Moisture Sorption Isotherms of Foods: Experimental Methodology, Mathematical Analysis, and Practical Applications

C. Caballero-Cerón, J.A. Guerrero-Beltrán, H. Mújica-Paz, J.A. Torres, and J. Welti-Chanes

Abbreviations

ΔG	Gibb's free energy value
ΔH	Enthalpy
ΔS	Entropy
A	Constant of Halsey equation
ASE	Average standard error
a_w	Water activity
$a_{w,calc.}$	Water activity values estimated with the model
$a_{w,exp}$	Experimental water activity values
B	Constant of Halsey equation
BET	Brunauer-Emmett-Teller equation
C	Adsorbent constant, interaction energy constant

C. Caballero-Cerón
Centro de Biotecnología FEMSA, Escuela de Biotecnología y Alimentos,
Tecnológico de Monterrey, Av. Eugenio Garza Sada 2501 Sur, Col. Tecnológico,
Monterrey, N.L. 64849, Mexico

J.A. Guerrero-Beltrán (✉)
Departamento de Ingeniería Química, Alimentos y Ambiental, Universidad de las
Américas-Puebla, Sta. Catarina Mártir, Cholula, Puebla 72820, Mexico
e-mail: joseangel150@hotmail.com

H. Mújica-Paz • J. Welti-Chanes (✉)
Escuela de Ingeniería y Ciencias, Tecnológico de Monterrey, Av. Eugenio Garza Sada 2501
Sur, Col. Tecnológico, Monterrey, Nuevo León 64849, México
e-mail: h.mujica@itesm.mx; jwelti@itesm.mx

J.A. Torres
Food Process Engineering Group, Department of Food Science and Technology,
Oregon State University, 100 Wiegand Hall, Corvallis, OR 97331, USA

DDI	Dynamic dew point isotherm method
Ds	Dried solids
DSC	Differential scanning calorimetry
DVS	Dynamic vapor sorption method
F, G, and H	Constants of Lewicki equation
GAB	Guggenheim, Anderson, and De Boer equation
H_1	Condensation heat of pure water (J mol-1)
H_m	Total sorption heat of the monolayer (J mol-1)
H_q	Total sorption heat of subsequent water layers (J mol-1)
K	Interaction energy constant
k and n	Constants of Henderson equation
M	Linearized portion slope of the sorption isotherm in the range of interest
MRD	Measurements of deviation between predicted data
Q	Isosteric heat of sorption
$-Q/R$	Slope in the lineal relationship of ln a_w against the inverse absolute temperature
q_{st}	Isosteric heat of sorption
R	Ideal gas constant
R	Ideal gas constant
R^2	Coefficient of determination
RH	Relative humidity
RMSE	Measurements of deviation between experimental data
T	Absolute temperature
T_B	Isokinetic temperature
T_g	Glass transition temperature
T_{hm}	Harmonic temperature
X	Moisture content
X_i	Average moisture content values
$X_{i,\ calc.}$	Calculated moisture content values
$X_{i,\ exp}$	Experimental moisture content values
X_m	Monolayer moisture values

1 Introduction

Knowing the moisture content of a product is insufficient to predict its stability, making it necessary to also know its water activity (a_w), a thermodynamic property describing the interactions between water molecules and the food matrix. Moisture sorption isotherms, i.e., the relationship between moisture content and a_w at constant pressure and temperature describing the sorption process of water molecules into a specific material, are useful when identifying optimal food dehydration and storage conditions. Moisture sorption properties affect physicochemical and biological phenomena such as enzymatic degradation, microbial activity, food

microstructure, sensory quality deterioration, nutrient losses, and other changes limiting the shelf life of food products. Some of these phenomena are associated with water mobility, which is also related with the phase transitions from a "glass" or amorphous to a "rubbery" state. Glass transition is a second order phase transition associated with time, temperature, and moisture content. When fresh foods are dried, water removal leaves behind an amorphous material. A desirable final product moisture level is one that corresponds to a glass transition temperature (T_g) higher than the product storage temperature. Therefore, knowing T_g helps in setting the food storage and/or process conditions required to retain textural properties and to predict the shelf life of low and intermediate moisture content foods.

The aim of this work is to present information on food moisture sorption isotherms and their relationship with product composition and temperature. Advantages and disadvantages of experimental methods available to obtain sorption isotherms are reviewed, equations describing experimental data are then discussed, and finally, practical applications to shelf life estimations due to moisture gain or loss are presented.

2 Moisture Sorption Isotherms

Moisture sorption isotherms are a graphical representation of the thermodynamic equilibrium between moisture content and the water activity at a given temperature and pressure (Iglesias and Chirife 1982). The shape of the moisture sorption isotherms changes with temperature, composition, pressure, physical state of the components, and the process of dehydration/humidification used; every product isotherm is unique (Goula et al. 2008; Vega-Gálvez et al. 2009). Moisture sorption isotherms describe how water molecules are adsorbed by a specific material, and are used to predict the shelf life of food and pharmaceutical products due to moisture gain (adsorption) or loss (desorption), and also to define storage, transport, and process conditions, or to estimate the energy requirements of a dehydration process (Arlabosse et al. 2003; Iglesias and Chirife 1982; Lewicki 2000). The adsorption/desorption process is not fully reversible (Fig. 1), i.e., at the same a_w a larger moisture content is observed during the desorption process, a phenomenon called hysteresis (Basu et al. 2006; Al-Muhtaseb et al. 2002).

Five isotherm types have been reported (Fig. 2). Type I or Langmuir isotherms are observed when water molecules are absorbed by materials mostly as a single monolayer; Type II, shown by soluble materials, are sigmoidal isotherms with an asymptotic tendency when a_w approaches 1.0; Type III corresponds to high sugar concentration products; Type IV describes hydrophilic solids; and Type V represents adsorption of water molecules as multilayers (Basu et al. 2006; Al-Muhtaseb et al. 2002). Most food products exhibit Type II or III.

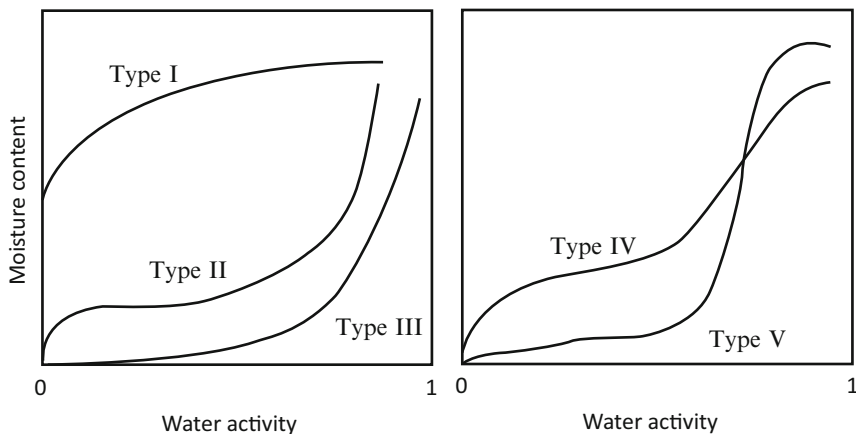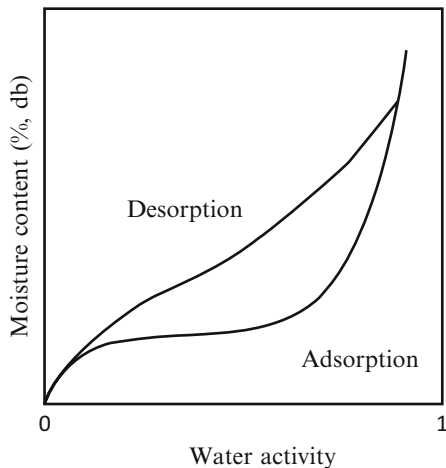**Fig. 1** Schematic representation of moisture sorption isotherms for food products showing hysteresis phenomenon

Fig. 2 Five types of sorption isotherms

2.1 Monolayer Moisture Content

The monolayer moisture content is defined as the water necessary to cover by absorption to hydrophilic and polar groups the entire food surface, including pores and capillaries (Rahman 2009; Furmaniak et al. 2009). This moisture level is used as a stability parameter for dried products, since this bound water can be assumed as being unavailable to participate in reactions requiring water as a solvent or to exert a plasticizing role (Bell and Labuza 2000; Basu et al. 2006). Water absorbed in excess of the monolayer value is arranged into multilayers bound by hydrogen bonds, and can interact with other chemical compounds of the food matrix or participate in the transport of soluble compounds (Rahman 1995; Furmaniak

et al. 2009). From a practical point of view, the monolayer value is a reference parameter defining for dried products a moisture content value for maximal product stability.

2.2 Temperature and Composition Effects on Moisture Sorption Properties

Many factors affect the sorption isotherm, but the most important ones are food composition and temperature (Goula et al. 2008; Vega-Gálvez et al. 2009).

2.2.1 Chemical Composition and Moisture Sorption Properties

Food systems are complex matrices constituted by a continuous aqueous phase and a small fraction of dispersed solids. Soluble compounds in the aqueous phase consist of sugars, salts, and others, while the solid phase is constituted by insoluble polymers such as starch, proteins, and insoluble fiber (Moreira et al. 2009). The relationship of moisture and water activity depends on the food composition and how water molecules interact with food compounds, i.e., how many polar sites are available for the binding of water molecules (Iglesias and Chirife 1982; Kingsly and Ileleji 2009; Moreira et al. 2009; Myhara et al. 1998). While water soluble molecules such as sugars, salts, or soluble fibers bind water molecules contributing to vapor pressure reduction, insoluble solids with no binding sites do not, thus higher values of a_w are reached at the same equilibrium moisture content (Goula et al. 2008; Moreira et al. 2009).

2.2.2 Effect of Temperature on Sorption Isotherms

Temperature influences the water molecular mobility in a food system, as well as the dynamic exchange between the vapor and the absorbed phases. In addition, the binding energy between molecules decreases when temperature increases, so a reduction in the adsorption capacity of water molecules is observed, leading to changes in the sorption isotherm (Quirijns et al. 2005; McMinn et al. 2003). As shown in Fig. 3, temperature increases a_w at the same equilibrium moisture content, reflecting a reduction in the total number of active sites for water adsorption as a result of physical and/or chemical changes due to the temperature increase (Goula et al. 2008; Quirijns et al. 2005).

Fig. 3 Effect of
temperature on moisture
sorption isotherms
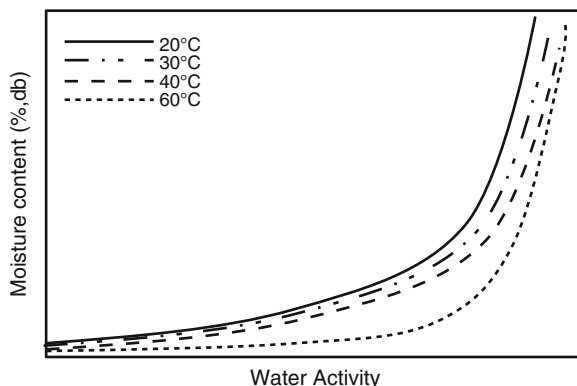
3 Experimental Methods for the Determination of Moisture Sorption Isotherms

Experimental methods are divided into those with the air relative humidity and/or temperature continuously changing, and those known as dynamic methods, in contrast with static methods where air properties are kept constant during a_w determination.

3.1 Static Methods

In static methods, samples in hermetic and closed vessels are kept in contact with air at constant relative humidity (RH) and temperature until equilibrium between the sample and air is reached. These methods can be classified as hygrometric, manometric, and gravimetric (Iglesias and Chirife 1982). In hygrometric methods, the surrounding food atmosphere vapor pressure is measured using dew point and electrical sensors (Spiess and Wolf 1987). In manometric methods, air vapor pressure in equilibrium with the food sample is measured (Goula et al. 2008; Spiess and Wolf 1987). In gravimetric methods, equilibrium is evaluated by following weight changes (Iglesias and Chirife 1982) in samples (2 g approx.) with known moisture content in contact with air at constant RH and temperature. Weight loss (desorption) or gain (adsorption) is evaluated until equilibrium is reached, i.e., when the difference between two consecutive measurements is approximately ± 0.0010 g. The measuring system consists of a series of hermetic containers (glass jars or desiccators), a glass or plastic base (usually a petri dish), and weighing bottles where samples are placed (Iglesias and Chirife 1982; Bell and Labuza 2000; Spiess and Wolf 1987). Hermetic flasks (or desiccators) are placed in a constant room temperature or in an incubator. Saturated salt solutions, sulfuric acid, or glycerol solutions are used to control the RH. Saturated salt solutions are

Table 1 Water activity generated by oversaturated salt solutions at different temperatures (adapted from López-Malo et al. 1994)

Salt	Water activity Temperature (°C)		
	25	30	35
Lithium chloride, LiCl	0.111	0.112	0.113
Potassium acetate, CH_3COOK	0.252	0.244	0.237
Magnesium chloride, $MgCl_2$	0.325	0.322	0.319
Potassium carbonate, K_2CO_3	0.434	0.432	0.431
Magnesium nitrate, $Mg(NO_3)_2$	0.524	0.511	0.499
Sodium bromide, NaBr	0.573	0.559	0.545
Potassium iodide, KI	0.686	0.676	0.669
Strontium chloride, $SrCl_2$	0.707	0.691	0.676
Sodium chloride, NaCl	0.755	0.753	0.752
Ammonium chloride, NH_4Cl	0.777	0.763	0.754
Ammonium sulfate $(NH_4)_2SO_4$	0.807	0.801	0.798
Potassium chloride, KCl	0.843	0.836	0.830
Barium chloride, $BaCl_2$	0.904	0.901	0.898
Potassium nitrite, KNO_2	0.931	0.917	0.906
Potassium sulfate, K_2SO_4	0.976	0.974	0.972

preferred, as they are thermally stable and show small RH variation with temperature changes, as well as being stable to changes in sample moisture content (Greenspan 1977; Rockland 1960; Spiess and Wolf 1987). Table 1 shows the most common salts employed in the 0.11–0.976 a_w interval (López-Malo et al. 1994).

Static methods are simple to operate and allow multiple samples to be analyzed simultaneously, but determination times are long, samples must be removed from the system for weighing which may modify their equilibrium moisture, requiring large sample quantities for a complete isotherm, and determination points are discrete (Yu et al. 2008a, b; Lewicki 2000). Long determination times are required to ensure that thermodynamic equilibrium between samples and air is reached (Spackman and Schmidt 2010). However, these long times may result in mold growth in samples with RH greater than 75 %, causing the loss of experimental data (Bell and Labuza 2000; Yu et al. 2008a, b; Baucour and Daudin 2000). Automatic and dynamic methods have been developed to avoid these experimental limitations.

3.2 Dynamic Methods

Samples are placed on a microbalance and an air stream with known RH and constant temperature passes continuously over them. Constant exposure to air flow and the small sample weight reduce the determination time from days to hours, making it possible to measure points at high a_w levels without the risk of microbial growth or physicochemical changes in the sample (Rahman and

Al-Belushi 2006; Arlabosse et al. 2003; Spackman and Schmidt 2010; Yu et al. 2008c). Only one sample is needed for the complete sorption isotherm, weight is automatically recorded, and sample handling is reduced (Rahman and Al-Belushi 2006; Yu et al. 2008b). The automated equipment most frequently used is based on the gravimetric method and uses dew point sensors (Carter and Fontana 2008; Spackman and Schmidt 2010).

3.2.1 Dynamic Vapor Sorption Method (DVS)

In this method, sample weight is continuously recorded at a constant RH and temperature. RH is controlled by using a continuous gas flow mix of dry nitrogen and water vapor. RH changes are programmed as fixed steps controlled by time or RH values, while weight is continuously measured until equilibrium is reached for each RH evaluated (Rahman and Al-Belushi 2006; Li and Schmidt 2011). Equipment consists of two symmetric chambers kept at the same RH and temperature, one for the sample and the other as an empty cell used for reference (Rahman and Al-Belushi 2006; Roman-Gutierrez et al. 2002). The sample size is small (mg), reducing the equilibrium time from days to hours for each point in the sorption isotherm (Arlabosse et al. 2003; Spackman and Schmidt 2010; Rahman and Al-Belushi 2006). Other DVS method applications include determination of drying microkinetics and evaluation of time-depending phase changes such as glass transitions, deliquescence points, crystallizations, and others physicochemical changes (Yu et al. 2008b; Rahman and Al-Belushi 2006; Spackman and Schmidt 2010). In some cases, thermodynamic equilibrium is not reached due to the fast exposure of the sample to the gas flow leading to sorption isotherm differences with those obtained by other methods (Roman-Gutierrez et al. 2002).

3.2.2 Dynamic Dew Point Isotherm Method (DDI)

Water activity and sample weight changes due to continuous flow of a saturated vapor stream (adsorption) or dried air (desorption) over the sample are measured directly (Schmidt and Lee 2012; Carter and Fontana 2008). Air flow stops after a_w changes of 0.015 units approximately, and weight and water activity are measured for each point. Thermodynamic equilibrium may not be reached during measurement, and thus results may differ from those obtained by other methods, particularly for samples with a slow rate of water diffusion (Schmidt and Lee 2012; Carter and Fontana 2008). This method has been used to evaluate time-depending phase changes (Yao et al. 2011; Yuan et al. 2011). The sample chamber in the isotherms generator consists of a precision balance, a standard mirror dew point sensor, inflow ports for dry air and water saturated air, and an infrared temperature sensor. Dry air is obtained by air circulation through a packed desiccant column, while the water
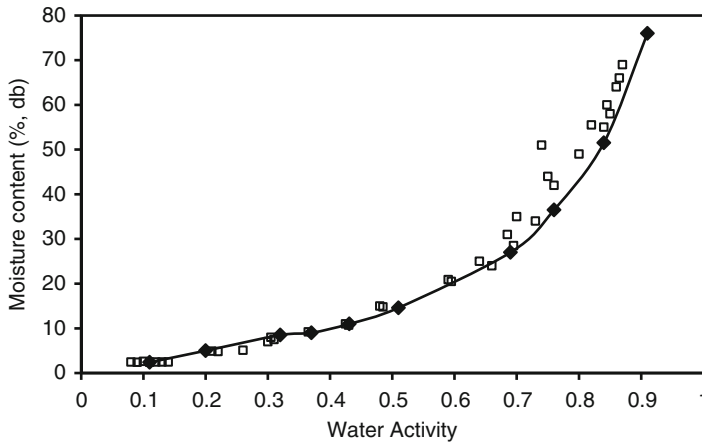
Fig. 4 Sorption isotherm at 32 °C of apple obtained by DDI method (*open square*) and gravimetric static method (*filled diamond*) (unpublished data)

saturated air is obtained by air circulation through a water reservoir (Schmidt and Lee 2012; Carter and Fontana 2008). The DDI method is designed to obtain a complete sorption isotherm (adsorption and desorption) with one sample in a short time period of approximately 24 h, obtaining a high resolution isotherm (>50 points for isotherm). As more data become available, isotherms can be used to obtain additional information on the adsorption of water molecules, as well as phase changes due to moisture content changes. Apple moisture isotherms at 32 °C obtained by conventional static and DDI methods show the same behavior, but the resolution is higher for the latter (Fig. 4). Studies on phase changes such as crystallization, glass transition, and deliquescence points have been reported (Carter and Fontana 2008; Schmidt and Lee 2012; Yao et al. 2011; Yuan et al. 2011; Spackman and Schmidt 2010; Carter and Schmidt 2012). Yuan et al. (Yuan et al. 2011) evaluated the polydextrose glass transition, obtaining T_g values similar to those determined by differential scanning calorimetry (DSC). Yao et al. (2011) measured the deliquescence point for crystalline sucrose at 15, 25, and 35 °C. Although T_g values obtained by the DDI method are restricted to the 15–40 °C equipment operation limits, these are the most common temperature storage conditions; thus; results will be useful when setting food storage and shipping conditions. Schmidt and Lee (2012) observed that sorption isotherms for corn starch, isolated soy protein, microcrystalline cellulose, and crystalline sucrose obtained by DDI and static gravimetric methods were similar. However, those for lactose and corn flakes differed, which was assumed to be associated with phase transitions or slow water diffusion rate, respectively (Carter and Fontana 2008). Diffusion rate can be increased by decreasing the particle size or reducing air flow, yielding DDI results in agreement with those obtained by other methods (Schmidt and Lee 2012).

4 Modeling Sorption Isotherms

Mathematical models proposed to describe experimental sorption isotherms for food products can be classified according to the number of parameters used, or on whether they are based on theoretical or empirical assumptions (Basu et al. 2006; Bhandari and Adhikari 2008). Most models used 2–3 parameters, and the one selected should describe the experimental data well, have less mathematical complexity, and provide mechanistic information on the food hygroscopic properties (Basu et al. 2006). Foods are complex systems, and thus a single model cannot describe all products (Al-Muhtaseb et al. 2002; Bhandari and Adhikari 2008). In the mathematical models presented next, X and X_m are the moisture content and monolayer moisture values (gH$_2$O/100 g dried solids), respectively.

4.1 Brunauer-Emmett-Teller (BET) Equation (Brunauer et al. 1938)

The BET equation, a semiempirical 2-parameter model, describes the $a_w < 0.5$ region (Al-Muhtaseb et al. 2002; Bhandari and Adhikari 2008) as follows:

$$X = \frac{X_m C a_w}{(1 - a_w)[1 + (C - 1)a_w]} \tag{1}$$

where C is an adsorbent constant. This model assumes that the sorption heat in the monolayer is constant and equal to the water vaporization heat plus a constant related to the interaction site, the sorption heat for water molecules above the monolayer value is equal to that for pure water, water sorption occurs only on specific food structure sites, and the sorption surface is homogeneous. The monolayer moisture content defines the moisture content for the maximum stability of dehydrated products.

4.2 Guggenheim, Anderson, and De Boer (GAB) Equation (van den Berg and Bruins 1981)

The GAB model, a semi-theoretical 3-parameter equation, describes water adsorption as a multilayer phenomenon (van den Berg and Bruins 1981; Jouppila and Roos 1997) as follows:

$$X = \frac{X_m C K a_w}{(1 - K a_w)[1 + (C - 1)K a_w]} \tag{2}$$

where C and K are interaction energy constants for the monolayer and the other water molecules are adsorbed on individual sites, respectively. Equations (3) and (4) are the temperature functions used to evaluate the constants C and K:

$$C = C_0 \exp\left(\frac{H_1 - H_m}{RT}\right) \tag{3}$$

$$K = K_0 \exp\left(\frac{H_1 - H_q}{RT}\right) \tag{4}$$

where H_1, H_m, and H_q are, respectively, the condensation heat of pure water (J/mol), total sorption heat of the monolayer (J/mol), and total sorption heat of subsequent water layers (J/mol), T is the absolute temperature (K) and R is the ideal gas constant (8.314 J/mol/K) (Talla et al. 2005). X_m is considered temperature independent, but in some cases it has been shown to decrease when temperature increases (Goula et al. 2008; Quirijns et al. 2005). This monolayer moisture content decrease may be due to a reduction of the active binding water sites as a result of physical or chemical changes induced by temperature. The temperature function for X_m can be expressed as:

$$X_m = X_{m,0} \exp\left(\frac{\Delta H_X}{RT}\right) \tag{5}$$

where $X_{m,0}$ and ΔH_X (J/mol) are constants. The GAB model assumes that water adsorption is a multilayer phenomenon without lateral interactions of water molecules. The monolayer covers the complete sorbent surface with water molecules bound very tightly in the monolayer, whereas the subsequent 2–9 multilayers have less interaction with the sorbent (Quirijns et al. 2005). Timmermann et al. (2001) observed that the GAB parameters are more representative than the corresponding BET parameters for food products, whereas Singh and Singh (1996) showed that it can describe different food isotherm types. The temperature, moisture content, and a_w intervals tested in this latter work were 4–140 °C, 2–77 %, and 0.059–0.99, respectively.

4.3 Halsey Equation (Halsey 1948)

This model overcomes BET limitations (Rahman 1995) by assuming that the potential energy of water molecules varies with the inverse of their distance from the food surface and can describe a wide variety of food isotherms in the 0.1–0.8 a_w interval and is expressed as follows:

$$X = \left[\frac{-A}{RT\ln a_w}\right]^{1/c} \tag{6}$$

where A and C are constants, and T is the absolute temperature (K). As the term RT does not eliminate the temperature dependence of constants A or B, this expression is simplified as follows (Iglesias and Chirife 1976; Basu et al. 2006):

$$X = \left[\frac{-A'}{\ln a_{\mathrm{w}}}\right]^{1/B} \tag{7}$$

where A' is a new constant and may be related to temperature as an exponential function:

$$X = \left[\frac{-\exp(A + BT)}{\ln a_{\mathrm{w}}}\right]^{1/C} \tag{8}$$

where A, B, and C are constants for each isotherm.

4.4 Henderson Equation (Henderson 1952)

The Henderson model, an empirical relationship between adsorbed moisture and a_{w} used to describe moisture sorption isotherms of food products, but with rather limited applicability as compared with other models, is expressed as (Rahman 1995):

$$1 - a_{\mathrm{w}} = \exp(-kTX^n) \tag{9}$$

where k and n are constants and T is the temperature (°C). The following expression is a modification of the original Henderson equation considering k as temperature function:

$$1 - a_{\mathrm{w}} = \exp[-A(T + B)X^n] \tag{10}$$

where A, B, and C are model constants.

4.5 Kühn Equation (Kühn 1964)

This theoretical model, based on a capillary condensation concept and applied most frequently to vegetable and animal products (Akanbi et al. 2006; Escobedo-Avellaneda et al. 2011a, b), is expressed as follows:

$$X = -\frac{k}{\ln a_{\mathrm{w}}} + B'$$ (11)

where k and B' are constants.

4.6 Oswin Equation (Oswin 1946)

The Oswin equation, an empirical model to describe sigmoidal moisture isotherms, can be represented as follows:

$$X = A\left[\frac{a_{\mathrm{w}}}{1 - a_{\mathrm{w}}}\right]^{B}$$ (12)

where A and B are constants. Applications of this equation include high starch content products and also different vegetable products (Al-Muhtaseb et al. 2002).

4.7 Lewicki Equation (Lewicki 1998, 2000)

Assuming that food moisture can be described as pure and hydration water, Lewicki (2000) proposed the following 2-parameter model related to Raoult's law:

$$X = A\left[\frac{1}{a_{\mathrm{w}}} - 1\right]^{b-1}$$ (13)

where A and b are constants. This equation can yield better results than the GAB model, especially when a_{w} is close to 1.0. Although this equation is similar to the Oswin model (Eq. 12), some differences between these two equations can be noted. In contrast with the 2-parameter Lewicki expression (Eq. 13), the Oswin equation is an empirical model, and thus its constants have no physical meaning. In addition, the point $a_{\mathrm{w}} = 1$ is excluded (Lewicki 2000; McMinn et al. 2004). Lewicki (1998) proposed the following 3-parameter model based on a 2-function expression to describe processes occurring in parallel, the first one predominating at high a_{w}, with the second being more important at low a_{w}:

$$X = \frac{F}{(1 - a_{\mathrm{w}})^{G}} + \frac{F}{1 + a_{\mathrm{w}}^{H}}$$ (14)

where F, G, and H are constants. This equation was tested using 31 sorption isotherms reported for various food products yielding better results than those obtained for the GAB, but not as good as those for the Peleg model (Eq. 16).

McMinn et al. (2004) showed that while the 2- and 3-parameter Lewicki equations well describe experimental data for high starch products, the 3-parameter equation gives better results for food products with Type II isotherms within the 30–60 °C temperature range, and the 2-parameter equation was superior to the GAB equation. However, sorption isotherms of potato, high amylose, and high amylopectin starch powders cannot be described using the Lewicki equations.

4.8   Smith Equation (Smith 1947)

The Smith model, an empirical equation describing the high a_w portion of sorption isotherms for products containing high molecular weight solutes (Rahman 1995), can be represented as follows:

$$X = A + B\log(1 - a_w) \tag{15}$$

where A and B are constants, A is the moisture fraction absorbed on the first fraction, and B is the water in the multilayer fraction. This model, limited to the 0.5–0.95 a_w interval (Al-Muhtaseb et al. 2004; Rahman 1995), assumes that there are two fractions of water molecules adsorbed on the food surface. The first fraction with a condensation heat higher than the one for pure water follows the Langmuir model, while the second fraction consisting of a multilayer of condensed water molecules formed only after the first is absorbed, preventing any evaporation from the first fraction. The Smith model describes only the behavior of the second fraction (Al-Muhtaseb et al. 2002).

4.9   Peleg Equation (Peleg 1993)

The Peleg model is a semiempirical 4-parameter equation describing sigmoidal and non-sigmoidal isotherms as follows:

$$X = K_1 a_w^{n_1} + K_2 a_w^{n_2} \tag{16}$$

where K_1, K_2, n_1, and n_2 are constants and $n_1 < 1$ and $n_2 > 1$. When $a_w \rightarrow 1$, $X \rightarrow K_1 + K_1$; however, the adsorbed moisture content values do not reach these values at a_w values close to 1.0. Therefore, this equation is used for $a_w < 0.95$ (Lewicki 1998).

5 Analysis of Applicability for Modeling of Food Sorption Isotherms

Models selected to describe experimental sorption data must be evaluated using statistical indices such as the coefficient of determination (R^2, Eq. 17), root mean squared error (RMSE, Eq. 18), mean relative deviation (MRD, Eq. 19), and average standard error (ASE, Eq. 17):

$$R^2 = 1 - \frac{\sum_{i=1}^{n} \left(X_{i,\text{calc}} - X_{i,\text{exp}}\right)^2}{\sum_{i=1}^{n} \left(X_{i,\text{exp}} - \overline{X}_{i,\text{exp}}\right)^2} \tag{17}$$

$$\text{RMSE} = \sqrt{\sum_{i=1}^{n} \left(X_{i,\text{calc}} - X_{i,\text{exp}}\right)^2} \tag{18}$$

$$\text{MRD} = \frac{1}{n} \sum_{i=1}^{n} \left|\frac{X_{i,\text{calc}} - X_{i,\text{exp}}}{X_{i,\text{exp}}}\right| \tag{19}$$

$$\text{ASE} = \frac{100}{n} \sum_{i=1}^{n} abs \left[\frac{a_{\text{w,calc}} - a_{\text{w,exp}}}{1 - a_{\text{w,exp}}}\right] \tag{20}$$

where $a_{\text{w,calc.}}$ and $a_{\text{w,exp}}$, are the a_w values estimated with the model and experimental value, respectively, while $X_{i,\text{exp}}$, $X_{i,\text{calc}}$, $\overline{X}_i$ are the experimental, calculated, and average moisture content values, respectively, and n is the number of experimental data points. R^2 quantifies the portion of the total variation explained by regression, so when R^2 is closer to 1, the model better fits the experimental data. RMSE and MRD values are measurements of deviation between experimental and predicted data, and low values of RMSE and MRD are expected for equations best describing the experimental data. When MRD < 10 %, the equation can be used to describe experimental data (Ruiz-López and Herman-Lara 2009; Basu et al. 2006). Plotting the residuals ($X - X_{\text{calc}}$) against the independent variable is also a measure of error distribution, i.e., when the model suitably describes the experimental data, the residuals should be randomly independent errors with a zero mean, constant variance and arranged in a normal distribution. If residual plots have a clear pattern, the model should be rejected (Basu et al. 2006).

6 Models Used to Describe Food Moisture Sorption Isotherms

Examples of mathematical models describing sorption isotherms for fruit products, as summarized in Table 2, show the GAB equation as the most widely used, since this theoretical 3-parameter equation provides estimates of monolayer moisture values and is able to take temperature effects into consideration. Reported MRD values for fruit sorption data under 10 % indicate a good fitness to experimental data. On the other hand, the BET equation describing only the low a_w isotherm portion is used by most authors to estimate moisture monolayer values, which are

Table 2 Mathematical equations used to describe fruit moisture sorption isotherms

Equation	Samples
GAB	Grapes (Kaymak-Ertekin and Sultanoğlu 2001), apricots (Kaymak-Ertekin and Sultanoğlu 2001), apple (Duarte Goneli et al. 2010; Kaymak-Ertekin and Sultanoğlu 2001; Spiess and Wolf 1987), mango (Rockland 1960; Timmermann et al. 2001; Hossain et al. 2001), banana (Ferro-Fontan et al. 1982; Jouppila and Roos 1997; Kaya and Kahyaoglu 2007; Moreira et al. 2009; Timmermann et al. 2001; Yan et al. 2008a, b), pineapple (Iglesias and Chirife 1976; Timmermann et al. 2001), gnetum (Eim et al. 2011), strawberries (Moraga et al. 2006), kiwi (Moraga et al. 2011), blue berries (Liu et al. 2010; Vega-Gálvez et al. 2009), dates (Belarbi et al. 2000), persimmon (Benedetti et al. 2011), papaya (Lewicki 1998)
BET	Grapes (Kaymak-Ertekin and Sultanoğlu 2001), apricots (Kaymak-Ertekin and Sultanoğlu 2001), apple (Kaymak-Ertekin and Sultanoğlu 2001), mango (Rockland 1960; Timmermann et al. 2001), banana (Ferro-Fontan et al. 1982; Jouppila and Roos 1997; Moreira et al. 2009; Timmermann et al. 2001; Yan et al. 2008a), pineapple (Timmermann et al. 2001), strawberries (Moraga et al. 2006), kiwi (Moraga et al. 2011), blue berries (Vega-Gálvez et al. 2009), dates (Belarbi et al. 2000)
Halsey	Grapes (Kaymak-Ertekin and Sultanoğlu 2001), apricots (Kaymak-Ertekin and Sultanoğlu 2001), apple (Kaymak-Ertekin and Sultanoğlu 2001), mango (Rockland 1960), banana (Ferro-Fontan et al. 1982; Jouppila and Roos 1997; Yan et al. 2008a), blue berries (Vega-Gálvez et al. 2009)
Henderson	Grapes (Kaymak-Ertekin and Sultanoğlu 2001), apricots (Kaymak-Ertekin and Sultanoğlu 2001), apple (Kaymak-Ertekin and Sultanoğlu 2001), mango (Quirijns et al. 2005; Rockland 1960), banana (Ferro-Fontan et al. 1982; Jouppila and Roos 1997; Yan et al. 2008b), pineapple (Iglesias and Chirife 1976), blue berries (Vega-Gálvez et al. 2009), persimmon (Benedetti et al. 2011)
Künh	
Lewicki	Persimmon (Benedetti et al. 2011)
Oswin	Grapes (Kaymak-Ertekin and Sultanoğlu 2001), apricot (Kaymak-Ertekin and Sultanoğlu 2001), apple (Kaymak-Ertekin and Sultanoğlu 2001), mango (Rockland 1960), banana (Ferro-Fontan et al. 1982; Yan et al. 2008b), blue berries (Vega-Gálvez et al. 2009), persimmon (Benedetti et al. 2011)
Peleg	Persimmon (Benedetti et al. 2011)
Smith	Mango (Rockland 1960), banana (Ferro-Fontan et al. 1982), pineapple (Iglesias and Chirife 1976), blue berries (Vega-Gálvez et al. 2009)

Table 3 Mathematical equations used to describe vegetables moisture sorption isotherms

Equation	Samples
GAB	Tomato pulp (Greenspan 1977), potato (Kaymak-Ertekin and Sultanoğlu 2001; McMinn and Magee 2003; Medeiros et al. 2006), mushrooms (Sharma et al. 2009), onion (Talla et al. 2005; Viswanathan et al. 2003), red pepper (Kim et al. 1991; Kingsly and Ileleji 2009), raw bamboo (Corey et al. 2011), gluten potato (Viollaz and Rovedo 1999), green pepper (Kingsly and Ileleji 2009), tomato slices (Akanbi et al. 2006), carrot (Escobedo-Avellaneda et al. 2011a), Mexican red sauce (Escobedo-Avellaneda et al. 2011b)
BET	Tomato pulp (Greenspan 1977), mushrooms (Baucour and Daudin 2000), potato (Kaymak-Ertekin and Sultanoğlu 2001; Medeiros et al. 2006), onion (Viswanathan et al. 2003), red pepper (Kingsly and Ileleji 2009), raw bamboo (Corey et al. 2011), green pepper (Kingsly and Ileleji 2009), tomato slices (Iglesias and Chirife 1982), Mexican red sauce (Escobedo-Avellaneda et al. 2011b)
Halsey	Mushrooms (Sharma et al. 2009), potato (Kaymak-Ertekin and Sultanoğlu 2001; McMinn and Magee 2003; Medeiros et al. 2006), onion (Viswanathan et al. 2003), green pepper (Greenspan 1977), tomato slices (Akanbi et al. 2006), carrot (Escobedo-Avellaneda et al. 2011a), Mexican red sauce (Escobedo-Avellaneda et al. 2011b)
Henderson	Potato (Kaymak-Ertekin and Sultanoğlu 2001), mushrooms (Sharma et al. 2009), onion (Viswanathan et al. 2003), carrot (Escobedo-Avellaneda et al. 2011a), Mexican red sauce (Escobedo-Avellaneda et al. 2011b)
Künh	Tomato slices (Akanbi et al. 2006), mushrooms (Sharma et al. 2009), Mexican red sauce (Escobedo-Avellaneda et al. 2011b)
Lewicki	
Oswin	Tomato pulp (Greenspan 1977), potato (Kaymak-Ertekin and Sultanoğlu 2001; Medeiros et al. 2006), mushrooms (Sharma et al. 2009), tomato slices (Akanbi et al. 2006), carrots (Escobedo-Avellaneda et al. 2011a)
Peleg	Tomato pulp (Greenspan 1977), turnip top leaves and stems (Moreira et al. 2005), carrots (Escobedo-Avellaneda et al. 2011a), Mexican red sauce (Escobedo-Avellaneda et al. 2011b)
Smith	Tomato pulp (Greenspan 1977), mushrooms (Sharma et al. 2009), carrot (Escobedo-Avellaneda et al. 2011a)

then compared to those obtained with the GAB model. The reported values of MRD above 15 % for the Halsey, Henderson, and Oswin equations show that these equations are not suitable for high sugar content products such as fruits.

The mathematical description of sorption isotherms for vegetable products, particularly spray dried tomato pulp (Table 3), shows that in the 20–60 °C temperature range the GAB model best describes the experimental data (MRE < 4 %) followed by the Peleg equation (MRE < 11 %). The Halsey, Henderson, and Oswin equations were not successful in showing MRE values reaching 86 % for the Halsey equation. In contrast, for green pepper, red pepper, and samples with high starch content such as potato, the Halsey and Oswin equations showed better results with MRE values in the 3.7–10.0 % range, while for mushrooms and carrots, the Henderson model was the most suitable with MRE of 0.42 % and 4.7 %, respectively. Table 4 summarizes equations describing the moisture isotherm for other

Table 4 Mathematical equation used to describe diverse food products moisture sorption isotherm

Equation	Samples
GAB	Cocoa beans (Menkov 2000; Sá and Sereno 1994), millet flour (Jamali et al. 2006), Basundi ready to use (Schmidt and Lee 2012), *Chenopodium ambrosioides* (pazote) (Johnson and Brennan 2000), cowpea and its protein insolated (Ayranci and Duman 2005), bitter orange leaves (Moraga et al. 2004), curd powder (Varghese et al. 2008), rice crackers (Singh and Singh 1996), maltodextrin (Lim et al. 1995), safflower petals and tarragon (Kaymak-Ertekin and Gedik 2003), fish flour (Lemus-Mondaca et al. 2009), cornmeal (Gabas et al. 1999), freeze-dried milk products (Katekawa and Silva 2007), starch gels (McMinn et al. 2004), potato starch (Al-Muhtaseb et al. 2002), bean flour (Mohamed et al. 2005), amaranth grains (Peleg 1993), macaroni (Arslan and Toğrul 2005), rice (Tonon et al. 2009), lentil seeds (Menkov et al. 2004), corn starch (Pott et al. 2005)
BET	Cocoa beans (Menkov 2000; Sá and Sereno 1994), millet flour (Jamali et al. 2006), Basundi ready to use (Schmidt and Lee 2012), cowpea and its protein insolated (Ayranci and Duman 2005), walnut flour (Menkov et al. 2005), curd powder (Varghese et al. 2008), safflower petals and tarragon (Kaymak-Ertekin and Gedik 2003), fish flour (Lemus-Mondaca et al. 2009), cornmeal (Gabas et al. 1999), freeze-dried milk products (Katekawa and Silva 2007), bean flour (Mohamed et al. 2005), macaroni (Arslan and Toğrul 2005), rice (Tonon et al. 2009), lentil seeds (Menkov et al. 2004), corn starch (Pott et al. 2005)
Halsey	Cocoa beans (Sá and Sereno 1994), cowpea and its protein insolated (Ayranci and Duman 2005), curd powder (Varghese et al. 2008), safflower petals and tarragon (Kaymak-Ertekin and Gedik 2003), freeze-dried milk products (Jamali et al. 2006), starch gels (McMinn et al. 2004), potato starch (Al-Muhtaseb et al. 2002), corn starch (Pott et al. 2005)
Henderson	Curd powder (Varghese et al. 2008), cocoa beans (Sá and Sereno 1994), cowpea and its protein insolated (Ayranci and Duman 2005), freeze-dried milk products (Katekawa and Silva 2007), starch gels (McMinn et al. 2004), macaroni (Arslan and Toğrul 2005), rice (Tonon et al. 2009), potato starch (Al-Muhtaseb et al. 2002), corn starch (Pott et al. 2005)
Künh	Cocoa beans (Sá and Sereno 1994), cowpea and its protein insolated (Ayranci and Duman 2005), freeze-dried milk products (Katekawa and Silva 2007)
Lewicki	Corn starch (Pott et al. 2005)
Oswin	Cowpea and its protein insolated (Ayranci and Duman 2005), curd powder (Varghese et al. 2008), safflower petals and tarragon (Kaymak-Ertekin and Gedik 2003), freeze-dried milk products (Katekawa and Silva 2007), macaroni (Arslan and Toğrul 2005), rice (Tonon et al. 2009)
Peleg	Starch gels (McMinn et al. 2004), macaroni (Arslan and Toğrul 2005), rice (Tonon et al. 2009), potato starch (Al-Muhtaseb et al. 2002)
Smith	Cocoa beans (Sá and Sereno 1994), cowpea and its protein insolated (Ayranci and Duman 2005), curd powder (Varghese et al. 2008), starch gels (McMinn et al. 2004), potato starch (Al-Muhtaseb et al. 2002), macaroni (Arslan and Toğrul 2005), rice (Tonon et al. 2009), corn starch (Pott et al. 2005)

food products. For amaranth grains and bean flour, the Henderson, Halsey, and Oswin models had MRD < 10 %, confirming that these equations can be used to describe high starch products. In conclusion, the models best describing moisture isotherms vary with the product type and composition.

7 Thermodynamic Properties: Sorption Heat, Enthalpy (ΔH), and Entropy (ΔS)

The determination of thermodynamic sorption properties can lead to an understanding of the molecular interactions between water molecules and the sorbent (Aguerre et al. 1986; Beristain et al. 1996). Enthalpy changes (ΔH) measure energy changes due to the molecular interaction between water molecules and sorbent during sorption processes, while entropy changes (ΔS) can be associated with binding or repulsive forces in the system. Finally, Gibb's free energy (ΔG) is associated with water affinity and provides a criterion to assess whether water sorption occurs as a spontaneous process (Beristain et al. 1996; Apostolopoulos and Gilbert 1990).

Thermodynamic sorption properties can be obtained when moisture isotherms are available at two or more temperature values. Food moisture sorption capacity may decrease with temperature, indicating that the hygroscopic characteristics of the sorbent decreases as well, which can be explained thermodynamically by using the Clausius-Clapeyron relationship (Aguerre et al. 1986; Gabas et al. 1999):

$$\ln a_{\mathrm{w}} = -\frac{Q}{R}\frac{1}{T} \tag{21}$$

where a_{w} is water activity, $-Q/R$ is the slope in the lineal relationship of $\ln a_{\mathrm{w}}$ against the inverse absolute temperature (T), Q is isosteric heat of sorption, and R is the ideal gas constant. The net isosteric heat of adsorption is used to calculate the binding energy between water molecules as follows:

$$\ln a_{\mathrm{w}} = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{22}$$

A linear relationship between the enthalpy and entropy of the moisture sorption forces has been shown for several products where the slope represents the isokinetic temperature (T_{B}) and the intercept is the Gibb's free energy value (ΔG_{B}) (Aguerre et al. 1986; Beristain et al. 1996; Ferro-Fontan et al. 1982). This relationship (Eq. 23) is known as the enthalpy-entropy compensation or isokinetic theory. This relationship determines if sorption phenomena are controlled by enthalpic or entropic processes. T_{B}, defined as the temperature at which all reactions in the series proceed at the same rate, can be compared to the harmonic temperature (T_{hm}, Eq. 24) to confirm the existence of enthalpy-entropy compensation. When $T_{\mathrm{B}} > T_{\mathrm{hm}}$, the sorption process is enthalpy controlled, while $T_{\mathrm{hm}} > T_{\mathrm{B}}$ indicates that the process is entropy controlled (Aguerre et al. 1986; Gabas et al. 2000).

$$\Delta H = T_{\mathrm{B}}\Delta S + \Delta G_{\mathrm{B}} \tag{23}$$

Fig. 5 Schematic representation of isosteric heat of sorption against moisture content in food products
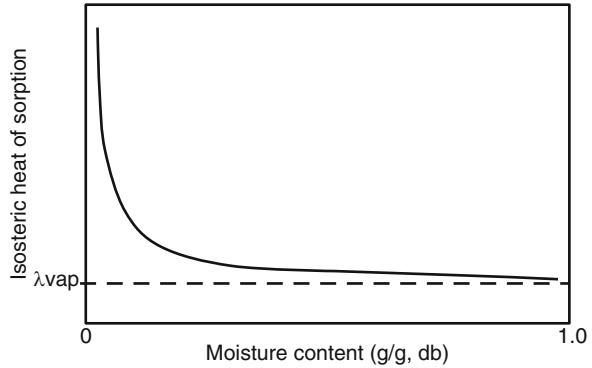
$$T_{hm} = \frac{n}{\sum\limits_{i=1}^{n} \left(1/T \right)} \qquad (24)$$

Beristain et al. (1996) observed the existence of two different mechanisms of moisture adsorption in potato and macadamia nuts. At low a_w, the process was enthalpy controlled, while subsequent moisture gain is entropy controlled. In contrast, in dried fruits (raisins, currants, figs, prunes, and apricots) the process was enthalpy controlled for the entire moisture content range. Enthalpy-controlled processes were also observed for plum pulp and skin (Gabas et al. 1999), spray dried tomato pulp (Goula et al. 2008), loquat and quince (Moreira et al. 2008), and other high sugar content products.

Isosteric heat of sorption (q_{st}) dependency on food moisture content (Fig. 5) shows that as moisture content increases and a_w approaches 1.0, it comes close to the vaporization heat of pure water. Values are higher at low moisture values (<20 %) because water molecules in this zone bind directly to the food components. In high sugar content products, q_{st} values are higher than in high insoluble fiber content products because in the former, water molecules form hydrogen bonds with sugar molecules and more energy will be required to break them. The isosteric heat of sorption should be considered when evaluating energy requirements in food drying processes (Gabas et al. 1999).

8 Applications of Moisture Sorption Isotherms

Sorption isotherms are used to predict the stability of foods sensitive to moisture changes during storage (Bell and Labuza 2000), including microbial activity prediction, evaluation of chemical changes due to moisture gain or loss, enzymatic

reactions, lipid oxidation, and nonenzymatic browning (Iglesias and Chirife 1982). Physical changes may take place during the adsorption process, including stickiness, caking, crystallization, and other alterations caused by a_w changes. Knowledge of moisture content or a_w value leading to undesirable changes in product quality, defined as the critical moisture sorption point (MSP), could improve food transport and storage to prevent undesirable product changes.

Product quality losses have also been related to the glass transition point of dehydrated products. An amorphous state is reached in foods with high sugar content when they have been dehydrated; however, when phase changes to a rubbery state, quality loss can occur within days and even hours. The viscosity of amorphous material is around 10^{12} Pa s, and the mobility of water molecules will be low enough to prevent microbial and enzymatic degradation reactions (Xie et al. 2010; Rahman et al. 2003; Liu et al. 2010). This phase change from a glassy state to a rubbery state is known as glass transition, which is a temperature, moisture content, and time dependent process.

Phase transitions can be accelerated by increasing temperature or adding a plasticizer. In high sugar products, water can serve as the plasticizer; thus, the increase in moisture content may decrease the glass transition temperature to the storage temperature (Yuan et al. 2011). The moisture content at which a glass transition takes place at a given storage temperature is a critical moisture content value. Estimations of the critical moisture content and a_w at the glass transition point are presented in Fig. 6 for structural or texture changes in the final product due to the gain of water (Tonon et al. 2009).
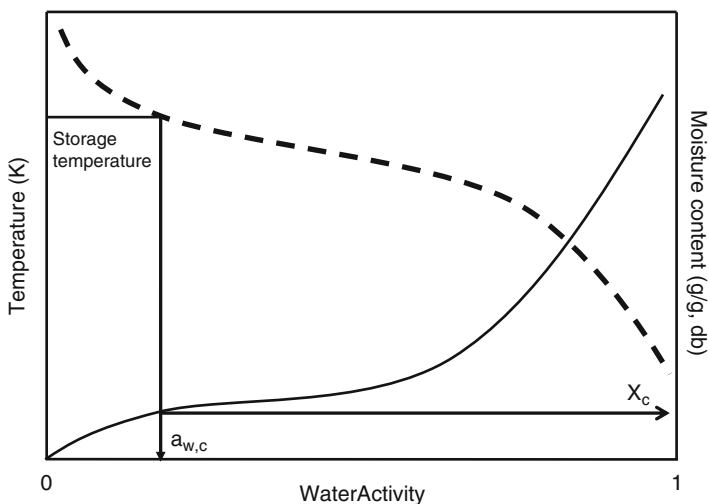

Fig. 6 Graphical representation of glass transition (*dashed line*) and moisture sorption isotherms (*solid line*) used to predict critical moisture content by dried products in order to prevent changes on structural or texture properties

9   Sorption Isotherms and Shelf Life Predictions Considering Parameter Variability

Moisture isotherms can be used to select the most appropriate packaging material to achieve a desired shelf life (Welti-Chanes et al. 2008; Escobedo-Avellaneda et al. 2011a). Since the adsorption and desorption processes are not the same due to the hysteresis phenomenon, it is important to use adsorption isotherms when analyzing moisture gain and desorption isotherms. An adequate predictive model is crucial to accurately predict the shelf life of products, such as the one proposed by Labuza and Altunakar (2007):

$$\ln\left(\frac{X_e - X_i}{X_e - X_c}\right) = \frac{k\,A \cdot p_v^0}{x\,\mathrm{ds} \cdot m}\theta \qquad (25)$$

where X is moisture content (g H_2O/g dried solids) with the subindices i and c corresponding to the initial and critical values, respectively, while e describes the equilibrium with the storage RH; k/x (g/m^2 dia mmHg) is the permeance of the packaging film, A (m^2) is the packaging area, ds (g solids) are the dried solids of the food, p_v^0 (mm Hg) is the water vapor pressure at the sorption isotherm temperature, m is the linearized portion slope of the sorption isotherm in the range of interest (Fig. 7), and θ (days) is the estimated shelf life (Bourlieu et al. 2009). Equation (24) allows estimations of shelf life time by considering initial moisture content, moisture content at which the product becomes unacceptable to the consumer, temperature and RH of storage, and packaging material. This equation can be used in a deterministic mode, i.e., when parameter variability is not considered in the calculation and therefore the predicted value does not include a shelf life confidence
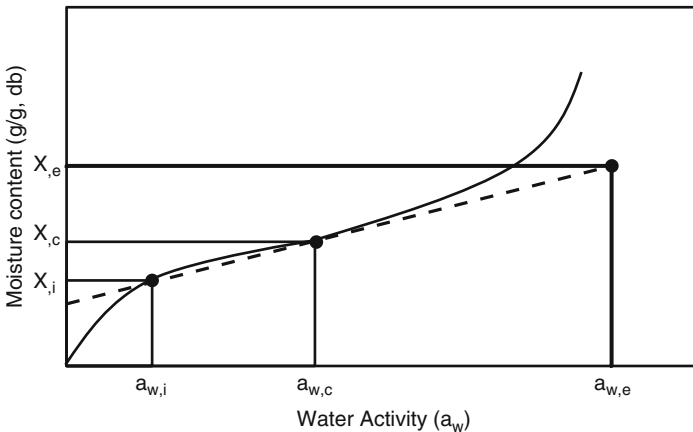

Fig. 7 Sorption isotherm (*solid line*) used to calculate parameters in shelf life equation for dried foods, where X_c, X_i, and X_e are the critical, initial, and equilibrium moisture content, respectively

assessment. On the other hand, a Monte Carlo procedure was recently used to consider the variability of the moisture isotherm to estimate frequency distributions for the shelf life of dehydrated tomato slices, chopped onions, and green beans slices (Escobedo-Avellaneda et al. 2011b). A Monte Carlo procedure is a statistical method that allows the generation of frequency distributions describing all possible values for a given outcome (Chotyakul et al. 2011, 2012). This procedure takes into account the statistical variability of all parameters used. Escobedo-Avellaneda et al. (2011b) showed a shelf life of 175.5, 62, and 57 days for tomato, onion, and green beans of intermediate and low moisture content when the variability of GAB parameters and a_w values was not taken into account. On the other hand, when the standard deviation of GAB parameters and a_w values was considered, shelf life frequency distributions of about 130–270 days, 55–69 days, and 51–65 days for tomato, onion, and green beans were obtained, respectively. If the accepted probability that the shelf life would fail before the time specified were 5 %, the recommended shelf life for tomato, onion, and green beans would be 150 days, 58 days, and 53 days, respectively. On the other hand, if the average values for the prediction model parameters were used to estimate shelf life, the probability of product failure before this value would be equal to or higher than 50 %. Therefore, the Monte Carlo method proposed by these authors is an effective tool to determine the shelf life of food products with an acceptable risk of product failure before the shelf life declared by the producer on its label.

10 Final Remarks

Sorption isotherms play a critical role in the description of the properties of hygroscopic materials and are used to establish proper handling and storage conditions to extend the shelf life of low and intermediate moisture content products. The described experimental methods for determination of sorption isotherms are critical for estimation of the hygroscopic properties of foods. Automatic equipment has been developed to facilitate obtaining sorption isotherms, reducing experimental times and even increasing the resolution of the experimental data obtained. However, studies with these units should be expanded to include more complex systems and improve their design and the procedures to follow when using them. Methods to determine which equations can best describe experimental moisture sorption data allow more accurate prediction of conditions of stability, and necessary processes in the study data have shown that no equation can describe all products and the entire a_w range. Adequate descriptions of the moisture data for various products in the 0.03–0.95 a_w range have been reported for the GAB, Peleg, and Lewicki 3-parameter equations. Thermodynamic properties from sorption isotherms can be used in drying process design, or in shelf life prediction for intermediate and low moisture content products, or in setting storage condition and selection of the properties of the packaging materials. Finally, nondeterministic

calculation procedures such as the Monte Carlo method represent a new opportunity to improve shelf life estimations.

References

Aguerre RJ, Suárez C, Viollaz PE (1986) Enthalpy-entropy compensation in sorption phenomena: application to the prediction of the effect of temperature on food isotherms. J Food Sci 51:1547–1549

Akanbi CT, Adeyemi RS, Ojo A (2006) Drying characteristics and sorption isotherm of tomato slices. J Food Eng 73:157–163

Al-Muhtaseb AH, McMinn WAM, Magee TRA (2002) Moisture sorption isotherm characteristics of food products: a review. Trans IChemE 80:118–128

Al-Muhtaseb AH, McMinn WAM, Magee TRA (2004) Water sorption isotherms of starch powders. Part 1: Mathematical description of experimental data. J Food Eng 61:297–307

Apostolopoulos D, Gilbert SG (1990) Water sorption of coffee solubles by frontal inverse gas chromatography: thermodynamic considerations. J Food Sci 55:475–477

Arlabosse P, Rodier E, Ferrasse JH, Chavez S, Lecomte D (2003) Comparison between static and dynamic methods for sorption isotherm measurements. Dry Tech 21:479–497

Arslan N, Toğrul H (2005) Modeling of water sorption isotherms of macaroni stored in a chamber under controlled humidity and thermodynamic approach. J Food Eng 69:133–145

Ayranci E, Duman O (2005) Moisture sorption isotherms of cowpea (Vigna unguiculata L. Walp) and its protein isolate at 10, 20 and 30 °C. J Food Eng 70:83–91

Basu S, Shivhare US, Mujumdar AS (2006) Models for sorption isotherms for foods: a review. Dry Tech 24:917–930

Baucour P, Daudin J (2000) Development of a new method for fast measurement of water sorption isotherms in the high humidity range validation on gelatin gel. J Food Eng 44:97–107

Belarbi A, Aymard C, Meot JM, Themelin A, Reynes M (2000) Water desorption isotherms for eleven varieties of dates. J Food Eng 43:103–107

Bell LN, Labuza TP (2000) Moisture sorption: practical aspects of isotherm measurement and use, 2nd edn. American Association of Cereal Chemists, St. Paul, MN

Benedetti PDCD, Pedro MAM, Telis-Romero J, Telis VRN (2011) Influence of encapsulating materials on water sorption isotherms of vacuum-dried persimmon pulp powder. J Food Process Preserv 35:423–431

Beristain CI, Garcia HS, Azuara E (1996) Enthalpy-entropy compensation in food vapor adsorption. J Food Eng 30:3–4

Bhandari BR, Adhikari B (2008) Water activity in food processing and preservation. In: Chen XD, Arun SM (eds) Drying technologies in food processing. Blackwell Publishing Ltd., West Sussex, pp 55–89

Bourlieu C, Guillard V, Vallès-Pamiès B, Guilbert S, Gontard N (2009) Edible moisture barriers: how to assess of their potential and limits in food products shelf-life extension? Crit Rev Food Sci Nutr 49:474–499

Brunauer S, Emmett PH, Teller E (1938) Adsorption of gases in multimolecular layers. J Am Chem Soc 60:309–319

Carter B, Fontana A (2008) Dynamic dewpoint isotherm versus other moisture sorption isotherm methods. Application note. Decagon Devices, Pullman, WA

Carter BP, Schmidt SJ (2012) Developments in glass transition determination in foods using moisture sorption isotherms. Food Chem 132:1693. doi:10.1016/j.foodchem.2011.06.022

Chotyakul N, Velazquez G, Torres JA (2011) Assessment of the uncertainty in thermal food processing decisions based on microbial safety objectives. J Food Eng 102:247–256

Chotyakul N, Pérez Lamela C, Torres JA (2012) Effect of model parameter variability on the uncertainty of refrigerated microbial shelf-life estimates. J Food Process Eng 35:829. doi:10.1111/j.1745-4530.2010.00631.x

Corey ME, Kerr WL, Mulligan JH, Lavelli V (2011) Phytochemical stability in dried apple and green tea functional products as related to moisture properties. LWT Food Sci Technol 44:67–74

Duarte Goneli AL, Corrêa PC, Horta De Oliveira GH, Ferreira Gomes C, Mendes Botelho F (2010) Water sorption isotherms and thermodynamic properties of pearl millet grain. Int J Food Sci Technol 45:828–838

Eim VS, Rosselló C, Femenia A, Simal S (2011) Moisture sorption isotherms and thermodynamic properties of carrot. Int J Food Eng 7(3):1. doi:10.2202/1556-3758.1804

Escobedo-Avellaneda Z, Pérez-Pérez MC, Bárcenas-Pozos ME, Welti-Chanes J (2011a) Moisture adsorption isotherms of freeze-dried and air-dried Mexican red sauce. J Food Process Eng 34:1931–1945

Escobedo-Avellaneda Z, Velazquez G, Torres JA, Welti-Chanes J (2011b) Inclusion of the variability of model parameters on shelf-life estimations for low and intermediate moisture vegetables. LWT Food Sci Technol 47:364–370

Ferro-Fontan C, Chirife J, Sancho E, Iglesias HA (1982) Analysis of a model for water sorption phenomena in foods. J Food Sci 47:1590–1594

Furmaniak S, Terzyk AP, Gołembiewski R, Gauden PA, Czepirski L (2009) Searching the most optimal model of water sorption on foodstuffs in the whole range of relative humidity. Food Res Int 42:1203–1214

Gabas AL, Telis-Romero J, Menegalli FC (1999) Thermodynamic models for water sorption by grape skin and pulp. Dry Tech 17:962–974

Gabas AL, Menegali FC, Telis-Romero J (2000) Water sorption enthalpy-entropy compensation based on isotherms of plum skin and pulp. J Food Sci 65:680–684

Goula AM, Karapantsios TD, Achilias DS, Adamopoulos KG (2008) Water sorption isotherms and glass transition temperature of spray dried tomato pulp. J Food Eng 85:73–83

Greenspan L (1977) Humidity fixed points of binary saturated aqueous solutions. J Res Natl Bur Stand 81a:89–112

Halsey G (1948) Physical adsorption in non-uniform surfaces. J Chem Phys 16:931

Henderson SM (1952) A basic concept of equilibrium moisture. Agric Eng 33:29–35

Hossain MD, Bala BK, Hossain MA, Mondol MRA (2001) Sorption isotherms and heat of sorption of pineapple. J Food Eng 48:103–107

Iglesias HA, Chirife J (1976) Equilibrium moisture contents of air dried beef. Dependence on drying temperature. Int J Food Sci Technol 11:565–573

Iglesias HA, Chirife J (1982) Handbook of food isotherms. Academic, New York, NY

Jamali A, Kouhila M, Mohamed LA, Jaouhari JT, Idimam AI, Abdenouri N (2006) Sorption isotherms of Chenopodium ambrosioides leaves at three temperatures. J Food Eng 72:77–84

Johnson P-NT, Brennan JG (2000) Moisture sorption isotherm characteristics of plantain (Musa, AAB). J Food Eng 44:79–84

Jouppila K, Roos YH (1997) Water sorption isotherms of freeze-dried milk products: applicability of linear and non-linear regression analysis in modeling. Int J Food Sci Technol 32:459–471

Katekawa ME, Silva MA (2007) On the influence of glass transition on shrinkage in convective drying of fruits: a case study of banana drying. Dry Tech 25:1659–1666

Kaya S, Kahyaoglu T (2007) Moisture sorption and thermodynamic properties of safflower petals and tarragon. J Food Eng 78:413–421

Kaymak-Ertekin F, Gedik A (2003) Sorption isotherms and isosteric heat of sorption for grapes, apricots, apples and potatoes. LWT Food Sci Technol 37:429–438

Kaymak-Ertekin F, Sultanoğlu M (2001) Moisture sorption isotherm characteristics of peppers. J Food Eng 47:225–231

Kim HK, Song Y, Yam KL (1991) Water sorption characteristics of dried red peppers (Capsicum annum L.). Int J Food Sci Technol 29:339–345

Kingsly ARP, Ileleji KE (2009) Sorption isotherm of corn distillers dried grains with solubles (DDGS) and its prediction using chemical composition. Food Chem 116:939–946

Kühn I (1964) A new theoretical analysis of adsorption phenomena. Introductory part: the characteristic expression of the main regular types of adsorption isotherms by single simple equation. J Coll Sci 19:685–698

Labuza TP, Altunakar B (2007) Water activity prediction and moisture sorption isotherms. In: Barbosa-Cánovas GV, Fontana AJ, Schmidt SJ, Labuza TP (eds) Water activity in foods: Fundamentals and applications. IFT/Blackwell, Ames, IA, pp 109–154

Lemus-Mondaca R, Betoret N, Vega-Galvéz A, Lara-Aravena E (2009) Dehydration characteristics of papaya (Carica pubescens): determination of equilibrium moisture content and diffusion coefficient. J Food Process Eng 32:645–663

Lewicki PP (1998) A three parameter equation for food moisture sorption isotherms. J Food Process Eng 21:127–144

Lewicki PP (2000) Raoult's law based food water sorption isotherm. J Food Eng 43:31–40

Li QE, Schmidt SJ (2011) Use of ramping and equilibrium water vapor sorption methods to determine the critical relative humidity at which the glassy to rubbery transition occurs in polydextrose. J Food Sci 76:149–157

Lim LT, Tang J, He J (1995) Moisture sorption characteristics of freeze dried blueberries. J Food Sci 60:810–814

Liu P, Yu L, Wang X, Li D, Chen L, Li X (2010) Glass transition temperature of starches with different amylose/amylopectin ratios. J Cereal Sci 51:388–391

López-Malo A, Palou E, Argaiz A (1994) Measurement of water activity of saturated salt solutions at various temperatures. In: Argaiz A, López-Malo A, Palou E, Corte P (eds) Proceeding of the session, ISOPOW Practicum II. Universidad de las Américas Puebla, Puebla, pp 113–116

McMinn WAM, Magee TRA (2003) Thermodynamic properties of moisture sorption of potato. J Food Eng 60:157–165

McMinn WAM, Al-Muhtaseb AH, Magee TRA (2003) Moisture sorption characteristics of starch gels. Part 1: Mathematical description of experimental data. J Food Process Eng 26:323–338

McMinn WAM, Al-Muhtaseb AH, Magee TRA (2004) Assessment of two- and three-parameter Lewicki models for description of sorption phenomena of starch materials. J Sci Food Agric 84:1695–1700

Medeiros ML, Ayrosa AMIB, Pitombo RNM, Lannes SCS (2006) Sorption isotherms of cocoa and cupuassu products. J Food Eng 73:402–406

Menkov ND (2000) Moisture sorption isotherms of lentil seeds at several temperatures. J Food Eng 44:205–211

Menkov ND, Durakova AG, Krasteva A (2004) Moisture sorption isotherms of walnut flour at several temperatures. Biotechnol Biotechnol Equip 18:201–206

Menkov ND, Durakova AG, Krasteva A (2005) Moisture sorption isotherms of common bean flour at several temperatures. Electron J Environ Agric Food Chem 4:892–898

Mohamed LA, Kouhila M, Jamali A, Lahsasni S, Mahrouz M (2005) Moisture sorption isotherms and heat of sorption of bitter orange leaves (Citrus aurantium). J Food Eng 67:491–498

Moraga G, Martıínez-Navarrete N, Chiralt A (2004) Water sorption isotherms and glass transition in strawberries: influence of pretreatment. J Food Eng 62:315–321

Moraga G, Martıínez-Navarrete N, Chiralt A (2006) Water sorption isotherms and phase transitions in kiwifruit. J Food Eng 72:147–156

Moraga G, Talens P, Moraga MJ, Martínez-Navarrete N (2011) Implication of water activity and glass transition on the mechanical and optical properties of freeze-dried apple and banana slices. J Food Eng 106:212–219

Moreira R, Chenlo F, Vázquez MJ, Cameán P (2005) Sorption isotherms of turnip top leaves and stems in the temperature range from 298 to 328 K. J Food Eng 71:193–199

Moreira R, Chenlo F, Torres MD, Vallejo N (2008) Thermodynamic analysis of experimental sorption isotherms of loquat and quince fruits. J Food Eng 88:514–521

Moreira R, Chenlo F, Torres MD (2009) Simplified algorithm for the prediction of water sorption isotherms of fruits, vegetables and legumes based upon chemical composition. J Food Eng 94 (3–4):334–343

Myhara RM, Taylor MS, Slominski BA, Al-Bulushi I (1998) Moisture sorption isotherms and chemical composition of Omani dates. J Food Eng 37:471–479

Oswin CR (1946) The kinetics of package life. III. The isotherm. J Soc Chem Ind 65(12):419–421

Peleg M (1993) Assessment of a semi-empirical four parameter general model for sigmoid moisture sorption isotherms. J Food Process Eng 16:21–37

Pott I, Neidhart S, Mühlbauer W, Carle R (2005) Quality improvement of non-sulphited mango slices by drying at high temperatures. Innov Food Sci Emerg Technol 6:412–419

Quirijns EJ, van Boxtel AJB, van Loon WKP, van Straten G (2005) Sorption isotherms, GAB parameters and isosteric heat of sorption. J Sci Food Agric 85:1805–1814

Rahman MS (1995) Food properties handbook. CRC, Boca Raton, FL

Rahman MS (2009) Food stability beyond water activity and glass transition: macro-micro region concept in the state diagram. Int J Food Prop 12:726–740

Rahman MS, Al-Belushi RH (2006) Dynamic isopiestic method (DIM): measuring moisture sorption isotherm of freeze-dried garlic powder and other potential uses of DIM. Int J Food Prop 9:421–437

Rahman MS, Kasapis S, Guizani N, Al-Amri OS (2003) State diagram of tuna meat: freezing curve and glass transition. J Food Eng 57:321–326

Rockland LR (1960) Saturated salt solutions for static control of relative humidity between 5° and 40°C. Anal Chem 32:1375–1376

Roman-Gutierrez AD, Guilbert S, Cuq B (2002) Distribution of water between wheat flour components: a dynamic water vapor adsorption study. J Cereal Sci 36:347–355

Ruiz-López II, Herman-Lara E (2009) Statistical indices for the selection of food sorption isotherm models statistical indices for the selection of food sorption isotherm models. Dry Tech 27:726–738

Sá MM, Sereno AM (1994) Glass transition and state diagrams for typical natural fruits and vegetables. Thermochim Acta 246:285–297

Schmidt SJ, Lee JW (2012) Comparison between water vapor sorption isotherms obtained using the new dynamic dewpoint isotherm method and those obtained using the standard saturated salt slurry method. Int J Food Prop 15:236–248

Sharma P, Singh RRB, Singh AK, Patel AA, Patil GR (2009) Sorption isotherms and thermodynamics of water sorption of ready-to-use Basundi mix. LWT Food Sci Technol 4:441–445

Singh PC, Singh RK (1996) Application of GAB model for water sorption isotherms of food products. J Food Process Preserv 20:203–220

Smith SE (1947) The sorption of water vapor by high polymers. J Am Chem Soc 69:646–651

Spackman CCW, Schmidt SJ (2010) Characterizing the physical state and textural stability of sugar gum pastes. Food Chem 119:490–499

Spiess WEL, Wolf W (1987) Critical evaluation of methods to determine moisture sorption isotherms. In: Rockland LR, Beuchat LR (eds) Water activity: theory and applications to food. Institute of Food Technologists, Chicago, IL, pp 215–233

Talla A, Jannot Y, Elambo Nkeg G, Puiggali J-R (2005) Experimental determination and modeling of sorption isotherms of tropical fruits: banana, mango, and pineapple experimental determination and modeling of sorption isotherms of tropical. Dry Tech 23:1477–1498

Timmermann EO, Chirife J, Iglesias HA (2001) Water sorption isotherms of foods and foodstuffs: BET or GAB parameters? J Food Eng 48:19–31

Tonon RV, Baroni AF, Brabet C, Gibert O, Pallet D, Hubinger MD (2009) Water sorption and glass transition temperature of spray dried açai (Euterpe oleracea Mart.) juice. J Food Eng 94:215–221

van den Berg C, Bruins S (1981) Water activity and its estimation in food systems: theoretical aspects. In: Rockland LR, Stewart GF (eds) Water activity: influence on food quality. Academic Press, Inc., New York, NY, pp 1–61

Varghese KS, Ramachandrannair SV, Mishra HN (2008) Moisture sorption characteristics of curd (Indian yogurt) powder. Int J Dairy Technol 62:85–92

Vega-Gálvez A, López J, Miranda M, DiScala K, Yagnam F, Uribe E (2009) Mathematical modeling of moisture sorption isotherms and determination of isosteric heat of blueberry variety O'Neil. Int J Food Sci Technol 44:2033–2041

Viollaz PE, Rovedo CO (1999) Equilibrium sorption isotherms and thermodynamic properties of starch and gluten. J Food Eng 40:287–292

Viswanathan R, Jayas DS, Hulasare RB (2003) Sorption isotherms of tomato slices and onion shreds. Biosyst Eng 86:465–472

Welti-Chanes J, Pérez E, Guerrero-Beltrán JA, Alzamora SM, Vergara-Balderas F (2008) Applications of water activity management in the food industry. In: Barbosa-Canovas GV, Fontana AJ, Schmidt AR, Labuza TP (eds) Water: activity in foods. Blackwell Publishing Ltd., Oxford, UK, pp 341–357

Xie F, Liu W-C, Liu P, Wang J, Halley PJ, Yu L (2010) Starch thermal transitions comparatively studied by DSC and MTDSC. Starch 62:350–357

Yan Z, Sousa-Gallagher J, Oliveira FAR (2008a) Sorption isotherms and moisture sorption hysteresis of intermediate moisture content banana. J Food Eng 86:342–348

Yan Z, Sousa-Gallagher MJ, Oliveira FAR (2008b) Effect of temperature and initial moisture content on sorption isotherms of banana dried by tunnel drier. Int J Food Sci Technol 43:1430–1436

Yao W, Yu X, Lee JW, Yuan X, Schmidt SJ (2011) Measuring the deliquescence point of crystalline sucrose as a function of temperature using a new automatic isotherm generator. Int J Food Prop 14:882–893

Yu X, Kappes SM, Bello-Pérez LA, Schmidt SJ (2008a) Investigating the moisture sorption behavior of amorphous sucrose using a dynamic humidity generating instrument. J Food Sci 73(1):25–35

Yu X, Martin SE, Schmidt SJ (2008b) Exploring the problem of mold growth and the efficacy of various mold inhibitor methods during moisture sorption isotherm measurements. J Food Sci 73:69–81

Yu X, Schmidt AR, Bello-Pérez LA, Schmidt SJ (2008c) Determination of the bulk moisture diffusion coefficient for corn starch using an automated water sorption instrument. J Agric Food Chem 56:50–58

Yuan X, Carter BP, Schmidt SJ (2011) Determining the critical relative humidity at which the glassy to rubbery transition occurs in polydextrose using an automatic water vapor sorption instrument. J Food Sci 76(1):78–89