# Novel Technologies for Food Processing and Shelf Life Extension Prof. Hari Niwas Mishra Department of Agricultural and Food Engineering Indian Institute of Technology, Kharagpur

# Lecture - 04 Role of Water in Food and Its Shelf Life

In this lecture, the role of water in food and its influence on the shelf life of the food materials is discussed.

Water
Water, next to oxygen, is important constituent of life.
<ul> <li>A person can live for a few weeks without food but only a few days without water.</li> </ul>
It is an integral part of animal and vegetable tissues.
Water is the medium through which all cellular reactions occur.
It helps in digestion, circulation and excretion processes.
Water helps in maintaining the electrolyte balance of the body and plays     a role in the maintenance of body temperature.
Water is not only a solvent but it also participates in several reactions either as a reactant or as a product.

Water is an important component of life, next to oxygen. A person can live for a few weeks without food, but it becomes very difficult to live a few days without water. Water is an integral part of all the animal and vegetable tissues. It is the medium through which different cellular reactions take place. Water helps in almost all body processes like digestion, circulation, excretion, etc. It helps in maintaining the electrolyte balance of the body and plays an important role in the maintenance of the body temperature. Water is not only a solvent, but it also participates or takes part in the several reactions either as a reactant or as a product.



It is one of the widely distributed compounds in the world and is found in all three states of matter i.e. liquid, solid and gas or vapour. It is one of the most important chemicals present in food and drinks. In fact, sometimes it is said that food is a mixture of chemicals or biochemicals in water. The foods contain wide-ranges of water in it. There are certain foods which contain water as low as may be 1 or 2 % e.g. crackers, 18 to 20 % e.g. figs, raisins, etc. On the other hand, there are certain foods which contain water contents as high as 96 or 98 % in case of fruits or vegetables like cucumber, tomato, etc. The water content influences appearance, texture, flavour and other characteristics of the food. It is not only the water content but the manner in which water is present in the food material gives its desired characteristics. Water is involved in most of the changes that take place when the food is cooked or processed. In fact, food spoilage also is related to the water content.



Even some of the desirable or undesirable changes that take place when the food is cooked are due to the property of water as a solvent. The characteristic colour and flavour in the coffee brew and tea brew is because of the ability of water to dissolve the colourings and flavourings. There are many water-soluble vitamins which are leached out during the cooking or washing processes depending upon their solubility in water.

Water also acts as a dispersion medium in food. Too much water in foods can be a danger, as it favours the growth of undesirable bacteria and other microorganisms. So, the aim of modern food technology is to keep the water content of foods as low as possible to maximize the shelf life of food.



### Physical properties of water

The physical constants of water are very different when compared with the other molecules of similar atomic composition and molecular weight such as H<sub>2</sub>S, HF, NH<sub>3</sub>, etc. Water has unusually different or sometimes higher values for physical constants such as melting point, boiling point, surface tension, specific heat, and dielectric constants, etc. Even the heat of fusion, vaporization, sublimation values for water are also high. Another unusual property of water is that it has a maximum density at 4 °C and not at 0 °C which is the freezing point of water. On the contrary, other materials of the foods normally are maximally dense at their freezing point. The two forms of the water i.e. the liquid form and solid form shows variation in their characteristics. The thermal conductivity of ice at 0 °C is approximately 4 times than that of water at the same temperature. It indicates that ice conducts heat at a faster rate than the immobilized water. And, this can be observed in the case of freezing and thawing. Freezing processes accomplish at a faster rate than the thawing process. During the freezing with the progress of time, the ice phase enlarges, which becomes the medium for heat transfer. Therefore, the freezing process can be conducted very quickly. But in thawing, with the progress of time, heat transfer medium becomes water. Water has less thermal conductivity than ice. So, it conducts energy at a lower rate which slowers down the thawing process in comparison to freezing.



### Structure of water molecule

Water is formed with 2 hydrogen atoms and 1 oxygen atom. The properties of the water are closely related to its structure. Its unusual properties suggest that there is existence of strong attractive forces among the water molecule. The observed differences between the properties of water and ice also indicate that the structure of water and ice are not common e.g. water and ice have different thermal conductivity properties. In a water molecule, two hydrogen atoms connected by a covalent bond with oxygen atoms and the bond angle is 104.5°.



Although the water molecule is considered to be an electrically neutral molecule, there is an imbalance of the charge because of the arrangement of atoms. The hydrogen atoms are placed on the same side of the oxygen atom. So, the side where hydrogen atoms are located is slightly more electropositive whereas, the other side is slightly more electronegative. That means, in the water molecule, both positive and negative charges are present at the oxygen atom. This imbalance of the electrical charge, in fact, attracts the other water molecule. In other words, it can be said that oxygen of one water molecule attracts the hydrogen of the other and joints it with the help of hydrogen bond. This type of attraction leads to multiple hydrogen bonds. This type of multiple hydrogen bonding on a three-dimensional basis actually gives the logical explanation for the characteristics of the water. In this structure (see Fig.), one water molecule can make a hydrogen bond with four other water molecules at the same time. The higher values of the physical constant are basically the energy required to break these hydrogen bonds and this provides a logical explanation for unusually higher physical constants of water molecule.



# Theories of water structure

There are two theories explained in this connection:

# (1) Homogeneous model

The homogeneous model explains that intermolecular hydrogen bonds are uniformly distributed throughout the water so that each water molecule has essentially the same environment.

# (2) Mixture model

Mixture model explains that the intermolecular hydrogen bonds are concentrated at any given moment, in localized multi-molecular clumps or clusters of a water molecule. In fact, the mixture model is the most widely accepted and valid model. This model explains the characteristics or reactions, etc. which are normally seen in the processes.



### Structure of ice

There is some structural difference between water and ice. The hydrogen bonding in water determines the structure of ice. The hydrogen bonded structure of water is an open structure. But, the structure of ice is a closed structure. When water is frozen, then a regular hexagonal pattern of hydrogen-bonded closed structure results. This structure actually accounts for the properties of the ice.

In the structure of ice, there is ample amount of empty space which makes the ice structure less dense, lower in weight than water. Therefore, the ice floats in water and this is in fact, a natural defence mechanism provided by nature particularly to the aquatic lives. Otherwise, the situation would be different, if the solid water i.e. ice is not floating on water in seas, in rivers, etc. during the winter season, when the temperature drops, this enables the aquatic lives to comfortably live in the warm water below the blanket of the ice on the surface of the water.



### Effect of solutes on structure of water

Water is called as the universal solvent and there is considerable justification for this. Because the substances that are themselves polar or ionic are readily soluble in water e.g. sodium chloride or such other components when put into water, it may dissociate into sodium ion and chloride ion.

There might be another type of solutes like inert solute or the solute which can form a hydrogen bond. Different types of solutes when come in association with water, they influence the characteristics of water differently. Normally, hydrogen bonded structure of pure water is disrupted by the association of dissociable solutes. Some ion in dilute solution break the hydrogen bonds of pure water whereas, the other have a net structure forming effect.

Ions which are normally smaller and/ or multivalent (mostly positive ions) like lithium, sodium, potassium, hydronium, calcium, etc. are net structure formers. On the other hand, the large and monovalent ions (mostly negatively charged ions and large positive ions) such as potassium, rubidium, ammonium, chloride, bromide, and iodide are the net structure breakers. In a concentrated salt solution, the structure which is common in the vicinity of ions is likely to predominate.



Solutes capable of forming hydrogen bonds such as urea may be expected to enhance or at least not to disturb the normal structure of water. However, the distribution and orientation of the solutes' hydrogen bonding sites may be geometrically incompatible with the normal hydrogen-bonded structure of water. This may cause disruption of some of the hydrogen bonds of water like water-water hydrogen bonds.

However, a total number of hydrogen bond per mole of the solution will not be substantially changed because the solute has the capacity to form hydrogen bond. So, when it is introduced into water, the water-water hydrogen bonds might be replaced with the water-solute hydrogen bonds. This newly formed water solute hydrogen bonds are of particular importance when macromolecules are involved. If in a macromolecule, the hydrogen bonding sites are uniformly distributed on the surface, then it is conceivable that, a structured zone of water exists at the macromolecule water interface. A considerable number of carbohydrate, proteins, steroids, hormones, etc. appear to have hydrogen bonding sites.



Solutes which are inert in nature such as hydrocarbons and the non-polar groups of compounds like fatty acids, amino acids, protein, etc. have a structure forming action when introduced into water. Solutes of this nature situate themselves at the boundary of the bulky hydrogen-bonded cluster of the water molecule and thereby encourage the formation of more extensive water-water hydrogen bond.

This causes the solute to become partly surrounded by water with a greater than normal amount of structure. In most proteins, about 40 % of the total amino acids have non-polar side chains. These non-polar groups have a structure forming action on the adjacent water and the interaction between the water and non-polar groups has an important influence on the reactivity of the proteins as well as on their native tertiary conformations.



### **Bound water**

Food and living systems contain bound water molecules due to their biological structure or the presence of solutes. The intensity of binding varies, but only those molecules of water that are mobile and bound least firmly determine the observed water activity. In fact, bound water behaves differently from that of pure water. The type of water or the form of water present in food determines its availability for the chemical and microbiological processes.

Depending on the extent of boundness, water is grouped into four types such as type IV, type III, type II and type I bound water. Distinct boundary might not be there, but in all the four types of water, there is presence of intermediate stages of boundaries.

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### (i) Type IV bound water

Type IV bound water is the one which has full activity and it does not exist except in the free state. The other types such as type III, type II and type I bound water are found in biological matter.

### (ii) Type III bound water

Type III bound water is present physically entrapped in tissue matrix as well as in solutions. This type of water represents the majority of water in plant and animal food tissues. The activity of this type of water is only slightly reduced than normal water or water in the free state. This type of water is actually available for the growth of microorganism, enzyme activity (hydrolytic and oxidative) as well as non-enzymatic browning. The water content of the food can be brought to about 15 to 20 %, if type III bound water is removed, depending upon the type of the food. If type III bound water is removed, it indicates that the growth of the microorganism, enzymatic activity, non-enzymatic browning, etc. will be eliminated.

# Type II bound water This is more firmly bound than type III and its activity is reduced substantially. It permits enzymatic activity (only hydrolytic) and non-enzymatic browning. Removal of this eliminates the possibilities of microbial growth and greatly reduces most of the chemical reactions. Type I bound water It is more firmly bound than Type II and the water activity is further reduced. Partial removal of this type of water can be accomplished by conventional dehydration. The degree of binding is such that any reaction depending upon solution is so slow as to be immeasurable. At this stage, there is an acceleration of lipid phase reactions, such as oxidative rancidity.

### (iii) Type II bound water

Type II bound water is more firmly bound than the type III, and its activity is further reduced substantially. It permits enzymatic activity (only hydrolytic enzymatic activity) and non-enzymatic browning. Removal of this type of water eliminates the possibility of microbial growth and greatly reduces most of the chemical reaction processes.

### (iv) Type I bound water

Type I bound water is more firmly bound than type II and the water activity of this is further reduced. Even only partial removal of this type of water can be accomplished by the conventional dehydration processes. The degree of binding, in this case, is such that any reaction depending upon the solution is so slow that it becomes very difficult to measure. At this stage, there is an acceleration of the lipid phase reaction such as oxidative rancidity.



### Water activity (a<sub>w</sub>)

By considering the nature and type of water, another parameter which actually plays an important role in food is water activity.

The ratio of partial pressure of water above the sample to the ratio of the vapour pressure of pure water at the same temperature is defined as water activity. Mathematically, it is expressed as:

$$a_w = \frac{p}{p_0}$$

Where p is the partial pressure of water above the food sample and  $p_0$  is the vapour pressure of pure water at the same temperature.

Water activity can also be defined as equilibrium relative humidity expressed in decimals.

$$a_w = \frac{ERH}{100}$$

Water activity is the intrinsic property of the food sample whereas; equilibrium relative humidity is a property of the atmosphere in equilibrium with the food sample.

To find out the water activity in terms of equilibrium relative humidity, the experiment has to be conducted which becomes generally time-consuming and tedious. Even a smaller sample (1 g) takes a very long time to equilibrate the humidity of the food with that of the environment. In the case of larger sample, it becomes completely impossible. The latest instruments made it possible to measure water activity within a short time.



### Water activity and food stability

The water activity influences the stability or storage life of the food material. Food stability and  $a_w$  are closely related in many (but not all) situations (Figures A-F). Here, there are plots of reaction rate against  $a_w$  indicating the rates of the microbial growth processes, enzymatic reactions, oxidation reactions, Maillard reaction like brown colour development, lysine loss and sorption isotherm, chlorophyll loss, vitamin B<sub>1</sub> loss, etc.

In figure C, the oxidation reaction in the lipid (potato chips), deserves comment. It can be observed that the lipid oxidation reaction is running or taking place at a comparatively faster rate when water activity is very low. When water activity increases or addition of water up to the boundary layer of zone I and zone II, the lipid oxidation comes to the minimum, and further addition of water or increase in the water activity results into the increase in the reaction rate of lipid oxidation. When it comes to the boundary zone II and zone III i.e. intermediate moisture food (IMF) a<sub>w</sub> range, the rate reaches to the maximum. Although it is not shown in the figure, further increase in the water results into the decrease of the lipid oxidation reaction.



It has been suggested that, water added in this region of the isotherm may accelerate oxidation by increasing the solubility of oxygen and by allowing macromolecules to swell, thereby exposing more catalytic sites. At still greater  $a_w$  values (more than about 0.80) the added water may retard rates of oxidation and the suggested explanation is that dilution of catalysts reduces their effectiveness.



In figure A, D and E which are basically microbial growth, Maillard reaction and other miscellaneous reaction like chlorophyll loss and vitamin  $B_1$  loss, exhibited the maximum activity towards the intermediate  $a_w$  level (0.75 to 0.85).

Two possibilities have been advanced to account for the decline in reaction rate that sometimes accompanies increase in  $a_w$  in foods with moderate to high moisture.

- (i) For those reactions in which water is a product, an increase in water content can result in product inhibition.
- (ii) When the water content of the sample is such that solubility, accessibility (surface of macromolecules), and mobility of rate enhancing constituents are no longer rate limiting, the further addition of water will dilute the rate enhancing constituents and decrease the reaction rates.



Further, in almost all chemical reactions shown in Figures A, B, C, D, E, & F, it can be observed that the typical minimum reaction rate is present towards the first zone i.e. the interface of the zone I and zone II of the isotherm ( $a_w 0.2 - 0.3$ ). That means, at this water activity, the reactions are typically occurring at a very low rate. At this stage, all the reactions remain minimum. So, this water content of the food corresponding to this first encountered minimum desorption is called as monolayer moisture content. This monolayer moisture content provides a good estimate of the water content providing the maximum stability of the dried product.



The following equation can be used to compute the monolayer moisture content

$$\frac{a_{w}}{m(1-a_{w})} = \frac{1}{m_{1}C} + \frac{C-1}{m_{1}C} a_{w}$$

Where  $m_1$  is the monolayer moisture content, m is the initial moisture content (g/g dry matter) of the food and C is a constant, and  $a_w$  is the water activity.

From the equation, a plot of  $[a_w/m(1-a_w)]$  vs  $a_w$  known as BET plot should yield a straight line.

In addition to the chemical reaction and microbial growth,  $a_w$  also influences the texture of dry and semi-dry foods. The  $a_w$  and water content must be maintained to the desired level. For example, suitably low  $a_w$  are required if crispiness of crackers, popcorn, potato chips are to be retained, if caking of granulated sugar, dry milk and instant coffee is to be avoided, and if stickiness of the hard candy is to be prevented.

The maximum  $a_w$  that can be tolerated in dry materials without incurring a loss of desirable properties range from 0.35 - 0.5, depending on the product. Suitably high  $a_w$  of soft textured foods are needed to avoid undesirable hardness.

These two aspects need to be looked into simultaneously i.e. the control of water activity (increasing, decreasing or maintaining) and its effect on the food quality such as textural, sensory and organoleptic qualities.