29) PRESERVATION OF FRUITS AND VEGETABLES BY DRYING

III EQUILIBRIUM MOISTURE CONTENT AND SORPTION ISOTHERMS

Air is the most commonly used gas for drying foods and the humidity content is important when predicting the drying conditions. When air is brought in contact with a wet food material, equilibrium between the air and food material is eventually reached. The moisture content of food under such a condition is called the equilibrium moisture content. A plot of the equilibrium moisture content versus humidity at different temperatures is often used to illustrate the effect of temperature. The equilibrium moisture content usually decreases with an increase in temperature and is dependent on whether the amount of humidity is shifted from high to low (drying) or from low to high. Hence different curves are plotted for desorption and adsorption. The difference in the equilibrium moisture content between the adsorption and desorption curves is called hysteresis. Hysteresis is generally observed in most hygroscopic products. A product is hygroscopic if it is able to bind water when the vapour pressure is lowered. The degree of water interactions with the food is determined by moisture content and water activity.

A typical sorption isotherm for food products is shown in Fig. 1. The curve is divided into three regions. In region A, the water is tightly bound to the food product. In region B, the water is less tightly held and usually present in small capillaries. In region C, the water is held loosely in large capillaries, or is free. Foods high in protein, starch, and high-molecular-weight polymers have higher equilibrium moisture contents than those high in soluble solids, crystalline salts, and sugars. Sorption isotherms vary drastically from one food product to another, shown in Fig. 2.

Water sorption by foods is a process wherein water molecules progressively and reversibly combine with food solids via chemi-sorption, physical adsorption, and multilayer condensation.

Figure 1. Typical moisture equilibrium vs. water activity for foods and critical moisture content.
Figure 2. Typical moisture equilibrium contents of food materials at 25°C.

The sorption isotherm of a food material is a curve showing the equilibrium moisture content versus the relative humidity or water activity of the vapour space surrounding the material (Fig. 3). The concept of water activity that is used most commonly by researchers and processors in the food industry can be defined by following equation:

\[ Aw = \frac{p}{p_0} = \frac{ERH}{100} \]

where \( p \) is the water vapour pressure in food material, \( p_0 \) the vapour pressure of pure water, and \( Aw \) the water activity.

Figure 3. General type of sorption isotherm for food products.

An isotherm can be divided into three regions, as shown in Fig. 3. The water in region A represents strongly bound water with an enthalpy of vaporisation considerably higher than that of pure water. These first water molecules are sorbed at hydrophilic, charged, and polar groups of food components (protein, polysaccharides), which include structural water (H-bonded water), monolayer water, and hydrophobic hydration water. Usually, they are un-freezable and are not available for chemical reactions or as plasticizers. In region B, water molecules bind less firmly than the first. The vaporisation enthalpy is little greater than that for pure water. This water is available as a solvent for low-molecular-weight solutes and for some biochemical reactions. This class of constituent water can be looked upon as the continuous transition of the bound to the free type of water. The properties of water in region C are pretty close to those of the free water and no excess heat of binding can be detected. Free water may be held in voids, crevices, capillaries, and loosely bind to the food materials.

The process of increasing moisture content (water gain) is termed adsorption, and, that of decreasing moisture content (water loss), desorption. The term describing the differences between adsorption and desorption is hysteresis. Generally, adsorption isotherms exhibit a lower moisture content than do desorption isotherms at a given water activity. In foods, a variety of hysteresis loop shapes can be observed, depending on the type of food and the temperature. In both adsorption and desorption, the isotherms retain the characteristic sigmoid shape for proteins. In starchy foods, a large hysteresis loop occurs with a
maximum at about $aw = 0.70$, which is within the capillary condensation region. Increasing temperature decreases the total hysteresis. Desorption isotherms usually give a higher water content than do adsorption isotherms. In general, the type of changes encountered upon adsorption and desorption will depend on the initial state of the sorbent (amorphous versus crystalline), the transitions taking place during adsorption, and the speed of desorption. Hysteresis seems to be reproducible and persistent over many adsorption-desorption scans, especially at low temperatures and over relatively short periods of time. However, at higher temperatures, this may not be the case, due probably to denaturation. Elimination of hysteresis upon the second or subsequent cycles may take place for a variety of reasons, such as change in the crystalline structure when a new crystalline form persists upon subsequent cycles, swelling, and increased elasticity of capillary walls, resulting in a loss of water-holding capacity. Another factor involved in determining the shape of the curve is temperature. Increased temperature decreases the moisture content. Also, as the moisture content decreases, the heats of vaporization increase.

In addition to the physical factors in sorption isotherms, chemical factors influence water activity. Hydrogen-bond formation is one such factor. Also, the presence of dissolved solutes affects water activity. Differences between electrolytic and non-electrolytic solutions as well as amount of positively and negatively charged ions play a role in the sorption process.

**Bound Water**

Many experimental results show that some water molecules have different kinetic and thermodynamic properties from ordinary water (e.g., they exhibit a lower vapour pressure, lower mobility, greatly reduced freezing point, etc.). Such water has frequently been referred to as *bound water* (Fig 3, point A). This definition is an operational one that depends on the physical properties studied and the techniques used. Bound water contents may be different for the same foods with different criteria. Kuprianoff (1958) stated that bound water might best be determined by measuring the water that cannot be frozen at subfreezing temperatures. Under this definition, Toledo et al. (1968) measured the unfreezable water content in wheat flour with wide-line NMR. The results showed that the signals from all samples with different moisture content remained constant as the temperature decreased to less than -2°C (28°F). Below this temperature, the bound water fell to a common value that is equivalent to 25% (db) moisture. Berlin et al. (1970) assessed the amount of unfreezable water in proteins (Bovine casein) and found such bound water was to be 50 to 60% of the dry weight of protein. From the water sorption isotherms of these materials, interestingly, it can be seen that unfreezable water of foods corresponds to equilibrium moisture content at water activity of 0.8 to 0.9. Thus unfreezable water is not strongly bound to food materials and is available for chemical reactions and microbial growth.

**MEASUREMENT OF SORPTION ISOTHERMS**

Many methods are available for determining water sorption isotherms. Basically, these methods can be classified under three categories: (1) gravimetric, (2) manometric, and (3) hygrometric. Gravimetric methods involve the registration of weight changes. Weight changes can be determined both continuously and discontinuously in static and dynamic systems. Continuous methods employ the use of electro balances or quartz spring balances. In the discontinuous systems, sulphuric acid or salt solution is placed in a vacuum with the food material to give a measure of the equilibrium relative humidity.
As the name implies, manometric methods involve the use of sensitive manometers. To improve accuracy, the fluid selected for the manometer is often oil instead of mercury. The relative displacement of oil is an order of magnitude greater than that of mercury. Manometric devices measure the vapour pressure of water in equilibrium with a food material at a given moisture content.

Hygrometric methods measure the equilibrium relative humidity of air in contact with a food material at given moisture content. Dew-point hygrometers detect the condensation of cooling water vapour. Electric hygrometers measure the change in conductance or capacitance of hygrosensors. Most hygrosensors are coated with a hygroscopic salt, such as LiCl, which absorbs moisture from the food sample. Another hygrometric device is the hair hygrometer. Measurements are determined by the stretching of human hair as it is exposed to high water activities.

Mathematical Description of Isotherms

Food isotherm is first obtained in graphical form from experimental data. These water sorption isotherm data have almost always been fitted to one or more of a host of theoretical and empirical models. No single equation has been found to depict accurately the sorption isotherms of all types of foods in the entire range of water activity. Such being the case, isotherm data are studied individually and the model that describes the behaviour most accurately is used to report the water activity and moisture content for a specific food. Following is a list of equations that have been studied, as well as a definition of the terms used in the models.

Bradley’s equation (1936) is based on the theory of polarization. The dipoles induced in the first layer of absorbed molecules induce more dipoles, and so on. These constants are temperature dependent and this equation is not very accurate above 0.7 to 0.85 \( A_w \).

Tests by Lomauro et al. (1985) showed that the GAB equation gave good fits to over 75% of food isotherms studied. The Oswin equation fits 57% of the food isotherms. The Iglesias and Chirife equations require knowledge of moisture content at 0.5 \( A_w \). This value is difficult to determine; thus guesswork is involved when using the Iglesias and Chirife equations.

Isotherm Data

Isotherm sorption data have been published for many different foods. Reports have been submitted in many journals for various types of foods. Handbook of Food Isotherms: Water Sorption Parameters for Food and Food Components, a text authored by Iglesias and Chirife (1982), is a source of information regarding many foods, ranging from beef to yoghurt. All water sorption data contained therein are presented both graphically and statistically. Water activity values of some foods are given in Table 1 for quick reference.

A source of information regarding food isotherms is Sorption Isotherms and Water Activity of Food Materials. This book is a bibliography compiled by Wolf et al. (1985) and can be used to reference the concepts of the sorption process as well as sorption data of food products. An article by van den Berg and Bruin (1981) lists 77 mathematical models for food sorption isotherms. These constants were obtained from Handbook of Food Isotherms (Iglesias and Chirife, 1982). In addition, the GAB isotherm equation has been fitted to sorption isotherm data of a variety of food products.

<table>
<thead>
<tr>
<th>Food</th>
<th>Moisture Content</th>
<th>Aw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice (0°C)</td>
<td>100</td>
<td>1.00</td>
</tr>
<tr>
<td>Fresh Meat</td>
<td>70</td>
<td>0.985</td>
</tr>
<tr>
<td>Food</td>
<td>Quantity</td>
<td>Water Activity</td>
</tr>
<tr>
<td>---------------------</td>
<td>----------</td>
<td>----------------</td>
</tr>
<tr>
<td>Bread</td>
<td>40</td>
<td>0.96</td>
</tr>
<tr>
<td>Marmalade</td>
<td>35</td>
<td>0.86</td>
</tr>
<tr>
<td>Wheat Flour</td>
<td>14.5</td>
<td>0.72</td>
</tr>
<tr>
<td>Hazelnuts</td>
<td>5</td>
<td>0.70</td>
</tr>
<tr>
<td>Raisins</td>
<td>27</td>
<td>0.60</td>
</tr>
<tr>
<td>Macaroni</td>
<td>10</td>
<td>0.45</td>
</tr>
<tr>
<td>Biscuits</td>
<td>5</td>
<td>0.20</td>
</tr>
<tr>
<td>Roasted hazelnuts</td>
<td>2.5</td>
<td>0.35</td>
</tr>
<tr>
<td>Dried Milk</td>
<td>3.5</td>
<td>0.11</td>
</tr>
<tr>
<td>Potato chips</td>
<td>1.5</td>
<td>0.08</td>
</tr>
</tbody>
</table>

**IMPORTANCE OF SORPTION ISOTERMS**

Water activity levels of some foods and growth minima’s of micro-organism are given in Figure 4. Water activity effect food stability and therefore it must be brought to a suitable level at the conclusion of drying and maintained within an acceptable range of activity values during the storage. Therefore sorption isotherms are very useful during design of concentration or dehydration processes since water removal depends on the pressure of water over the food and on the energy of binding of water in the food.

**Figure 4.** Water activity levels of some foods and growth minima’s of micro-organism
FACTORS AFFECTED BY WATER ACTIVITY

Water activity and moisture content are very important parameters in food unit operations. During processing and storage, many chemical and physical factors are influenced by the water activity and moisture content level. Chemical changes that are enhanced by water activity include enzymatic reactions, nonenzymatic browning, and microbial. In many food products, enzymes are not inactivated during the heating process. Consequently, enzymatic reactions can take place even at low moisture contents. Water activity also affects the nonenzymatic browning reactions in foods. When water is present, carboxyl and amino compounds are involved as reactants, products, or catalysts in the browning process. At low aw; below the BET monolayer value enzymatic and browning reaction rate is slow due to low substrate solubility and mobility (substrates are enable to diffuse to the active sites of enzymes). At high aw water dilutes the reactants and the rate of browning falls.

Bacterial growth is affected at fairly high water activity levels. If water activity is maintained at a value below 0.90, most bacteria remain dormant. Most yeast and moulds, however, can proliferate at water activity levels as low as 0.80. The water activity levels for minimal growth of micro-organisms are given in Fig. 5.

Physical changes such as texture and aroma can depend greatly on water activity. Textural changes are most often seen in freeze drying and subsequent storing of foods, particularly meats and fish. The water activity in dried foods can also affect the retention of aroma. Different foods that are stored together will be altered if their individual relative humidities are different. The foods will follow their own isotherm curve until an equilibrium humidity is found.

With such factors dependent on water activity, much work needs to be done to determine water sorption data accurately. Studies have been done to determine the effect of different constituents on water activity. Fat content, for example, apparently has no effect on water activity. Most other composition variables exhibit conflicting results when their importance to water activity is determined. Oxidation of lipids occurs at low aw due to the action of free radicals. At high aw metal catalyst becomes soluble and the structure of the food swells to expose more active sites.
FACTORS AFFECTING WATER BINDING

Temperature

The amount of water adsorbed usually decreases as temperature increases. In the sorption isotherm, this effect shows a downward shift. Noguchi (1981) reported that hydrophobic hydration of biopolymers (dextran) decreases rapidly with increasing temperature (e.g., the water content decreased from 4 mol per mole sorbate to 2 as temperature was increased from 20°C to 40°C. There is a possibility that high temperature/high humidity conditions may cause degradation in the substrate.

In describing a moisture sorption isotherm, one must specify the temperature and hold it constant. Because of the nature of water binding, at constant Aw, foods that follow a Type II isotherm (Figure 3) hold less water at higher temperatures than at lower ones.

In general, the effect of temperature on increasing the Aw at constant moisture content is greatest at lower to intermediate water activities. As seen in Figure 6, Aw increases as T increases for a constant moisture content.

As noted earlier, the moisture sorption isotherm is dependent on temperature. Of concern to the food technologist is the fact that, during storage, a product in a sealed package may be exposed to long periods at a temperature higher than the temperature at which it is as packaged. Thus, if the moisture content remains the same, the product will increase to a higher Aw (Figure 6).
Thus, any reactions that can lead to quality loss will be increased in rate by an increase in both Aw and temperature. For example, if Aw increases by 0.1, which doubles the rate of quality loss, and if the 10°C shift has a $Q_{10}$ effect of 4, then shelf life would be decreased by $2 \times 4$ or a factor of eighth times. Therefore it is imperative to do moisture sorption isotherms for sensitive dry products at a minimum of two temperatures to determine the magnitude of the shift. For intermediate moisture foods, this should not be a problem, as the different isotherms generally join above an Aw of 0.7.

**Composition**

The composition of the foodstuffs affects their water sorption properties. The basic components in a food system usually include proteins, lipids, polysaccharides, and so on. The binding energy of water depends on the nature of water interaction with food constituents. The stronger the interaction, the higher is the binding energy. Water: carbohydrate interactions were considered to consist of hydrophilic interaction, hydrophobic interaction, gel forming, and so on. Numerous hydroxyl groups, which make them hydrophilic, interact with water molecules by hydrogen bonding, and this leads to solvation and/or solubilization of sugar and many of their polymers. The structure of carbohydrates can greatly affect the rate of water binding and the amount of water bound. The starch gelatinisation and the minimum water content necessary for it to occur were studied. It is the order-disorder phase transition when starch granule is heated in the presence of enough water.

![Figure 6. Shift in Aw for a food in a sealed pouch subjected to a temperature shift.](image)

One factor that influences the extent and manner of water-protein interaction is the amino acid composition of the proteins. Bull and Breese (1968) studied the hydration properties of various globular proteins with an isoplectic technique. They found that protein hydration correlated strongly with the sum of the polar residues (hydroxyls, carboxyls, and basic groups) minus the amides. Amides were observed to inhibit water binding. Kuntz (1971) used an NMR technique to study the hydration of some synthetic polypeptides and showed that the bound water content decreased in the order ionic groups > polar groups > nonpolar groups. The sorptive capacity of these materials for water vapour were starch > flour >
gluten, and the effect of temperature on adsorption was greater at low water activity and became almost negligible as the saturation pressure was approached, but they did not investigate in detail how starch and gluten as individual components influence the water sorption in a food system containing these components.

REFERENCES


