FOOD CHEMISTRY II – UNIT I –WATER

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Dear Students, I welcome you all for our lecture series on FOOD TECHNOLOGY. In today’s lecture, let’s make an attempt to know about ‘**Water’.**

Introduction

Water is an important basic element in all foods. Water is called as the universal solvent and it is a basic necessity for the growth & metabolism of microbes and various chemical reactions that occur in food products. Water occurs in food systems as free water and bound water. Water is found as an intracellular and extracellular component in foods. The importance of water as a crucial component necessitates the understanding of the properties and behavior in food systems. The way water behaves in foods can provide information on the stability of a product as well as its shelf life.

The following topics will be dealt in this chapter-

1. Definition of water in food
2. Structure of water and ice
3. Types of water
4. Water activity and sorption phenomena
5. Water activity and shelf life
6. Water activity and packaging

1. Definition of water in food

Water is a chemical compound composed of two hydrogen atoms and one oxygen atom. The liquid stage of this compound is termed as water, the solid state as ice and gaseous state as steam. Water is also the most substantial component of foods and acts as a medium by supporting chemical reactions.

Water has an important role in the stability of most of the food products. The quantity and characteristic of water present in foods has an impact on the chemical processes of value in terms of food safety. The physical & chemical stability as well as growth of microbes in a food can be controlled by optimizing the water within foods by various methods.

Water content of a food product alone cannot provide a view of the potential microbial response and chemical reactions even though it is the most widely discussed concept in terms of water content of foods.Water content is measured by drying, infrared or nuclear magnetic resonance techniques but the measure of ‘water activity’ along with the total water is essential to describe its water status. The measurement of water activity is more relevant in understanding the quality and safety aspects of water.

2. **Structure of water and ice**

The function of water can be understood better when there is clear knowledge about its structure and the state it occurs in a food system.

2.1 Physical properties of water

Water exhibits various physical properties which can be understood on comparison to the properties of molecules similar to water. The physical properties of water are presented in table no 1.Water appears to have a high melting point of 0^0C and boiling point temperature of 100^0C. There is also a considerable difference in the density, vapour pressure, thermal conductivity of water at 0^0C & 100^0C and ice which further changes on freezing. The thermal diffusivity which is indicative of the rate at which a material can undergo a change in temperature or the rate at which heat moves inside a compound is 9 times higher in ice than water. This change causes freezing of water at a rate nine times faster than thawing. The reason for the unusual behavior of water and ice can be further understood by their chemical structure.

Table no 1. Physical properties of water and ice

Property	**Water**		**Ice**	
	0^0C	**100^0C**	**0^0C**	**-20^0C**
Density (g/cm^3)	0.9998	0.9583	0.9168	0.9182
Vapour pressure (kPa)	0.6113	101.3	0.6113	0.103
Thermal conductivity (W/m/K)	0.561	0.585	2.240	2.433

Thermal diffusivity(m^2/s)	$1.3*10^{-7}$	na	$11.7*10^{-7}$	$11.8-10^{-7}$
Ref: 1) Damodaran, S., Parkin, K. L., &Fennema, O. R. (Eds.). (2007). *Fennema's food chemistry*. CRC press.Pg 19 2) DeMan, J. M. (1976). *Principles of food chemistry*. AVI Publishing Co., Inc. pg 2				

2.2 Structure of water and ice

Each molecule of water is composed of twohydrogen atoms and a single oxygen atom.Each hydrogen atom is bound to the central oxygen atom by a pair of electrons which is usually termed as a covalent bond. There are six electrons in the outer shell of a water molecule out of which only two are engaged in covalent bonding. The remaining 4 electrons tend to be arranged far from each other to avoid or reduce the repulsion due to same charge thus providing a tetrahedral geometry. Since the two pairs of free bound electrons remain closer to the oxygen atom, they repel the electrons in the covalent bond thus pushing the two hydrogen bonds nearer to each other resulting in the arrangement of hydrogen and oxygen atoms at an angle of 105 degrees as shown in figure no 1.

Ice has a well-defined structure where each water molecule is surrounded by four neighboring water molecules. Two water molecules are bound to the oxygen atom directly and other two are bound to the hydrogen atoms as shown in figure no 2. This bridging breaks when ice melts leading to the formation of water in a liquid state.

3. Types of water

Water in foods and products can be discreetly classified into two forms namely bound water and free water. Bound water is that part of the total water bound by water soluble compounds such as sugar and salt or substrates that can forma matrix thus making it unavailable to any physical, chemical and microbial activity compared to free water which is the proportionof water inside foods that is available for such chemical reactions and growth of microbes. Major proportion of water is in the bound form i.e. bound to ions or bound to surfaces of large molecules or cell structures.The measurement of the intensity of binding of the water molecule is important in predicting the reactive nature of water in foods.

The free water has the ability to support microbial growth and participate in chemical,enzymatic reactions and spoilage activities. Thus the amount of free water is more important for understanding and analyzing the chemical and microbial stability of a food than its total water /moisture content.

Water content in food can be measured by gravimetric method where the food is dried till the moisture content is evaporated fully followed by measurement of the dry matter; Karl Fisher titration which involves the reduction of iodine by sulphur di oxide in the presence of water.

4. Water activity& Sorption Phenomena

Water activity (a_w) is defined as the ratio of the vapour pressure of water in a substance to the vapour pressure of pure water. It is calculated using the following formula-

$$a_w = p/p_o$$

where a_w is the water activity of a food, p is the partial pressure of water in a substrate and p_o is the vapour pressure of pure water in the same temperature.Water activity defines the efficacy of water in the food to take part in chemical reactions. The extent of unavailability has a negative impact on the water activity, in other words higher the proportion of bound water lower will be the water activity. The tightly bound water has less chances of escaping the food as vapour thus is devoid of partial pressure. When the partial pressure is zero, the water activitywill also be zero.Water activity ranges from 0 to1.0, where 1.0 is water activity of pure water.The water activity of a food will be closer or equal to 1.0 when the amount of moisture in it exceeds the solid content whereas the water activity will be lower than 1.0 when the solid content is more than moisture content of a food.The water activity is dependent on the temperature, boiling and freezing point, equilibrium relative humidityand osmotic pressure.

Relative humidity of a food product is the humidity of air surrounding the food. When this is in equilibrium with the environment, it is known as equilibrium relative humidity (ERH)at which the food product does not gain nor lose water. When the relative humidity increases than the ERH, the product gains moisture; when the relative humidity decreases below ERH, the product loses moisture and becomes drier. This confirms the relationship between ERH and water activity as both are based on vapour pressure. ERH is dependent on the chemical compound, temperature, water content, storage conditions, absolute pressure and packaging.

Water activitycan be derived from ERH using the following formula-

$$a_w = \text{equilibrium relative humidity (ERH)} / 100$$

The process of adsorption and desorption are not fully reversible thus the isotherms of each of these can be differentiated based on analysis of increase or decreasing moisture content of a food product. On adsorption the product becomes wet (gains moisture) and desorption the product becomes dry (loses moisture). Adsorption and desorption isotherms are used for observation of hygroscopic products and the process of drying respectively.Water sorption isotherms usually have a sigmoid shape curve which is attributed to the presence of three types of water – I – strongly bound monolayer of water molecules, II-weak but hard to remove multiple layers of water and III – loosely bound multilayered water condensed in the capillaries and pores of the food material. The typical shape of water adsorption and desorption isotherm is shown in figure no3.

The shape of the moisture isotherm typical for most foods is shown in figure no 4.

Hygroscopic foods have a steeply sloping curve whereas foods less sensitive to moisture or non-hygroscopic have a flat curve as shown in figure no 5.

The definition of conditions favouring the growth of microbes is of utmost importance in the food stability and food preservation process.Water activity can predict safety and stability with respect to microbial growth, chemical and biochemical reaction rates, and physical properties. Microbes have a critical water activity level below which they cannot grow or multiply.Growth of bacteria is inhibited at <0.75 a_w, growth of all microbes is inhibited at <0.6 a_w. Maillard reactions / browning occurs at a maximum rate at 0.6-0.7 a_w and inactivation of enzymes occurs at <0.75 a_w.Preservation of B-vitamins such as vitamin C, E and Thiamine is observed at lower a_w. The graphic representation of the reaction rates of the above discussed variables at various a_w levels is shown in figure no 6.

The measurement of water activity can be done by using a resistive electrolytic hygrometer, capacitance hygrometer or a dew point hygrometer. The principle involved in these hygrometers involves measurement of change temperature, pressure, mass or a mechanical or electrical change in a substance as moisture is absorbed or desorbed.

5. Water activity and shelf-life

Changes in the water activity by absorption of water when a product is exposed to a high humidity environment or loss of water when placed in a low humidity environment can cause undesirable changes in food products and can shorten the shelf life. Physical changes includeloss of crispness in dry products, caking and clumping of powders and loss of water from moist foods making them sticky. Other undesirable changes are acceleration of chemical deterioration or microbial growth. Moisture content and water activity affect the progress of chemical and microbiological spoilage reactions in foodswhich is discussed individually as follows-

5.1 Microbial growth

The shelf life of a product is an important aspect of food safety.Stability of a food depends on the water activity and pH in the food environment. Foods with higher a_w are highly perishable. Microbes able to cause food deterioration need certain conditions for growth namely available moisture, optimum pH, the right temperature and nutrients. The growth or microbes can be checked by controlling these factors and shelf life of a product can be increased. The shelf life of a food can be determined based on the ingredients used, pH, water activity and microbiological inhibitors. In general, bacteria require higher values of a_w for growth compared to fungi andgram-negative bacteria require higher water activity than gram-positive bacteria.

Dried or freeze dried foods have good shelf life and stability because their moisture content is between 5-15%. A moisture level of 20-40% and a_w of above 0.5 is found in intermediate moisture foods such as cakes.Refrigerated foods are especially vulnerable to microbial spoilage thus reducing their shelf life. They are at a higher risk of deterioration by microbes and may sustain pathogenic microbial growth. The growth of microbes in food can be monitored by microbiological methods. Reactions such as gas production, syneresisand changes in color or viscosity can also indicate changes in the stability of the product.

5.2 Chemical deterioration of foods

Water activity influences chemical and enzymatic reactivity apart from microbial spoilage. Water may influence chemical reactionsby serving asa solvent, reactant or by changing the mobility of the reactants by altering the viscosity etc. Chemical deterioration of packaged foods can be due to three major reactions in food namely Oxidation of lipids, Enzymatic degradation and Non-enzymatic browning. These reactions can occur simultaneously in foods and their rate is accelerated by increase in storage temperature.

Monitoring the level of lipid degradation products at elevated temperatures is one of the principal methods used in predicting the shelf life of a product. Lipid oxidation at these temperatures can occur due to the action of free radicals, enzymatic actionand oxidation by light leading to the formation of hydroperoxides.

Free radical synthesis is catalyzed by heat, light or metal ions for instance copper ions. Free radicals generated by oxidation reaction result in peroxides that are further converted into alcohols, aldehydes, ketones,and free fatty acids.Many of these compounds have strong flavors and odors referred to as rancid fat. The double bonds of unsaturated fatty acids mainly oleic C18:1, linoleic C18:2, and linolenic C18:3 are the targets of oxidation. The rate of oxidation occurs 64 times faster in linoleic acid and 100 times faster inlinolenicacid on comparison witholeic acid.

Photosensitive compounds found in foods such as riboflavin, chlorophyll, myoglobin, heavy metal ions etcare excited to a high-energy state on absorption of light. This energy reacts with the oxygen atoms and forms highlyreactive singlet oxygen which can cause oxidation of fatty acids leading to the formation of singlet oxygen in the formation of hydroperoxides.

Majority of the enzymes in food are inactive when the water activity falls below 0.85. Such enzymes include amylases, phenoloxidases, and peroxidases. Lipases can remain active at a_w values at 0.3 or 0.1. The enzymatic action of lipase with triglycerides in food leads to the formation of free fatty acids resulting in rancidity. These fatty acids have distinct flavour such as lauric acid which has a strong soapy flavour detectable at concentrations of 0.3%. Other fatty acids found in vegetable oils are capable of producing off flavour at 2% concentration. Another example is butyric acid found in rancid butter is capable of producing rancid flavour at minimal concentration.

The non-enzymatic browning or Maillard reactions are one of the most important factors leading to food spoilage. The water activity favouring this reaction is between 0.6-0.7. Browning reactions are slow at low level of humidity and are seen at maximum rate in intermediate-moisture foods.

Other chemical reactions influenced by the water activity are hydrolysis of protopectin, splitting and demethylation of pectin, autocatalytic hydrolysis of fats, and the transformation of chlorophyll into pheophytin.

6. Water activity and packaging

Water activity is a critical factor in determining the shelf life of products. The upper and lower water activity levels can be established keeping in mind the microbial, physicochemical, nutritional and characteristics of food products.The shelf life of a packaged food is determined by the rate of exchange of moisture through the package and rate of change in a_w. Data on the temperature, relative humidity and critical a_w values will aid in selection of a packaging techniqueand optimize the quality and shelf life of a product.

Sorption isotherms have animportant role in the selection of packaging materials. Hygroscopic products always have a steep sorption isotherm. Such foods require packaging material to be moisture proof for example glass containers with waterproof seals or thick polyvinylchloride material. Instant coffee for instance loses its flowability and cakes at critical limit of 50 percent relative humidity. Non hygroscopic products can be packaged in polyethylene containers as reactions do not occur at normal storage conditions.For some foods the equilibriumrelative humidity is more than the external climatic conditions. Such products require the packaging material to avoid the loss of moisture. Examples of such foods include processed cheese and baked goods.

Conclusion

Water apart from being the most important constituent of food has a crucial role in the stability and safety of a food product. Water and its behavior in food systems can direct many processes that can dictate the shelf life, microbial safety and sensory characteristics of a food product. Water activity of foods needs to be controlled based on the nature of the food product by optimum packaging materials and storage conditions.