Fundamentals of Moisture Sorption Isotherms

Water profoundly influences product attributes such as quality and safety. To completely understand water relations in a product requires an understanding of the amount of water (moisture content) that can be held at a given energy state (water activity). Moisture sorption isotherms describe the relationship between water activity and moisture content at a constant temperature. The nature of this relationship depends on the interaction between water and other ingredients. The amount of water vapor that can be absorbed by a product depends on its chemical composition, physical-chemical state, and physical structure. Consequently, the isotherm shape is unique to each product type due to differences in capillary, surface, and colligative effects (Figure 1). Products that lie in the low water activity portion of the isotherm are often referred to as dry, those in the range of 0.60 a_w to 0.90 aw are intermediate moisture products, and those having water activities higher than 0.90 are high water activity products.

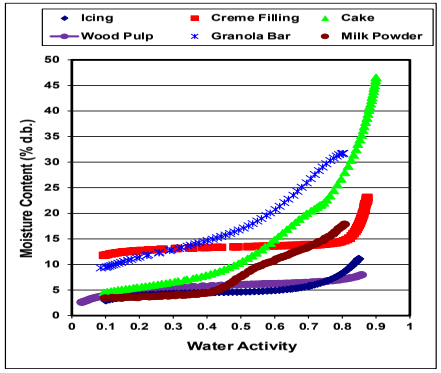

Figure 1. Moisture adsorption isotherms for icing, crème filling, cake, wood pulp, granola bar, and milk powder showing that the isotherm shape is unique to the product.

For ease of interpretation, isotherms are often identified by Brunauer classifications (Brunauer, 1945). Most food and pharmaceutical products fall under type I, II, or III. Type I isotherms are typical of very hygroscopic materials, Type II (sigmoidal) isotherms are typical for intermediate moisture products, and type III (J-shaped) isotherms are typical for crystalline and coated materials. These general classifications proved useful when conducting isotherms on every product was not feasible due to time and labor constraints. However, with automation and improved speed, isotherms can easily be conducted on any product and the uniqueness of each isotherm often proves more valuable than placing them in a common classification.

Hysteresis

Figure 2 shows two isotherms, one obtained by wetting a sample from a dry state and the other obtained by drying a sample from wet state. The arrows show the direction of the process. The moisture content at each water activity is higher during desorption (drying from high moisture content) than adsorption (wetting from low moisture content). The curves in Fig. 2 represent limits or bounding isotherms since they begin at water activities near zero and 1. If a drying process reduces the water activity of a sample only part way to dryness, and the sample is then rewet, it follows a path between the wetting and drying boundary curves, as shown in Fig. 3. These curves are called scanning curves, and there can be infinitely many of them depending on where drying stops and starts.

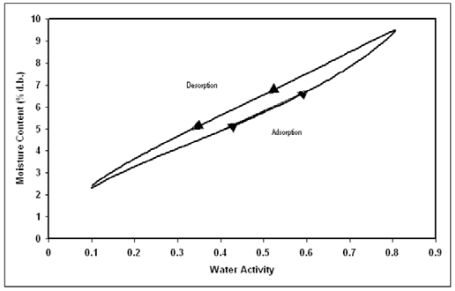

Figure 2. Full isotherm of microcrystalline cellulose showing hysteresis.

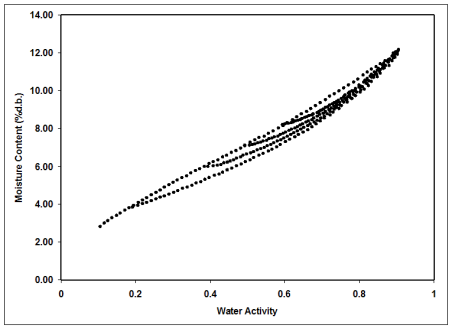

Figure 3. Scanning adsorption curves of microcrystalline cellulose resulting from drying to different water activities. Isotherm was started in adsorption at 0.2 aw, wetted to 0.90 aw, dried to 0.4 aw, wetted back to 0.90 aw, dried to 0.50 aw, wetted back to 0.90 aw, dried to 0.60 aw, wetted back to 0.90 aw, and then dried down to 0.10 aw.

For ease of interpretation, isotherms are often identified by Brunauer classifications (Brunauer, 1945). Most food and pharmaceutical products fall under type I, II, or III. Type I isotherms are typical of very hygroscopic materials, Type II (sigmoidal) isotherms are typical for intermediate moisture

As can be seen from these examples, an isotherm is not a single valued function but depends on the wetting and drying history of the sample. This phenomenon is called hysteresis.

It is possible to obtain isotherm data which appear to show hysteresis by failing to allow a sample to equilibrate at each step or by inducing changes in the water binding properties of the matrix by wetting or drying it. It is preferable to treat these cases separately, and reserve the term hysteresis for situations where equilibrium is obtained, but moisture contents of wetted and dried samples still differ because of their history.

Several plausible hysteresis models exist for samples wet enough for water to be held in the matrix by capillary forces. The “ink bottle” model pictures a pore with a narrow neck and a larger internal radius. Such a pore would fill when the water activity corresponding to the energy state of the larger, internal radius was exceeded, but would empty only when the water activity dropped below the energy state of the neck radius. The moisture content of a drying process would therefore always be greater than that for a wetting process. Another model relates to the contact angle of water with the surface during wetting and drying. At lower water activities typical of intermediate and low moisture foods these models appear less relevant, but the observed hysteresis is similar to that seen at higher water activity.

Non-Equilibrium

If diffusion of water into (adsorption) or out of (desorption) a material is slow and sufficient time is not allowed for complete diffusion, there will be a large amount of apparent hysteresis that could be reduced by allowing sample equilibration.

Matrix Changes

Figure 4 shows three different isotherm curves of spray-dried milk powder with different maximum water activities and different sorption histories. The boundary isotherm with a 0.80 a_w maximum experienced a phase change at 0.43 a_w, indicated by a sharp inflection point in the curve. The desorption curve for this isotherm appears to show hysteresis, especially below a water activity of 0.60. However, an isotherm, run on a sample wetted to a maximum water activity below the phase change, exhibits very little hysteresis. The lack of hysteresis in this isotherm indicates that the matrix changes that occur at 0.43 a_w are completely responsible for the apparent hysteresis.

Water in a sample is bound to particle surfaces by various bonding mechanisms. When the configuration of particle surfaces changes due to a phase change, binding sites change and the amount of water which can be bound at a given energy of water also changes. An isotherm curve of the phase changed sample does not show further phase transitions since simply drying the sample does not return it to an amorphous state.

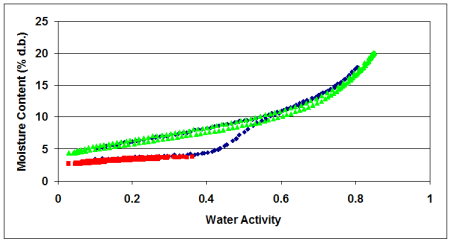

Figure 4. Moisture sorption isotherms for spray-dried milk powder showing a change in hysteresis due to a phase change at 0.43 aw. When the isotherm is ended prior to the phase change at 0.43 aw (■), there is little hysteresis. When the isotherm is ended above the phase change (♦), there is apparent, but not actual hysteresis due to the phase change. Subsequent isotherms run on the sample after experiencing a phase transition (▲) do not show an inflection point, are repeatable, and exhibit only small levels of hysteresis.

These matrix changes represent a true physical change in the material. They are not reversible by drying, no matter how many drying cycles occur. Differences between the adsorption and desorption curves in the inital isotherm is not true hysteresis since the sample matrix has experienced a physical change. Differences between sorption curves in the subsequent isotherms represents true hysteresis.

Working Isotherms

Full boundary isotherms give information about the physical characteristics of a product, show hysteresis, and are important in establishing critical control points, but in many cases a working isotherm will prove very useful. A working isotherm shows how a product adsorbs and desorbs water from its current or typical condition. To create a working isotherm, the product is processed as usual, and then a scanning curve is created by wetting one sample from that point and drying a different sample from that same point. Figure 5 shows a working isotherm for wood pulp superimposed over its full boundary isotherm.

The scanning curve the product will initially follow depends on whether the product was previously wetted or dried to its current state. If a product was wetted to a certain water activity and then is dried back down, there will be an initial transition period as the product moves from the adsorption curve to the desorption curve. The same is true for a product that was previously dried and then wetted up. There will be an initial transition period as the product moves from the desorption curve to the adsorption curve. This transition region can be observed at any point on the isotherm if the direction of the sorption is changed and the product exhibits hysteresis as can be observed in Figure 5.

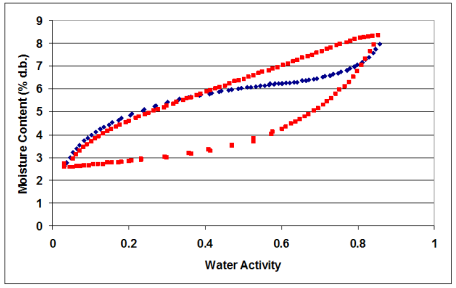

Figure 5. A working isotherm (♦) superimposed over a full isotherm (■) for wood pulp. There is a transition from the native starting point (0.60 aw) on the working isotherm in both adsorption and desorption until the curves meet the bounding adsorption and desorption curves of the full isotherm at which point the working isotherm follows the full isotherm.

TEMPERATURE

The amount of moisture that can be held at a given water activity changes (usually goes down) with increasing temperature (Figure 6). Likewise, water activity usually increases at a given moisture content with increasing temperature. These temperature dependent changes result in changes in the isotherm shape and provide valuable information about a products response to temperature fluctuations. The effect of temperature is unique to each product and follows the Clausius-Clapeyron equation which is:

$$\ln \frac{a_{w2}}{a_{w1}} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad (1)$$

Where a_{W2} and a_{W1} are water activities at temperatures (K) T_2 and T_1, respectively; ΔH is the heat of sorption in J/mol (as a function of moisture

content); and R equals 8.314 J mol^{-1} K^{-1}. The heat of sorption (ΔH) is the only unknown and must be determined empirically by regression analysis. Plotting $\ln(a_w)$ vs 1/T (K), the slope of the line is equal to ΔH /R. Once ΔH is known, the water activity at any temperature can be determined using equation 1.

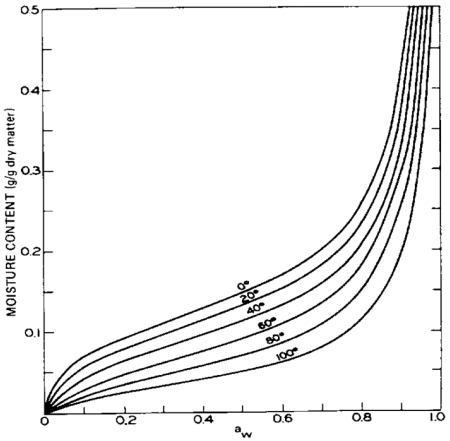

Figure 6. Desorption isotherms of potato slices at various temperatures (Gorling, 1958).

Measuring Moisture Sorption Isotherms

Constructing an isotherm consists of collecting water activity and moisture content values over a range of water activities. The range of water activities used depends on the situation, but normally is 0.10 a_w up to 0.90 a_w.

Traditional Desiccator Method

In the traditional isotherm method, each point on the isotherm is determined by equilibrating a sample to a known water activity and then determining its equilibrium moisture content by weight. Typically, the sample is placed in a sealed chamber over a saturated salt slurry in excess. Different water activity levels are achieved by using different salts. Alternatively, varying concentrations of acid or glycerol solutions, mechanical humidifiers, and adjusted mixtures of wet and dry air can be used. Equilibrium is reached when the weight of the sample stops changing. This equilibration process can take weeks. The temperature must be tightly controlled during equilibration and steps must be taken to prevent microbial contamination at water activities higher than 0.60.

Dynamic Vapor Sorption

The traditional method has been automated by instruments programmed to automatically change the water activity of a sample in a dynamic, stepwise progression. These instruments, often referred to as controlled atmosphere balances, utilize the Dynamic Vapor Sorption (DVS) method. The instrument holds the sample at one water activity level until the sample weight stops changing, measures the water content by weight, and then dynamically moves to the next water activity. Instrument temperature is held constant. Water activity levels are usually controlled by mixing dry and wet air.

Automatic isotherm generators are much faster and less labor intensive than traditional desiccator methods. They also make it possible to conduct sorption kinetic studies. However, like traditional dessicator methods, DVS instruments equilibrate the sample to a known water activity level. Since true equilibration between the sample and the vapor source requires an infinitely long period of time, they measure apparent equilibrium at the point when the change in sample weight is negligibly small. Increasing the tolerable weight change can speed up the isotherm process but calls into question the validity of the water activity values.

Dynamic Dewpoint Isotherm Method

The Dynamic Dewpoint Isotherm (DDI) method directly measures water activity while gravimetrically tracking weight, so there is no dependence on equilibration to known water activity levels to determine water activity. Adsorption occurs as saturated wet air is passed over the sample. Desorption is accomplished as desiccated air is passed over the sample. After

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Graphing isotherm temperature and critical water activity for spray dried milk powder gives a good linear relationship and Tg values from (Shrestha et al., 2007) at different water activities agree well with the data (Figure 16). This indicates that determining critical phase transitions using isotherm analysis is equivalent to determining them with DSC analysis. The linear relationship between isotherm temperature and water activity also makes it possible to predict the glass transition temperature at any water activity.

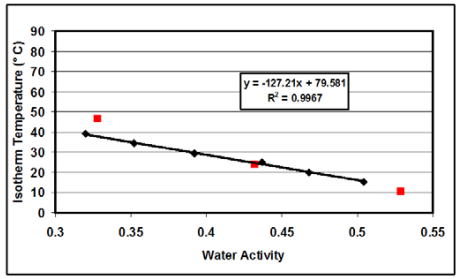

Figure 16. Water activity vs. isotherm temperature for spray dried milk powder (♦) showing a good linear relationship. Tg data taken from (Shrestha et al., 2007) (■) shows good agreement to the isotherm data.

The moisture sorption isotherm can also illustrate differences between amorphous and crystalline material and provide information about the level of each in a product (Figure 17). Amorphous material is much more hygroscopic initially and than undergoes a phase transition, clearly visible with a DDI isotherm. Crystalline material has a very flat isotherm with large changes in water activity vs. moisture content until the deliquescence point is reached and the curve changes to vertical while waters of hydration are added. The deliquescence point, represented by a sharp inflection in the isotherm curve from horizontal to vertical, is easily identified with isotherms of high resolution without requiring visual inspection of the sample.

Conclusion

Moisture sorption isotherms serve as a blueprint for moisture relations in products and modern instrumentation has made it possible for anyone to analyze the moisture relations of their product. The efficacy of isotherms in food engineering depends on being able to achieve high data resolution without drastically increasing isotherm test time. New methods such as DDI make it possible to achieve the necessary resolution while reducing test times to days instead of weeks. These high resolution moisture sorption isotherms make it possible to model and engineer food products in ways not previously possible. The rewards are products that maximize safety, quality, and profitability.

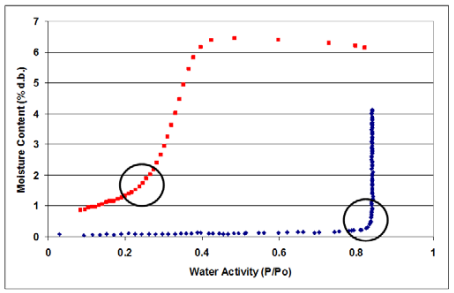

Figure 17. Moisture sorption isotherms at 25°C for crystalline (♦) and amorphous (■) sucrose showing a phase transition by the amorphous sucrose at 0.283 a_w and deliquescence of the crystalline sucrose at 0.815 a_w.

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roughly a 0.015 change in water activity, airflow is stopped and a snapshot of the sorption process is taken by directly measuring the water activity and the weight. Since the sample does not have to wait for equilibration to a known water activity, this method is faster without sacrificing accuracy. It is also able to produce an unmatched number of data points. Only water and desiccant are needed to run the isotherm.

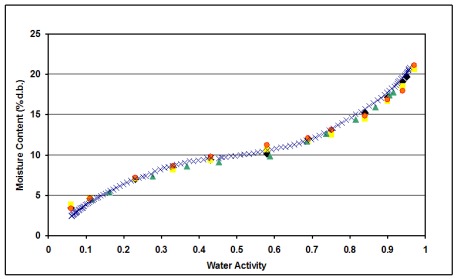

Figure 7. Dent Corn starch working isotherms when using desiccators with saturated salts (■), Proximity Equilibration Cell (●), DVS instrument 1 (♦), DVS instrument 2 (▲), and DDI (×) (DDI data from Decagon Devices in-house testing, data for all other methods taken from Xin Yu (2007).

The dynamic nature of the DDI method can present problems when trying to compare isotherms by DDI to isotherms created using other isotherm methods, especially traditional methods where equilibration times can be weeks. For most sample types, especially samples with fast vapor diffusion, penetration by water vapor into the whole sample is rapid and isotherms from DDI for these types of products will be comparable to other methods (Figure 7). However, for samples with slow diffusion rates, moisture movement through the sample is slow and complete diffusion of moisture into and out of the sample may be slow enough to give the appearance of vapor equilibrium in the headspace during water activity analysis. In reality, the moisture has not had time to be completely absorbed by the sample. Isotherms for these types of samples developed using the DDI method may have lower moisture contents during adsorption and higher moisture contents during desorption than isotherms constructed using other methods, resulting in higher levels of apparent hysteresis. Better agreement to other isotherms may be achieved by reducing the sample size, grinding the sample, and lowering the wet or dry air flow rate to allow more moisture penetration into slow diffusing samples.

Isotherm Models

Several different isotherm models have been proposed and compared in the literature. These models are necessary to predict the moisture content at a given water activity and are used to evaluate thermodynamic functions of water in foods. They are also necessary when using isotherm methods with low data resolution to interpolate between isotherm data points. While there are 270 proposed isotherm models, the most commonly used models are the GAB and BET. Since the BET model is only applicable up to 0.50 a_w, the GAB model is widely accepted as the most useful for characterizing isotherms across the entire water activity range. Its coefficients also have theoretical physical meaning such as providing monolayer moisture content. A new empirical model called the Double Log Polynomial (DLP), which is an adaptation of the Chi plot (Condon, 2006), has proven to be even better than the GAB at characterizing complex isotherms. The model equations are shown below:

BET $$m = \frac{a_w m_o c}{(1 - a_w)[1 + a_w(c - 1)]} \qquad (2)$$

Where m is the moisture in g/100 solids or g/g solids at water activity a_w and m_o is the monolayer value in the same units. The constant *c* is calculated by:

$$c = exp\left(\frac{Q_s}{RT}\right)$$

Where Q_s is the surface interaction energy in J/mole, *R* is the gas constant (8.314 J/mol K) and T (K) is the temperature:

GAB $$m = \frac{m_o k_b c\, a_w}{(1 - k_b\, a_w)(1 - k_b\, a_w + k_b c\, a_w)} \qquad (3)$$

Where *m* is the moisture in g/100 solids or g/g

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solids, k_b is a constant in the range of 0.70 to 1 and c is a constant in the range of 1 to 2000. In addition, m_o is the monolayer moisture content in the same units as m and a_w is the water activity at moisture m:

DLP $$m = b_3\chi^3 + b_2\chi^2 + b_1\chi = b_0 \quad (4)$$

Where m is the moisture in g/100 solids or g/g solids, $\chi = ln[-ln(a_w)]$ and $b_0 - b_3$ are empirical constants.

Uses For Moisture Sorption Isotherms

Moisture sorption isotherms are an important tool when formulating food to achieve specific qualities and attributes (Bell and Labuza, 2000). Despite their value, traditional isotherms have been limited by their low resolution. The high-resolution DDI method has opened up new and powerful possibilities. High resolution isotherms can reveal phase transition points—water activities at which products cake and clump, deliquesce, or go through glass transition. They can also be very helpful in making shelf life calculations, developing mixing models, modeling temperature abuse, determining the integrity of a protective coating or layer, determining monolayer values, and making accurate packaging calculations.

Drying and Wetting Curve

For a manufacturer drying a product, the sorption isotherm can be used to assist in process control by determining drying rates and optimal endpoints.

The isotherm will also show whether a product exhibits hysteresis and what impact that will have on water activity after drying to a given moisture content. In a hysteretic sample the moisture content will be higher at a given water activity for desorption than adsorption. The practical impact of hysteresis is that a moisture content that is safe when drying a sample because it corresponds to a safe water activity (0.6 a_w or below) may not be safe during adsorption because it corresponds to a higher water activity level. (above 0.70 a_w) (Figure 8).

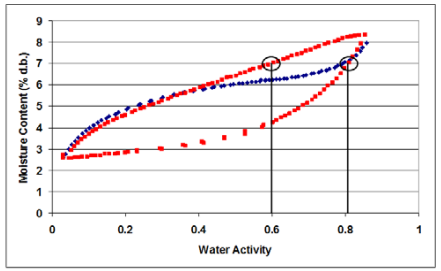

Figure 8. A working isotherm (♦) superimposed over a full isotherm curve (■) indicating that the working isotherm scans between the adsorption and desorption curves of the full isotherm. Also shown are the water activities associated with 7% moisture depending on whether the product has been wetted or dried. The isotherm is for wood pulp.

One of the practical impacts of hysteresis occurs when a product is dried to a safe water activity level and then exposed to humid conditions during storage. The impact of these events can be predicted. A working isotherm represents the drying and wetting characteristics of a product from its native state and is a scanning curve that connects the adsorption and desorption curves. It most correctly describes the changes experienced by a product when it wets or dries from its native state.

Moisture Content Prediction

An additional function of the isotherm is moisture content prediction. Since both water activity and moisture content are needed in certain situations, it is advantageous to measure both simultaneously. In addition, moisture content measurements can be inaccurate, time-consuming and require expensive instrumentation. As an alternative to moisture content measurement methods, the sorption isotherm can be used to determine moisture content based on water activity, usually with better repeatability than actually running a moisture content analysis and in much less time. This requires determination of a product's isotherm, characterization of the isotherm by a model or equation, and then loading that model into a specialized water activity instrument (see Decagon's AquaLab Series 4TE DUO).

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see that the water activity is 0.42 after 10 days, so 10.8 days seems reasonable.

Finally, assume we did a test with these same materials and conditions, but with a different package (but same surface area), and want to know the conductance of this new packaging material. Assume that we observe a water activity increase from 0.1 to 0.32 over a 20 day period when the package is placed in a environmental chamber at a humidity of 0.9 and a temperature of 40°C. The saturation vapor pressure of water at 40°C is 7.4 kPa (Campbell and Norman, 1998). The time constant is:

$$\tau = \frac{t}{-\ln\left(\frac{h_a - a_{wf}}{h_a - a_{wo}}\right)} = \frac{20}{-\ln\left(\frac{0.9-0.32}{0.9-0.1}\right)} = 62.2 days$$

To compute vapor conductance we use eq. 13:

$$g_v = \frac{\alpha\, p_a M}{e_s A \tau} = \frac{0.026(g/g)\,\mathrm{x}\,100(kPa)\,\mathrm{x}\,10(g)}{7.4(kPa)\,\mathrm{x}\,10^{-3}(m^2)\,\mathrm{x}\,5.4\,\mathrm{x}\,10^{6}(s)} = 6.5\,\mathrm{x}\,10^{-4} g\, m^{-2} s^{-1}$$

This new package material, under the conditions of the illustration above, would increase shelf life by giving a time constant of 154 days rather than 10.

Phase Changes and Critical Water Activities

When high resolution isotherms are available, such as those produced using the DDI method, the shape of the isotherm can provide information about critical water activities and phase transitions. Sharp inflection points in the isotherm indicate phase transitions (equivalent to a glass transition) and can provide information about critical water activities for maintaining textural properties and preventing caking and clumping (Figure 14). The exact inflection point in the curve, and hence the critical water activity, can be determined using second derivative curve smoothing strategies. Keep in mind that if data resolution of the isotherm is low, these inflection points cannot be identified. If the water activity of a product moves above the critical water activity for phase transition, the stability of the product will decrease as time dependent processes such as caking and crystallization speed up significantly.

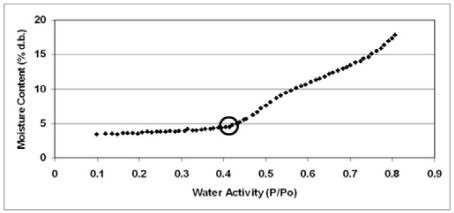

Figure 14. Moisture sorption isotherm for spray dried milk powder at 25°C showing a phase change occurring at a critical water activity of 0.43.

Increasing temperature will cause the critical water activity to go down and can also result in loss of stability with no change in water activity. Determining phase transitions using isotherms is similar to determining glass transition temperature (Tg) with Differential Scanning Calorimetry (DSC), except instead of holding water activity constant and scanning temperature, the isotherm analysis holds temperature constant and scans water activity (Figure 15). Consequently, the temperature of the isotherm when the critical water activity is determined should be similar to the Tg determined using DSC analysis for a sample at the critical water activity.

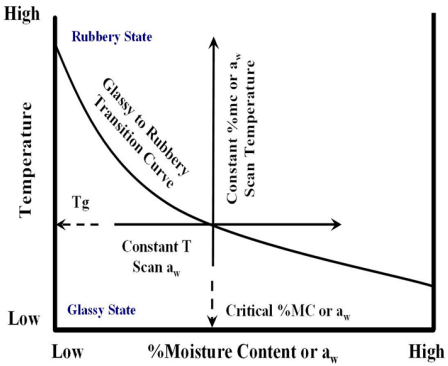

Figure 15. Diagram showing strategies used to determine glassy to rubbery phase transitions in amorphous material. The DSC strategy holds moisture or water activity constant and scans temperature while the isotherm strategy holds temperature constant and scans water activity (Figure courtesy of Shelly Schmidt).

Here, α is the slope of the isotherm (g/g), p_a is the atmospheric pressure (kPa), M is the total mass of product inside the package (g), e_s is the saturation water vapor pressure at package temperature (kPa), A is the package surface area (m^2), and g_v is the package conductance (g m^{-2} s^{-1}).

Equation 10 can be used in several different ways. As it stands, it can be used to find the water activity of a product over time when it is exposed, in a package, to humidity different from its starting water activity. For example, one might want to know the water activity of a bottle of tablets left on a bathroom shelf for an extended period of time.

A second way to use the equation is to compute the time for a packaged sample to reach a critical water activity when exposed to abuse conditions. The critical water activity would represent a loss in stability and this time would be equivalent to the shelf life of the product when exposed to the abuse conditions. Rearranging eq. 10 gives the shelf life:

$$t_{shelf} = -\tau \ln\left(\frac{h_a - a_{wc}}{h_a - a_{wo}}\right) \qquad (12)$$

Where a_{wc} is the critical water activity.

A third way to use eq. 10 is in determining the vapor conductance of a package. In that mode, a material of known water activity, with a known isotherm slope, is placed in a package and exposed to conditions of known humidity and temperature. After some period of time, the package is opened and the material water activity is re-measured. The measured values can be inserted into eq. 12 to give τ. This value is used with eq. 11 to solve for g_v:

$$g_v = \frac{\alpha\, p_a M}{e_s A \tau} \qquad (13)$$

Note that these equations suggest several ways to speed up package conductance testing. The tests could be run at a high temperature to increase saturation vapor pressure of water (es), or the M/A ratio could be made small to give good resolution.

One could also choose a material to put in the package with a low isotherm slope (α).
The following examples show how these calculations work. For all calculations an isotherm for powdered milk, shown in Fig. 13, will be used. A straight line fits the data well over the water activity range 0.1 to 0.4. Above that, at about 0.43 water activity is the critical value (see next section).

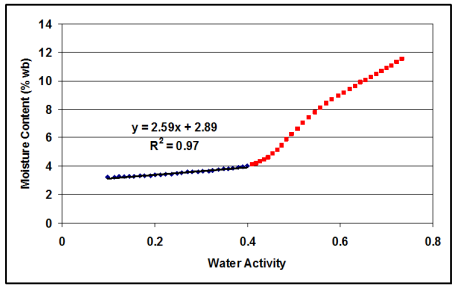

Figure 13. Adsorption isotherm for spray dried powdered milk showing a linear portion below 0.4 water activity and a phase transition at 0.43. The regression line is fit to the points below 0.4. Note that the y axis is again wet basis moisture content, which, again, is the appropriate measure of moisture content for these calculations.

For illustration, assume we have a package containing 10 g. of milk powder, initially at a water activity of 0.1. The slope of the isotherm from Figure 13 is 0.0259 g/g. The package has a surface area of 10 cm^2. Ambient and package temperature are 25°C, ambient humidity is 0.6, and atmospheric pressure is 100 kPa. The package permeability is 0.01 g m^{-2} s^{-1}. Saturation vapor pressure at 25 C is around 3 kPa (Table A3, (Campbell and Norman, 1998)). Putting these values into eq. 11 gives a time constant of 8.67 x 10^5 s, or around 10 days. Using this value in eq. 10, with the specified ambient humidity values shows that the sample will be at a water activity of 0.42 after 10 days, 0.53 after 20 days, and 0.58 after 30 days when exposed to 60% ambient humidity at 25°C.

If we take 0.43 as the critical water activity, the time to reach this value, as computed using eq. 12, is 10.8 days. From the previous calculation we

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Application Note

Temperature Abuse Modeling

Isotherms can be used to determine the effect of temperature on a product's water activity and moisture content. A product with a safe water activity at room temperature may become unsafe under temperature abuse conditions. Isotherms measured at several different temperatures will show the temperature at which a product in a sealed package (at constant moisture content) will be at unstable water activity levels. For example, granola bar at 25% moisture content will have a safe water activity (0.60) at 15°C and will not support mold growth. However, at 40°C, the water activity will be high enough (0.70) for mold to grow (Figure 9).

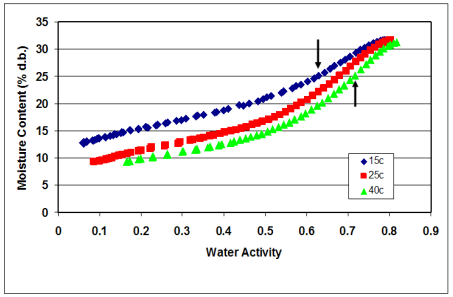

Figure 9. Moisture sorption isotherms of granola bar conducted at 15°C (♦), 25°C (■), and 40°C (▲) showing the differences in water activity at 25% moisture as temperature changes.

By plotting 1000/T(K) vs ln(a_w) for the data in Figure 9 at 25% moisture content, a linear relationship is generated (Figure 10).

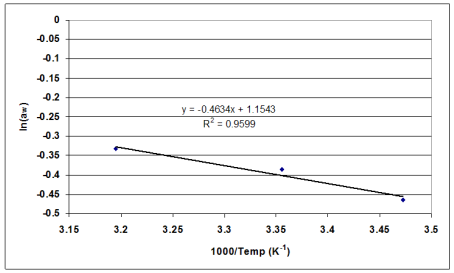

Figure 10. A plot of 1000/T(K) vs ln(a_w) for data taken from Figure 9 at 25% moisture content.

The negative slope of this line, multiplied by 1000, provides Q_s/R for this product, which can then be plugged into equation 1 to predict the water activity. Rearrangement of eq. 1 gives

(5)

$$a_{w2} = a_{wi}\, exp\left[\frac{Q_s}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] = a_{wi}\, exp\left[463\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

To find the water activity of the granola bar at, for example, 80°C, simply plug in 298 K (25°C for T_1, 0.680 for a_{w1} (data taken form Figure 9 at 25% moisture), and 353 K (80°C) for T_2 which gives 0.846 as the water activity at 80°C. The slope also gives the heat of sorption (Q_s) for this granola bar, which is 463 x 8.31 = 3852 J/mol.

Formulating For Water Activity Control

Isotherms can be valuable for formulation and product development. By comparing the isotherms of different formulations, it is possible to determine if a product can be adjusted to allow higher moisture content at a given water activity or a lower water activity at a given moisture content. The result can be a moister product that is still shelf stable.

Likewise, two ingredients at the same moisture content may not be compatible when mixed together. If two materials of differing water activities but the same moisture content are mixed together, the water will adjust between the materials until an equilibrium water activity is obtained. Thus, for a multi-component product, to prevent moisture migration, one should match the water activity of the two components. A great example of this type of product is a snack cake with a crème filling, cake, and icing covering. The crème filling, cake, and icing have very different moisture contents, and hence very different textures, but the same water activity (Figure 11). This provides a product with variety but is still stable because the water activities are in the safe range. In addition, the icing coating serves as a moisture barrier to the more moisture sensitive cake interior.

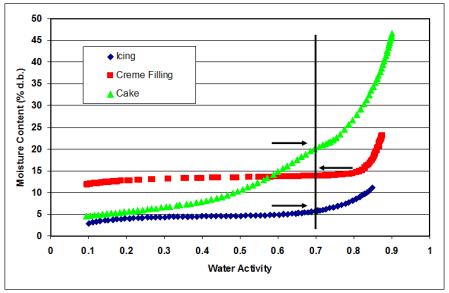

Figure 11. Working moisture sorption isotherms for icing (♦), crème filling (■), and cake (▲). The line at 0.70 aw represents the natural water activity of the product. Arrows indicate the direction water will move if cake and icing at water activities less than 0.70 aw are mixed with crème filling at a water activity greater than 0.70 aw.

Dry Ingredient Mixing

It is possible, using the isotherms of the components, to determine the final water activity of a mixture of ingredients without actually making the product. This works best by transforming the isotherm to a *chi* plot (chi being –ln[-ln(a_w)]) as shown in Fig. 12. The isotherm can then generally be fit by one or more straight lines. Figure 12 has some of the data from Fig. 11 for the snack cake ingredients. The *x* axis now is the chi variable. The y axis is the wet basis moisture content. The conversion from dry basis to wet basis is:

$$w = \frac{m}{1+m} \qquad (6)$$

Where *w* is mass of water divided by total product (water plus dry) mass, and *m* is mass of water divided by dry mass.

The conversion to wet basis moisture content makes the mixture calculations more convenient. The wet basis moisture content of a mixture is:

$$\bar{w} = \sum \phi_i w_i \qquad (7)$$

Where ϕ_i is the mass fraction of component *i* (the wet mass of the component divided by the total mass of the mixture) and w_i is the wet basis moisture content of the component.

Within the range of water activity for which the chi plot is a straight line the isotherm is described by:

$$w = \alpha\chi + \beta \qquad (8)$$

Where α and β are the slope and intercept of the chi plot.

As long as water is not gained or lost by the mixture, equation 7 gives the average moisture content at the time of mixing and also after equilibration has occurred among components. At equilibration, the water activity, and therefore the chi value of all components is equal, so eqs. 7 and 8 can be combined to find that chi value:

$$\chi = \frac{\bar{w} - \sum \phi_i \beta_i}{\sum \phi_i \alpha_i} \qquad (9)$$

Where the average moisture content is computed from the initial values and eq. 7. Once the chi value is known eq. 8 can be used to find the final moisture contents of the individual constituents.

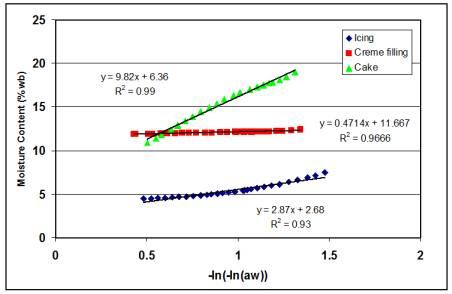

Figure 12. Chi plot of isotherm data for snack cake components showing linear fits to data.

Table 1 shows values of α and β from Fig. 12 for the snack cake components. To illustrate how these values can be used, assume we want to know the water activity of a mixture of 60% cake, 20% crème filling, and 20% chocolate icing. The starting moisture contents and their corresponding water activities are shown in the table. Using eq. 7 we compute that the average moisture content for the mix is 12.8%. Using eq. 9 we compute the final chi value to be 0.93, giving a final water activity of

$$a_w = exp[-exp(-\chi)] = exp[-exp(-0.93)] = 0.67$$

Ingredient	α	β	ϕ_i	*Initial %m.c	Initial aw	*Final %m.c
Icing	2.87	2.68	0.2	7	0.80	5.4
Creme	0.47	11.67	0.2	12	0.61	12.1
Cake	9.82	6.36	0.6	15	0.66	15.5

Ave mc	Final chi	Final a_w
12.8	0.93	0.67

Table 1. Values needed for snack cake inredients mixing problem.
*Moisture content is wet basis

Using eq. 8 and the α and β values for the components, we can now compute the final moisture contents of the components, as shown in the last column of the table. It may appear counterintuitive that the moisture content of both the crème and cake increased, while the moisture content of the icing decreased, in spite of the fact the icing was initially at a much lower moisture content that the crème and cake This should underline the concept that it is water activity, not moisture content that equilibrates between components.

Three final comments should be made with respect to calculating water activity of mixtures. First, we have used a linear approximation to the chi plot for the isotherm. That works well in most situations where water activity is not changing over a broad range, and gives nice, closed form equations for computing water activity. There is no problem, however, with using the full DLP isotherm equation to do these calculations. The equations are just messier and the solutions harder to obtain. The second point is that hysteresis could be an issue with these calculations unless you use the correct isotherm. Since some components are increasing in moisture content and some decreasing, a working isotherm is probably the best approximation. Finally, all of these calculations assume that the isotherm equation does not change with wetting or drying. If one of the ingredients undergoes a phase change during equilibration, its isotherm equation will change. Obviously the method would have problems if this were not taken into account.

Shelf Life Determination

Sorption isotherms are valuable for shelf life prediction. They can be used to determine a food's monolayer moisture content and the corresponding water activity, which represents its most stable state. The monolayer value is determined by modeling isotherm data using the GAB or BET equations. It is usually the moisture content around 0.2-0.3 a_w. An increase in water activity of 0.1 above the monolayer value will result in a decrease of shelf life by two to three times (Bell and Labuza, 2000).

Packaging Calculations

A product's isotherm can also be used to determine package requirements depending on the products sensitivity to moisture and the type of conditions it may be exposed to (Bell and Labuza, 2000). If we assume the product and the environment are at the same temperature, and that the permeability of the package is low enough so that changes in water activity are uniform over the entire product inside the package, then the water activity of the product can be predicted from:

$$a_w = h_a - (h_a - a_{wo})exp(-t/\tau) \qquad (10)$$

Where h_a is the humidity of the air, a_{wo} is the initial water activity of the sample, *t* is the time in the package, and the time constant, τ, is given by

$$\tau = \frac{\alpha\, p_a M}{e_s A g_v} \qquad (11)$$

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