WATER ACTIVITY FOR CONFECTIONERY QUALITY AND SHELF-LIFE

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Abstract

Water activity plays an important role in the safety, quality, processing, shelf life, texture and sensory properties of confections. Throughout history, the importance of controlling water in food by drying, freezing, or adding sugar or salt has been recognized for preserving and controlling food quality. Most scientists recognize the importance of water activity in predicting the growth of microorganisms. However, water activity is also useful in predicting quality and shelf-life with respect to physical properties and chemical reaction rates. Water activity is the driving force for moisture migration between components or layers within a sample. Water activity also impacts physical properties such as texture, crystallization, and powder flow properties. Finally, water activity influences chemical reactivity by acting as a solvent, reactant, or changing the mobility of the reactants by affecting the viscosity of the system. Measuring and controlling water activity facilitates the development and production of high quality confectionery products that are safe and shelf stable.

Introduction

Everyone Loves Candy! Traditionally, candy has been consumed as a treat for enjoyment. However, consumers today are expecting better nutritional value and healthful benefits from foods, including candy. Research has shown that chocolate contains some of the same heart beneficial polyphenols as red wine and phytochemicals contained in licorice may prevent cancer. Companies are developing products that are sugar-free, low calorie, or use “natural” and “healthful” ingredients. These products must still be able to be processed economically and they must be stable and safe. One of the most important ingredients in determining product stability and quality is water. Understanding water’s impact on candy quality and how to control these impacts facilitates product reformulation, novel product development, improved product quality, and extended shelf-life.

Water activity is the key to understanding water’s impact on confections. This paper will discuss the effect of water activity on microbial, physical, and chemical stability as it relates to the quality and shelf-life of candy. Selection of both major and minor ingredients impacts the product’s final water activity. Modification of a formulation to improve one aspect of quality, be it bacteriological, chemical, or physical, may well have either a positive or negative effect on another property of the product. Water activity provides insight into the likely physical and chemical effects that will be experienced during and following manufacture (Lees, 1995).

Confectionery products are typically made of sugars (sucrose, glucose, fructose, etc.) and water. These components are combined with some interfering or texturing agents, such as cocoa, fat, milk solids, or syrups. Candy begins with water being supersaturated with solute, usually sucrose. The variations between different types of confectionery depend mainly upon the moisture content and sugar type. Candies can be divided into two groups based on their sugar type, crystalline or noncrystalline. Hard and soft candies contain uncrystallized sugars in a very viscous solution, while fondant and other have crystals as an important structural component. Confectionery products cover a wide range of water activities from 0.2 to 0.9a_w. Table 1 lists the water activities of types of confectionery products. Although confectionery products have a large range of water activities, the moisture content is low, between 0 and 20%.

Table 1 – Water activity of confectionery products

Products	Water Activity	Moisture	Total sugars
Boiled sweets	0.25-0.40	2-5%	35-60%
Caramels Toffees Fudge	0.45-0.60	6-10%	40-70%
Chewy sweets	0.46-0.60	6-10%	40-60%
Nougat	0.40-0.65	5-10%	30-60%
Marshmallow	0.60-0.75	12-20%	40-65%
Gums Jellies Liquorices	0.50-0.75	8-22%	30-75%
Candied fruit	0.70-0.80	20-30%	35-100%
Jams	0.80-0.85	30-40%	0-70%
Fondants Creams	0.65-0.80	10-18%	15-30%
Chewing-gum	0.40-0.65	3-6%	20-35%
Soft coating	0.40-0.65	3-6%	20-30%
Hard coating	0.40-0.75	0-1%	0-20%
Lozenges Tablets	0.40-0.75	0-1%	0-5%

adapted from Bussiere & Serpelloni 1985.

Water Activity

Water activity (a_w) is a measure of the energy status of the water in a system. Water activity is defined as the ratio of the partial pressure of water above a product to that of pure water at the same temperature. Water activity is a thermodynamic concept related to free energy. There are several factors that control water activity in a system, colligative, capillary and matric interactions. Colligative effects depend on the number of solute particles present in solution and interfere with the kinetic motion of water molecules. Capillary effects cause the vapor pressure of water above a curved liquid meniscus to be less than that of pure water because of changes in the hydrogen bonding angle between water molecules. Matric or surface interaction results from water interacting directly with chemical groups from dissolved species (e.g. salt or sugar) or undissolved ingredients (e.g. starches and proteins) through hydrogen bonds, ionic bonds (H_3O^+ or OH^-), van der Waals forces (hydrophobic bonds), or dipole-dipole forces. It is a combination of these factors in a product that reduces the energy of the water and thus reduces the relative humidity as compared to pure water. These factors can be grouped under two broad categories: osmotic and matric effects.

Due to varying degrees of osmotic and matric interactions, water activity describes the continuum of energy states of the water in a system. However, water activity is not a measure of the “free” vs. “bound” water. Water appears “bound” by forces to varying degrees, but water activity exists in a continuum of energy states rather than a static “boundness”. Water activity is sometimes defined as “free”, “bound”, or “available water” in a system. Although “bound” vs. “free” are easier to conceptualize, they fail to adequately define all aspects of the concept of water activity. A better description is that water activity is the energy status of the water within a system. It has a fundamental relationship to the work required to remove an infinitesimal quantity of water from a sample. Note that a_w is not determined by the total quantity of water in a sample, but only by that which is *least* tightly bound. Water activity allows one to have knowledge of microbial stability, chemical reactivity, physical properties, moisture migration, and shelf-life.

Water activity and moisture content have an effect on each other. The relationship between water activity and moisture content at a given temperature is called the moisture sorption isotherm and is discussed in detail by Bell and Labuza, (2000). Each product has its own unique moisture sorption isotherm – due to different interactions (colligative, capillary, and surface effects) between the water and the solid components at different moisture contents. An increase in a_w is almost always accompanied by an increase in the water content, but in a nonlinear fashion. Moisture sorption isotherms are sigmoidal in shape for most foods (Figure 1), although foods that contain large amounts of sugar or small soluble molecules have a J-type isotherm curve shape.

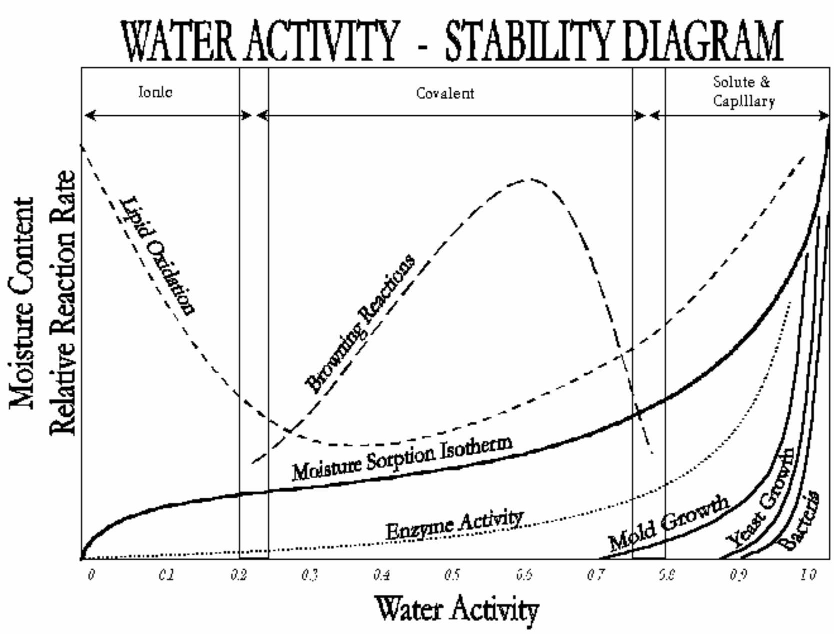

Figure 1. Water Activity – Stability Map (adapted from Labuza, (1970))

Microbial Stability

Low water activity imparts microbial safety to most confectionery products. Very few intrinsic properties are as important as water activity in predicting the survival of microorganisms in a food product. Scott (1953) showed that each microorganism has a limiting water activity below which it will not grow. Therefore, water activity, not water content, determines the lower limit of available water for microbial growth. Table 2 lists the water activity limits for growth of microorganisms important for food safety and quality and examples of foods in those ranges (Beuchat, 1981). Typically, most pathogenic bacteria stop growing at 0.90 except for *Staphyloccocus aureus* under aerobic conditions which grows to 0.86a_w. The "practical" limit for yeast is 0.88, for spoilage molds is 0.70 and the absolute limit for all organisms is 0.60a_w. Water activity also has a direct effect on the extent of sporulation, germination of spores, and toxin production.

It may be necessary at times to lower the a_w of a product to make it shelf stable. It is possible to lower a_w either by removing moisture or by the addition of humectants. Simple sugars are excellent humectants and are used to lower water activity for microbial control. The addition of monosaccharides to sucrose solutions will maximize the total soluble solids and lower the water activity, and hence combinations of sucrose with invert or glucose syrups, or both, are often used in jams and preserves (Herson & Hallard, 1980). From table 1 the major microbial concern for candies is mold growth. Fondants, creams, jellies, and icings may have mold growth if water activity rises due to temperature abuse or unwanted air pockets during fill or shrink.

Table 2 Water Activity and Growth of Microorganisms in Food*

Range of a_w	Microoranisms Generally Inhibited by Lowest a_w in This Range	Foods Generally within This Range
1.00 – 0.95	*Pseudomonas, Escherichia, Proteus, Shigells, Klebsiella, Bacillus, Clostridium perfringens,* some yeasts	Highly perishable (fresh) foods and canned fruits, vegetables, meat, fish, and milk
0.95 – 0.91	*Salmonella, Vibrio parahaemolyticus, C. botulinum, Serratia, Lactobacillus, Pediococcus,* some molds, yeasts (*Rhodotorula, Pichia*)	Some cheeses (Cheddar, Swiss, Muenster, Provolone), cured meat (ham)
0.91 – 0.87	Many yeasts (*Candida, Torulopsis, Hansenula), Micrococcus*	Fermented sausage (salami), sponge cakes, dry cheeses, margarine
0.87 – 0.80	Most molds (mycotoxigenic penicillia), *Staphyloccocus aureus,* most *Saccharomyces* (bailii) spp., *Debaryomyces*	Most fruit juice concentrates, sweetened condensed milk, syrups
0.80 – 0.75	Most halophilic bacteria, mycotoxigenic aspergilli	Jam, marmalade, marzipan, glacé fruits
0.75 – 0.65	Xerophilic molds (*Aspergillus chevalieri, A. candidus, Wallemia sebi*), *Saccharomyces bisporus*	Jelly, molasses, raw cane sugar, some dried fruits, nuts
0.65 – 0.60	Osmophilic yeasts (*Saccharomyces rouxii*), few molds (*Aspergillus echinulatus, Monascus bisporus*)	Dried fruits containing 15-20% moisture; some toffees and caramels; honey
0.60 – 0.50	No microbial proliferation	Dry pasta, spices
0.50 - 0.40	No microbial proliferation	Whole egg powder
0.40 - 0.30	No microbial proliferation	Cookies, crackers, bread crusts
0.30 - 0.20	No microbial proliferation	Whole milk powder; dried vegetables

* Adapted from Beuchat (1981).

Physical Properties

- Texture

Water activity affects the textural properties of foods (Troller & Christian, 1978a; Bourne, 1987 & 1992). Foods with high a_w have a texture that is described as moist, juicy, tender and chewy. When the water activity of these products is lowered, undesirable textural attributes such as hardness, dryness, staleness, and toughness are observed. Low a_w foods normally have texture attributes described as crisp and crunchy, while at higher a_w the texture changes to soggy.

The crispness intensity and overall hedonic texture of dry snack food products are a function of a_w (Katz & Labuza, 1981; Hough *et al*., 2001). Critical water activities are found where the product becomes unacceptable from a sensory standpoint. These fall into the a_w range where amorphous to crystalline transformations occur in simple sugar food systems and mobilization of soluble food constituents begins. Excessive and rapid drying or moisture reabsorption by a glassy material can cause the undesirable consequence of product loss by cracking and excessive breakage. Glass transition theory from the study of polymer science aids in understanding textural properties and explains changes which occur during processing and storage (Sperling 1986; Roos & Karel 1991; Roos 1993; Slade & Levine 1995). Physical structure is often altered by changes in water activity due to moisture gain resulting in a transition from the glassy to the rubber state.

The extent of moisture absorption from the surrounding air should never be underestimated. If a low water activity crispy wafer is exposed to a relative humidity of 50% ($0.50a_w$), within a short period of time, the wafer's moisture and water activity will increase. After exposure, the texture changes from crispy to hard and tough and with continued exposure to high humidity to soft and flexible. If exposed for long enough to high humidity structural collapse and shrinkage will occur. Many times edible coating such as chocolate are used to inhibit moisture absorption from the environment.

Many candy products will crystallize if a crystallization inhibitor is not used and a grainy texture will result. For example, crystallization will cause a hard candy to not be glassy or a fondant to not be soft. Measures such as adding invert sugar can be used to control and minimize crystallization, thus extending shelf life. The threshold moisture content for a sugar confectionery to be present as a glass is around 4% with the water activity value falling between 0.20 and 0.40 (Lees, 1996).

Raisins and other dried fruit may harden due to the loss of water associated with decreasing water activity, usually below 0.55 (Hyman & Labuza, 1998). Thus, dried fruit is often sugar coated to reduce the moisture loss rate or modified with glycerol to reduce the water activity thereby preventing moisture loss. Fruit pieces through osmotic dehydration may be purchased at specific water activity levels for unique applications.

- Moisture migration

Moisture migration is a common problem in multidomain foods that have regions of differing water activities (Labuza & Hyman, 1998). Moisture will migrate from the region of high a_w to the region of lower a_w, but the rate of migration depends on many factors. Moisture migration is controlled by minimizing the a_w differences among the components. Some confections contain components at different water activity levels, such as filled candies. Undesirable textural changes are often the result of moisture migration in multicomponent foods. Loss of crispness generally begins to happen when the water activity increases above 0.30 to 0.40 through environmental moisture uptake or moisture redistribution from other regions.

If a crispy wafer is combined with another fill material such as nougat, fondant, or creams, knowledge of the individual component water activity is critical for stability. If the water activity of the individual components are the same then the energy of the water is the same and there will be no exchange of moisture. The moisture content of the wafer and the fill material will be very different, but no moisture will exchange because the water activities are the same. Many times the water activity of the components cannot be made to the same water activity level and barriers or other techniques need to be used to retard moisture migration and prevent the equilibration of water activity between the wafer and filling.

Soft center cookies (crisp outer layer and soft inner layer) are an example of how to balance water activity and glass transition. The water activity of the center and outer layers of the cookie must be the same to prevent moisture migration and increase of glass transition. Since the glass transition temperature of sucrose is greater than that of fructose, sucrose is used in the outer layer and fructose in the inner layer. After baking, the sucrose in the outer layer is in the glassy state (crispy) and the fructose is in the rubbery state (soft).

- Caking and clumping

Water activity affects the stability, flow, and caking and clumping of powders during storage (Peleg & Mannheim, 1977; Saltmarch & Labuza, 1980; Chuy & Labuza, 1994; Aguilera & del Valle, 1995). Controlling water activity in a powder product below critical levels maintains proper product structure, texture, flowability, density, and rehydration properties. Knowledge of the water activity of powders as a function of moisture content and temperature is essential during processing, handling, packaging, and storage to prevent the deleterious phenomenon of caking, clumping, collapse, and stickiness. Caking is water activity, time, and temperature dependent and is related to the collapse phenomena of the powder under gravitational force (Chuy & Labuza, 1994).

In spray dried powders, the sugars are generally in the amorphous glassy state when they are dried to low moisture. Since amorphous sugars are very hygroscopic, if they are exposed to high humidity, caking and crystallization will occur resulting in state changes forming either a sticky texture or a hard, coarse, grainy texture (Saltmarch & Labuza 1980; Downtown *et al.* 1982). Makower and Dye (1956) looked at the state changes of pure amorphous sucrose. They determined the moisture uptake for sucrose at 35°C across different relative humidities or water activity levels (Figure 2). At $<0.12a_w$ (~2% moisture), the amorphous sucrose was stable for over 3 years. However, at $0.33a_w$ it gained about 4% moisture, re-crystallized, and lost that moisture in 3 days. Labuza and Labuza (2004) obtained similar results looking at the stability and storage of cotton candy, an amorphous sucrose product, as a function of water activity or relative humidity.

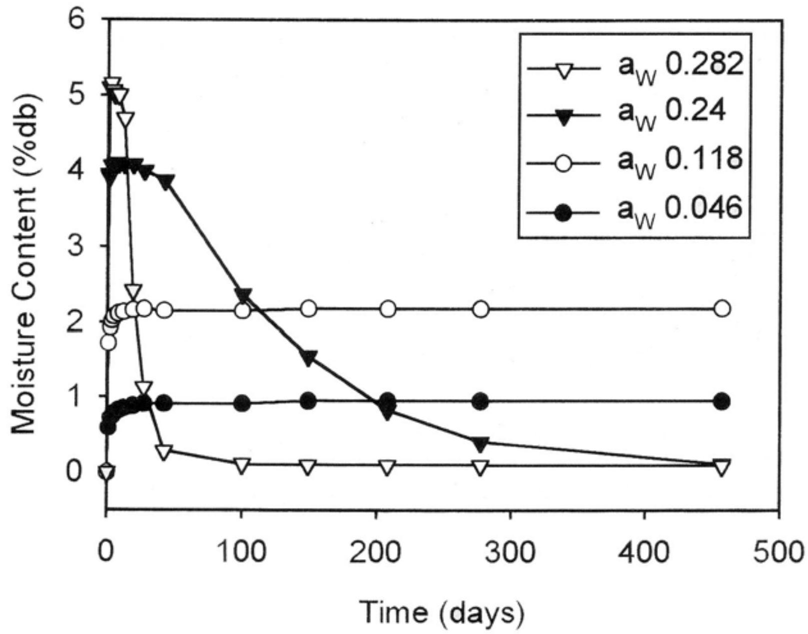

Figure 2. Adsorption of water by amorphous sucrose at several water activity levels (adapted from Makower and Dye, 1956).

Chemical Stability

Water influences chemical reactivity in different ways. It acts as a solvent, reactant, or changes the mobility of the reactants by affecting the viscosity of the system. Water activity influences non-enzymatic browning, lipid oxidation, degradation of vitamins, enzymatic reactions, protein denaturation, starch gelatinization, and starch retrogradation (see Figure 1).

Water activity influences the rate of non-enzymatic browning reactions, also called Maillard reactions (Troller & Christian 1978b; Labuza & Saltmarch 1981; Nursten 1986; Bell 1995). Non-enzymatic browning is an important reaction in food production and consists of a complex series of reactions between reducing sugars and free amine groups from proteins or amino acids. At high temperatures sugar-sugar caramelization occurs with many of the flavor compounds and end-products are similar to those observed for the Maillard reaction. Not all sugars are reducing sugars. Those that are effective reducing sugars are fructose, glucose, maltose, galactose, and lactose. Sucrose is not a reducing sugar unless it inverts.

The rate of non-enzymatic browning increases with increasing a_w, reaching a maximum at a_w in the range of 0.60 to 0.80 (Figure 1). Generally, further increases in water activity will hinder browning reactions due to a dilution effect. During confectionery processing, the product will move from right to left on the browning line shown in Figure 1. Thus, candies with a higher water activity will be more susceptible to the Maillard reaction than candies with a lower water activity, especially during storage. The use of certain compounds such as glycerol or sorbitol in confectionery products may change the rate/water activity profile (Davies & Labuza 1997). Figure 3 shows that glycerol shifts the rate maximum to a lower water activity as compared to a control while sorbitol seems to act as an inhibitor at all a_w values, probably due to its high viscosity.

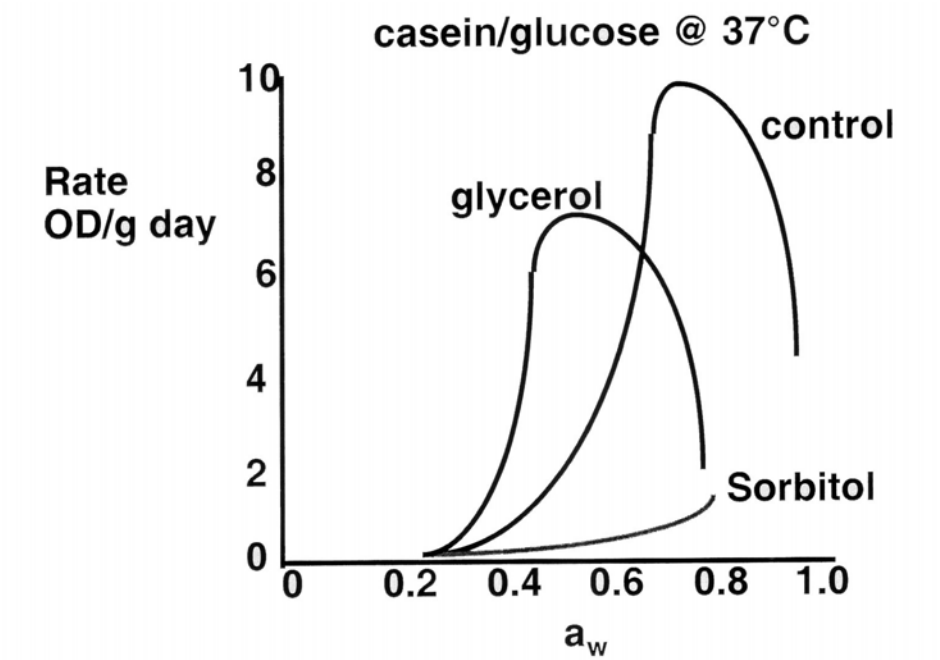

Figure 3. Effect of glycerol and sorbitol on the Maillard reaction rate as a function of water activity.

Lipid oxidation

Another concern in confection shelf-life is lipid oxidation. Lipid oxidation occurs by the reaction of oxygen with fatty acids, especially unsaturated fatty acids, to produce peroxides which form aldehyds and ketone breakdown products. Lipid oxidation has a minimum in the intermediate a_w range and increases at both high and low a_w values (Figure 1), although due to different mechanisms (Karel 1986; Troller & Christian 1978a). This type of spoilage results in loss of original flavor or formation of highly objectionable flavors and odors.

Enzymatic activity

Enzyme stability is influenced significantly by water activity due to their relatively fragile nature (Aker 1969; Potthast *et al.* 1975; Drapron 1985). Most enzymes and proteins must maintain conformation to remain active. Maintaining critical a_w levels to prevent or entice conformational changes in enzymes is important to food quality. Most enzymatic reactions are slowed down at water activities below 0.80, but some reactions occur even at very low a_w values.

A classic example of using enzymatic activity in candy production is with chocolate covered cherries. This product is made by adding the enzyme invertase to a fondant which, as a solid crystalline candy, is placed around the cherries and coated with chocolate. The cherries are allowed to sit while the invertase inside hydrolyzes the sucrose into fructose and glucose. The chemical reaction involved in the hydrolysis of sucrose requires water which is incorporated into the resulting glucose and fructose. The fructose and glucose combination is much more soluble than the sucrose and the syrup is less viscous. The result of this enzymatic process is to liquefy the fondant center and cause the total solulble sugar content to rise. The water activity of this product changes throughout the stroage life, especially during the ripening period.

Conclusion

Water activity is a powerful tool in understanding water's impact on confectionery products. As shown in figure 1, it is a key parameter for the microbial, physical, and chemical stability of confectionery products. Understanding water's impact on candy quality and how to control these impacts facilitates product reformulation, novel product development, improved product quality, and extended shelf-life. Water activity facilitates the development and production of high quality, safe, and shelf stable confectionery products with better nutritional value and healthful benefits.

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