coefficient at a reference temperature (m^2/s), E_D is the activation energy of the diffusion coefficient (kJ/mol), *R* is the universal gas constant, 0.00831447 kJ/mol·K, and *T* is temperature in K. To calculate the activation energy for moisture diffusion of normal corn starch, the natural log (ln) of *D* is plotted as a function of the inverse of temperature in K (**Figure 10**). The slope of the line fit to eq 8 is equal to −4672.1, with an $R^2 = 0.9782$. The activation energy was determined to be 38.85 ± 0.433 kJ/mol. Kim and others (*28*), studying the water and temperature (25, 35, and 45 °C) response of semi-IPN hydrogels composed of chitosan and poylacrylonitrile using the DVS, reported apparent activation energies of 32.4−34.8 kJ/mol depending on the composition of the semi-IPN (CSPA11, 13, and 31). These values are somewhat lower than, but still comparable with, those obtained for dent corn starch in this study.

Conclusions. In this study, we investigated the use of an automated water sorption instrument to determine the adsorption and desorption bulk moisture diffusion for dent corn starch as a function of relative humidity and the effect of temperature on the adsorption bulk moisture diffusion coefficient at a constant relative humidity. The automated water sorption instrument was found to be a convenient tool for measuring the bulk moisture diffusion coefficient; however, thorough consideration must be given to the selection of the appropriate diffusion model(s) for data analysis, based on the type and geometry of the sample, the DVS pan used, and the diffusion mechanism (case I or case II diffusion). The desorption bulk moisture diffusion coefficient values were found to be significantly different than the adsorption bulk moisture diffusion coefficient values as a function of relative humidity. Through this study, the DVS was found to be a very efficient method (more data in less time) compared to the saturated salt solution method for obtaining the kinetic moisture sorption profiles needed for calculating the bulk moisture diffusion coefficients. However, further research is merited to investigate an appropriate solution to the violation of the instantaneous boundary condition inherent in automated water sorption instruments discussed in the text.

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