

Structure of water

Introduction

Water is relatively small inorganic molecule, but organic life is highly dependent on this tiny molecule. It is the only substance on the earth that occurs abundantly in all three physical states (gas, liquid and solid).

Water is essential for life as:

- (1) regulator of body temperature
- (2) solvent
- (3) carrier of nutrients and waste products
- (4) reactant and reaction medium
- (5) lubricant and plasticizer
- (6) stabilizer of biopolymer conformation
- (7) facilitator of the dynamic behavior of macromolecules (e.g. catalytic activity)

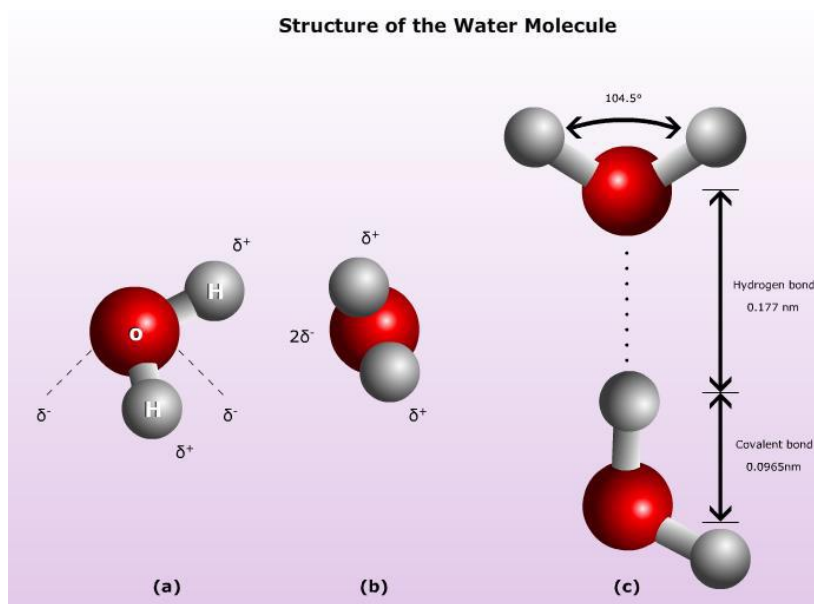
Most of the fresh foods contain large amounts of water. It is one of the major component in composition of many foods. Each food has its own characteristic amount of this component. Effect of water on structure, appearance and taste of foods as well as their susceptibility to spoilage depends on its amount, location, and orientation. Therefore, it is essential to know its physical properties.

Water has unusually high melting point, boiling point, surface tension, permittivity, heat capacity, and heat of phase transition values. Other unusual attribute of water include expansion upon solidification, large thermal conductivity compared to those of other liquids, moderately large thermal conductivity of ice compared to those of other nonmetallic solids.

Water Molecule

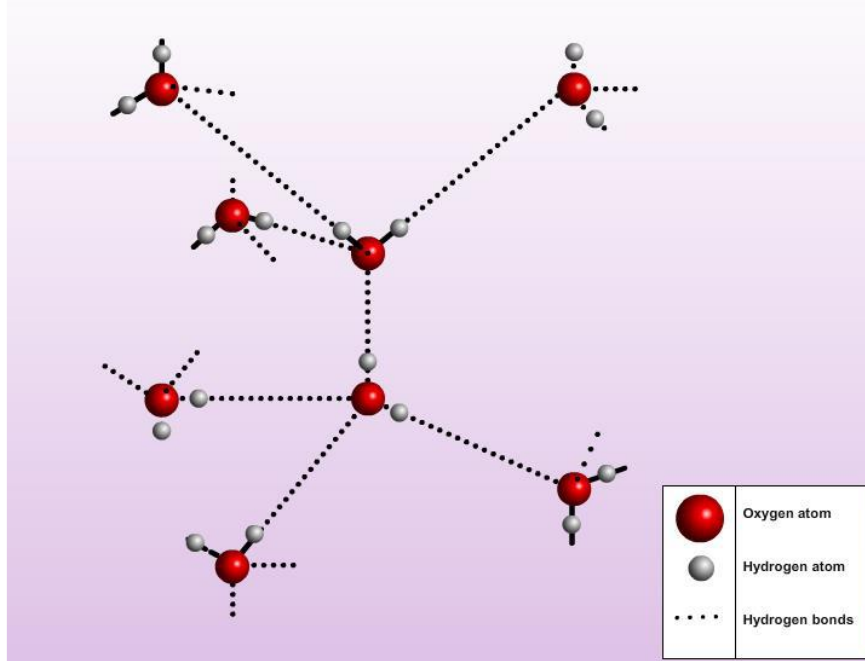
Some the unusual properties of water are due strong intermolecular attractive forces among molecules of water. The unusual properties of water can be explained from nature of water molecules. In formation of water molecule, two hydrogen atoms form covalent bonds with oxygen. The highly electronegative oxygen of the water molecule pulls the single electron from each of the two covalently bonded hydrogen atoms towards its self, as a result each hydrogen atom becomes partially positively charged and oxygen becomes partially negatively charged.

Consequently, resultant covalent bond formed between oxygen and hydrogen atoms acquires partial ionic character. The bond angle of individual water molecule in vapor state is 104.5° .



Structure of the water molecule

Hydrogen Bonding of Water Molecules in a Tetrahedral Configuration

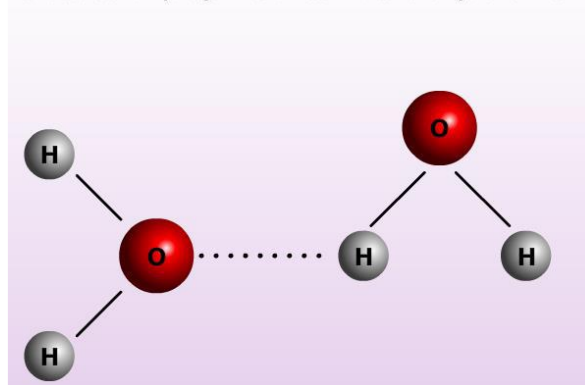


Hydrogen bonding of water molecules in a tetrahedral configuration

Association of Water Molecules

The shape of water molecule and the partial polar nature of the O-H bond in the water molecule create intermolecular attraction force. Such inter molecular attraction, results in to formation of hydrogen bonds between the water molecules. Therefore, water molecules associate with considerable tenacity.

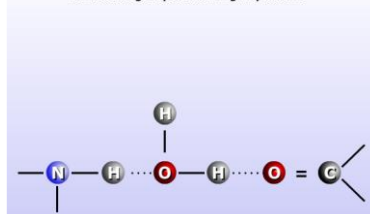
Structure and Hydrogen-Bond Possibilities for a Hydronium ion



Hydronium ion

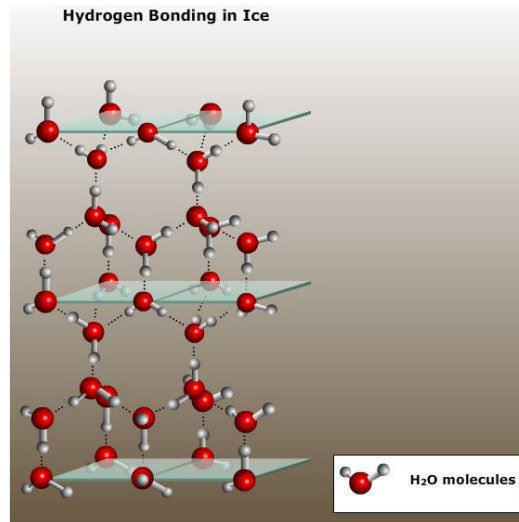
Each water molecule involves in four hydrogen bonds with neighboring water molecules. Multiple hydrogen bonding between water molecules, forms a structure of three-dimensional network.

Hydrogen bonding (dotted lines) of water to two kinds of functional groups occurring in proteins

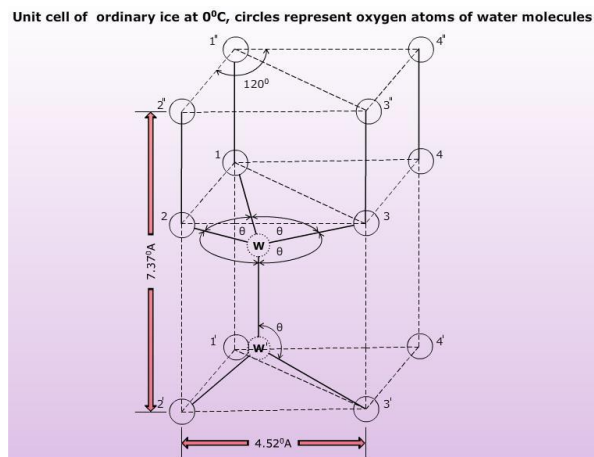


Hydrogen bonding of water to two kinds of functional groups occurring in proteins

Existence of three-dimensional hydrogen bonded structure of water is responsible for many of its unusual properties. The extra energy needed to break intermolecular hydrogen bonds. This leads to large values for heat capacity, melting point, boiling point, surface tension, and enthalpies of various phase transitions of water. The dielectric constant (permittivity) of water is influenced by hydrogen bonding. Hydrogen-bonded multi-molecular dipoles increase the permittivity of water. The hydrogen bonded arrangement of water molecules is highly dynamic, allowing individual molecules to alter their hydrogen-bonding relationships with neighboring molecules. This phenomenon facilitates mobility and fluidity of water. The open, hydrogen-bonded, tetrahedral structure of water molecules in ice is responsible for low density of water in ice form. The extent of intermolecular hydrogen bonding among water molecules depends on temperature.



Hydrogen bonding in ice



Unit cell of ordinary ice

With input of heat melting of ice occurs; that is, some hydrogen bonds are broken distance between nearest neighbor increases. The latter factor predominates at temperatures between 0 and 4°C, which causes net increase in density. Further warming increasing distance between nearest neighbors (thermal expansion) predominates above 4°C, which causes net decrease in density.

Water binding and chemical reactions mediated by water

Introduction

Mixing of solutes and water alters properties of each other. Hydrophilic solutes cause changes in structure and mobility of water and water causes changes in the reactivity, and structure, of hydrophilic solutes. Hydrophobic groups of solutes interact only weakly with water. In interaction of solute with water, various bonding forces existing between water and solutes. To understand interaction between water and solutes at the molecular level, it is essential to knowledge about water-related phenomena and related terms like water binding, hydration, and water holding capacity. The terms “water binding” and “hydration” are often used to represent tendency of water to associate with hydrophilic substances in foods. The extent and tenacity of water binding or hydration depends on several factors like nature of solute, salt composition, pH, and temperature.

Water holding capacity

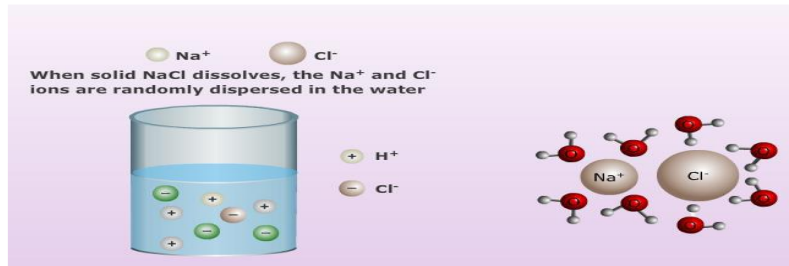
Term generally used to describe ability of a matrix of molecules to physically entrap large amounts of water in such a way that prevents exudation of the water. The food matrices that entrap water in this manner include pectin and starch gels and tissue cells of plant and animal. This physically entrapped water does not flow from food even when they are cut or minced. But this water behaves almost like pure water during food processing operations like drying, freezing, etc. it is also available as a solvent. Thus, bulk flow of this water is restricted, but movement of individual molecules almost remains same as that of water molecules in a dilute solution. Impairment in this entrapment of water (*i.e.* holding capacity) of foods has a significant effect on quality of food. Some of the typical examples are oozing out of liquid from gel (syneresis) and exudation of liquid on thawing of frozen foods.

Bound Water

Bound water is not a easily identifiable entity. It is poorly understood term. Number of definitions proposed. The bound water is that water which is in equilibrium water of sample at appropriate temperature and relative humidity does not contribute significantly to permittivity and has restricted mobility does not freeze at low temperature (*e.g.* 40°C) unavailable as a solvent to dissolve additional solutes migrate with a macromolecule during sedimentation or flow The bound exists in vicinity of solutes molecules. Properties of this water are significantly different from that of the “bulk” water in the same system. In high water content foods, the bound water account for very minute amount of the total water present. Generally, the first layer of water molecules adjacent to hydrophilic groups comprises the bound water.

Interaction between water and ions

Ions and ionic groups of organic molecules hinder mobility of water molecules to a greater extent than other types of solutes. The strength of water-ion interaction is greater than that of hydrogen bonds, between the water molecules, however, it is much less than that of covalent bonds. Water and inorganic ions (*e.g.* NaCl) undergo dipole-ion interactions.



Water as solvent

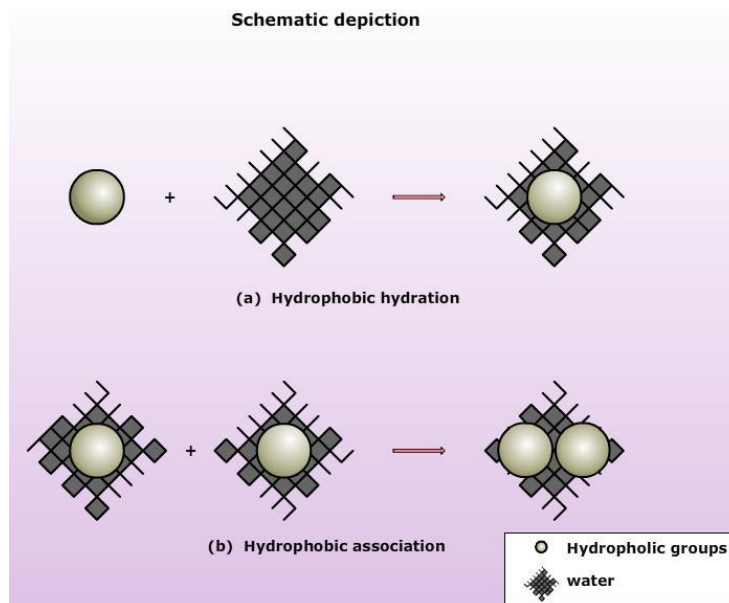
The ions compete for water and alter water structure, influence the permittivity of the aqueous medium and influence thickness of the electric layer around colloids particle “degree of hospitality” provided to other nonaqueous solutes and to substances suspended in the medium. Thus, conformation of proteins and stability of colloids are profoundly influenced by nature and concentration of ions present in the system. Salting-in and salting-out of protein are the important examples of such effect of ions.

Interaction between water and hydrophilic solutes forming hydrogen bond

Interactions between water and nonionic, hydrophilic solutes are weaker than that of the interactions between water and ions and of the almost same strength as that of the hydrogen bonds between water molecules. Solute capable of hydrogen bonding enhance or at least not disrupt the normal structure of pure water. However, in some instances solutes have a disruptive influence on the normal structure of water. Urea is good example which markedly disrupts normal structure of water.

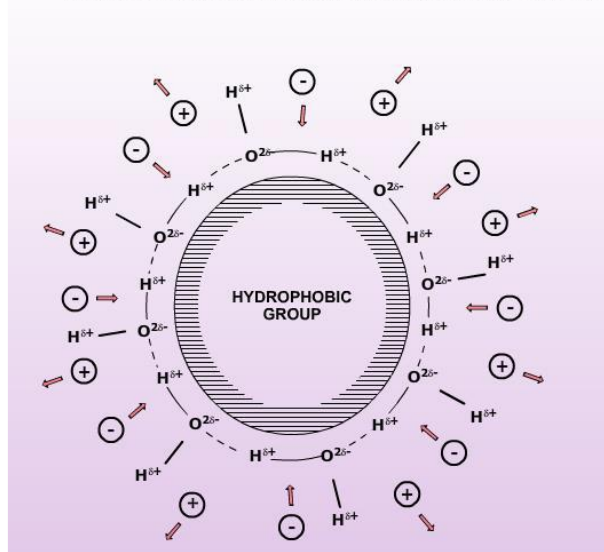
Interaction between water and non-polar substances

The mixing of water and hydrophobic substances (*e.g.* apolar groups of fatty acids, amino acids, proteins, etc.) is thermodynamically unfavorable event ($\Delta G > 0$). Water forms a special structure in vicinity of the incompatible apolar entities. This process has been referred to as hydrophobic hydration. Since hydrophobic hydration is thermodynamically unfavorable, water tends to minimize its association with the apolar entities. Therefore, the incompatible aqueous environment will encourage two separate apolar groups to associate, to decrease waterapolar interfacial area. This process is termed as “hydrophobic interaction”.



Hydrophobic interaction

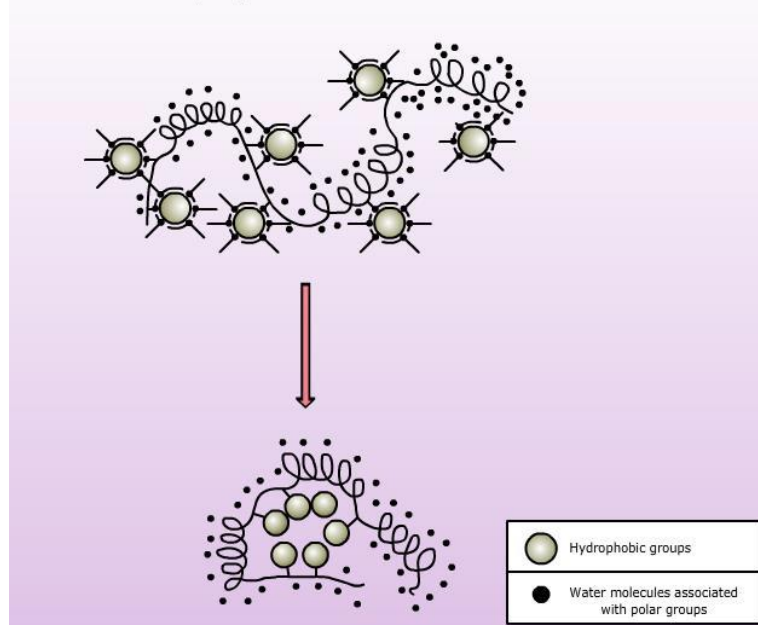
Proposed water orientation at a hydrophobic surface



Water orientation at hydrophobic surface

A clathrate hydrate is a cage-like structure inclusion compound, in which hydrogen-bonded water layer entraps a small apolar molecule. Formation of clathrate hydrates is an extraordinary ability of water to minimize contact with hydrophobic groups. This structure influences conformation, reactivity, and stability of molecules like proteins. Hydrophobic interaction is of primary importance in maintaining the tertiary structure of most proteins. It provides a major driving force for protein folding, causing many hydrophobic residues to assume positions in the protein interior. Such association of water with hydrophobic groups of proteins has an important influence on functionality of the protein.

Schematic depiction of a globular protein undergoing hydrophobic interaction



Globular protein undergoing hydrophobic interaction

The non-polar groups of other compounds such as alcohols, fatty acids, and free amino acids also can participate in hydrophobic interactions. Therefore, association of water with hydrophobic groups in proteins is very important in food. Reduction in temperature causes hydrophobic interactions to become weaker and hydrogen bonds to become stronger.

Water Activity

A definite relationship exists between water content of food and its perishability. Concentration and dehydration of food is carried out primarily to decrease its water content, with a view to increase concentration of solutes and thereby increase shelf life of the food. However, various foods with same amount of water content may differ significantly in perishability, which indicates that the water content alone is not a reliable indicator for susceptibility of food towards perishability. This is largely due to differences in intensity of association of the food constituents with water molecules. Water having strong associations with food constituents has lower ability to support deteriorative activities like microbial growth and chemical degradation reactions (*e.g.* hydrolysis), than that of the weakly associated water. Consequently, term water activity (a_w) was developed to account for the intensity with which water associates with various nonaqueous constituents. Food stability, safety and other properties can be predicted far more reliably from a_w than from water content. The term “activity” was derived from laws of equilibrium thermodynamics by G. N. Lewis and its application to foods was pioneered by Scott.

Definition

Water activity may be defined as ratio of tendency of a solvent to escape from solution (f_0) to tendency of the solvent to escape from pure solvent (f). At ambient pressure, f/f_0 is almost equal to relative vapour pressure of the solution. Therefore, a_w may also be defined as ratio of relative vapour pressure of solvent upon dissolving nonvolatile solute to the vapour pressure of pure solvent. Therefore, relative vapor pressure is also used interchangeably for a_w . The relative vapour is related to per cent equilibrium relative humidity (ERH) of the product environment.

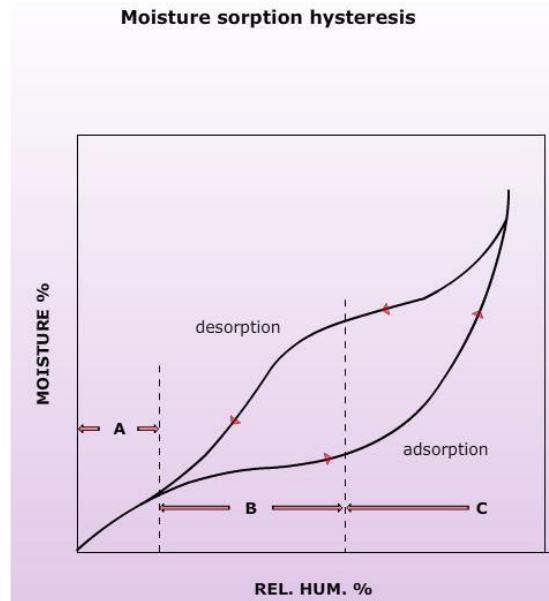
Temperature Dependence

Relative vapor pressure is temperature dependent. The degree of temperature dependence is a function of moisture content. This behavior can be important for a packaged food because it will undergo a change in relative vapour with a change in temperature, causing the temperature dependence of its stability to be greater than that of the same product unpackaged.

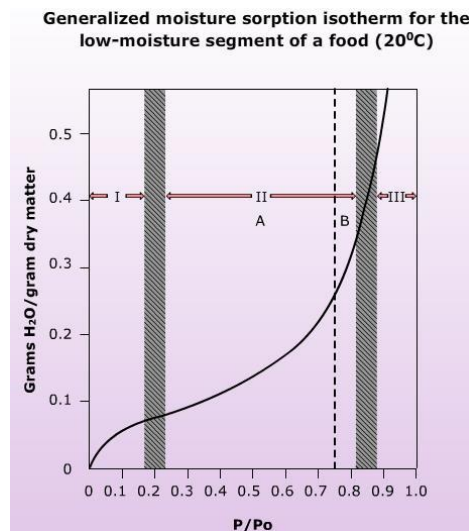
Moisture sorption isotherms

A plot of water content of a food (g water/g dry material) versus a_w at constant temperature is known as a moisture sorption isotherm (MSI). Information derived from MSIs are useful for concentration and dehydration processes, formulation of food mixtures so as to avoid moisture transfer among the ingredients, determination of moisture barrier properties needed in a packaging material, determination of what moisture content will curtail growth of microorganisms of interest and prediction of the chemical and physical stability of food as a function of water content.

Resorption (or adsorption) isotherms are prepared by adding water to previously dried samples. Desorption isotherms are isotherms prepared by removing water from samples. Isotherms with a sigmoidal shape are characteristic of most foods. Foods such as fruits, confections, and coffee extract that contain large amounts of sugar and other small, soluble molecules and are not rich in polymeric materials exhibit a J-type isotherm.



Moisture sorption hysteresis



Generalized moisture sorption isotherm

As water is added (resorption), sample composition moves from Zone I (dry) to Zone III (high moisture). Properties of water associated with each zone differ significantly.

Water in Zone I of the isotherm

The water in Zone I of the isotherm is most strongly sorbed and least mobile, associated with accessible polar sites by water-ion or water-dipole interactions, unfreezable at -40°C, not able to dissolve solutes, not present in sufficient amount to have a plasticizing effect on the solid, behaving simply as part of the solid and constituting a tiny fraction of the total water in a high-moisture food material.

Water in Zone II of the isotherm

Water in Zone II of the isotherm occupies first-layer sites that are still available, associates with neighboring water molecules and solute molecules primarily by hydrogen bonding, slightly less mobile than bulk water, most of it is unfreezable at - 40°C, exerts a significant plasticizing action on solutes, lowers their glass transition temperatures and causes swelling of the solid matrix. This action, coupled with the beginning of solution processes, leads to acceleration in the rate of most reactions. Water in Zones I and Zone II usually constitutes less than 5% of the water in a high moisture food material.

Water in Zone III of the isotherm

Water in Zone III of the isotherm causes glass-rubber transition in samples containing glassy regions, very large decrease in viscosity, very large increase in molecular mobility and commensurate increases

in the rates of many reactions. This water is referred to as bulk-phase water, having properties of bulk-phase water and will not alter properties of existing solutes, freezable, available as a solvent, readily supports the growth of microorganism and constituting more than 95% of the total water in a high-moisture food. It is the most mobile fraction of water existing in any food sample governs stability.

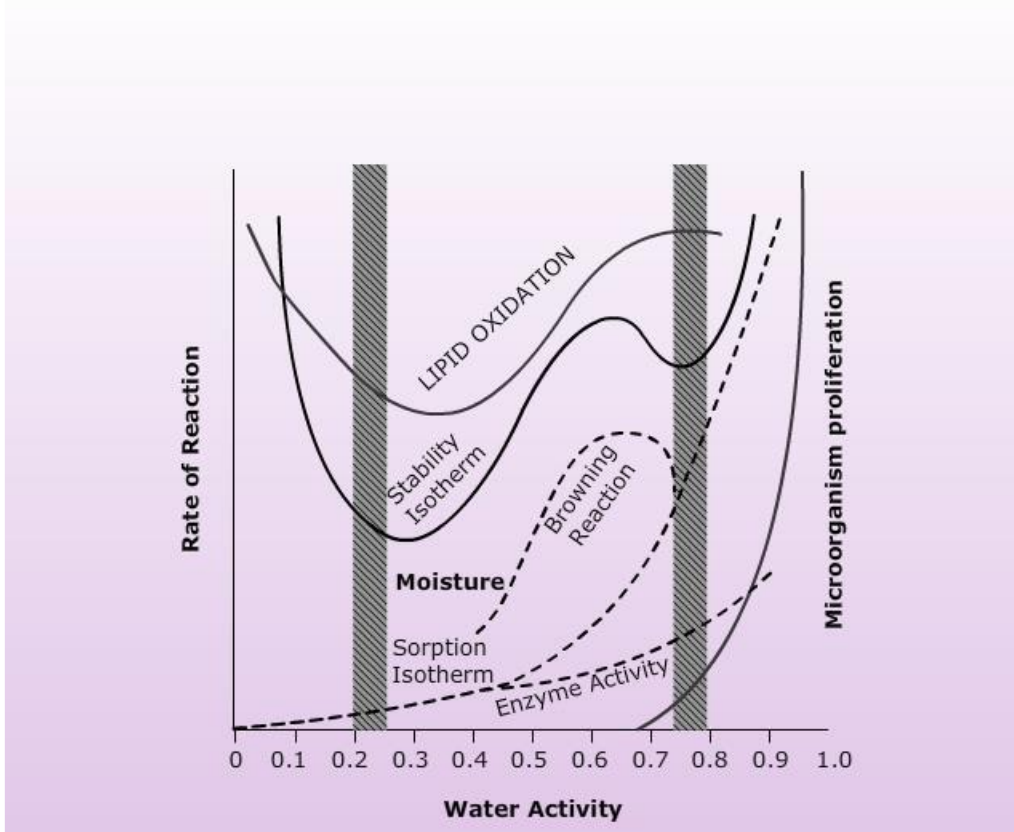
Hysteresis

An additional complication is that an MSI prepared by addition of water (resorption) to a dry sample will not necessarily be superimposable on an isotherm prepared by desorption. This lack of superimposability is referred to as “hysteresis”. The magnitude of hysteresis, the shape of the curves, and the inception and termination points of the hysteresis loop can vary considerably depending on factors such as nature of the food, physical changes it undergoes when water is removed or added temperature, rate of desorption and degree of water removal during desorption.

Relation of food stability with its water activity

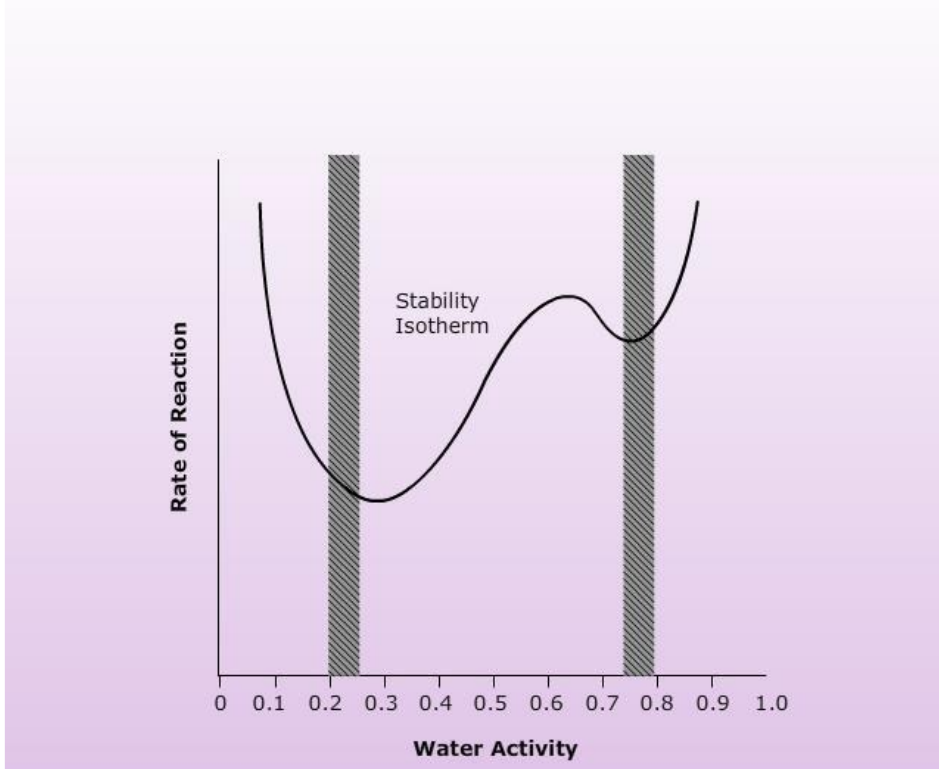
Food stability and its a_w are closely related in many situations. The rates of many reactions are influenced by the extent of water binding in food in which water content is less than TS (<50%). The effect of water activity on processes that influence quality of food is depicted in figure. It is clear that water activity has profound influence on the rate of many chemical reactions in food as well as on the rate of microbial growth.

Relationship Between Water Activity and a Number of Reaction Rates



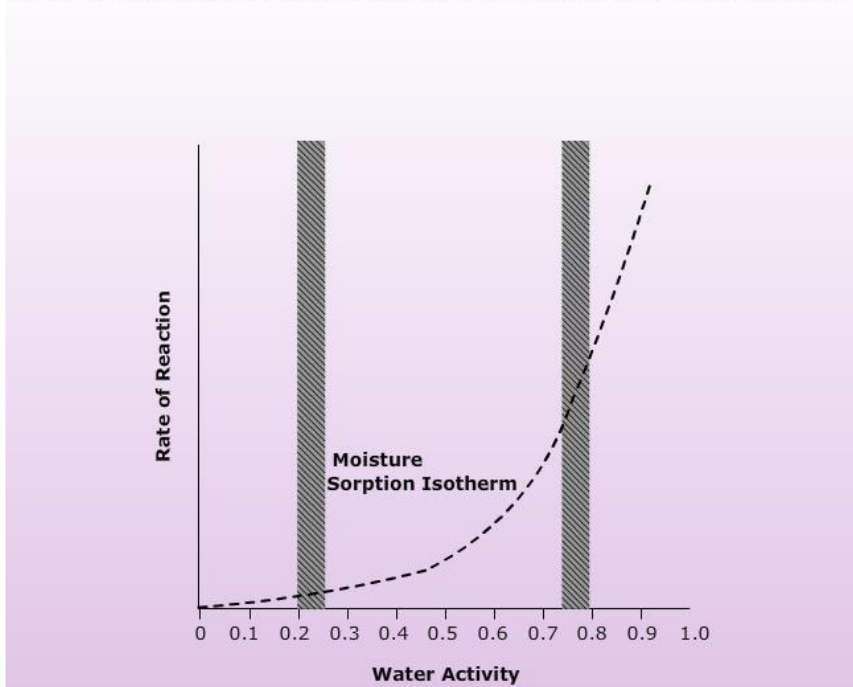
Water activity and a number of reaction rates

Relationship Between Water Activity and a Number of Reaction Rates



Water activity and a number of reaction rates-stability isotherm

Relationship Between Water Activity and a Number of Reaction Rates

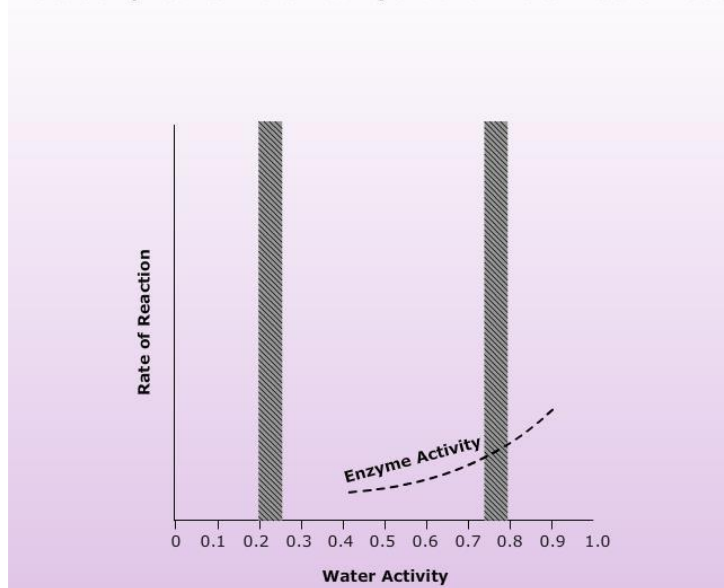


Water activity and a number of reaction rates-moisture sorption isotherm

Decreased water activity retards growth of microorganisms slows enzyme catalyzed reactions and also retards non-enzymatic browning. Enzyme activity is virtually non-existent in monolayer water ($a_w < 0.25$). Therefore growth of microorganisms at this level of activity is also zero. Mold and yeast start to grow when water activity reaches between 0.7-0.8, which is the upper limit of capillary water. Bacterial growth takes place when water activity reaches 0.8, which is the limit of loosely bound water.

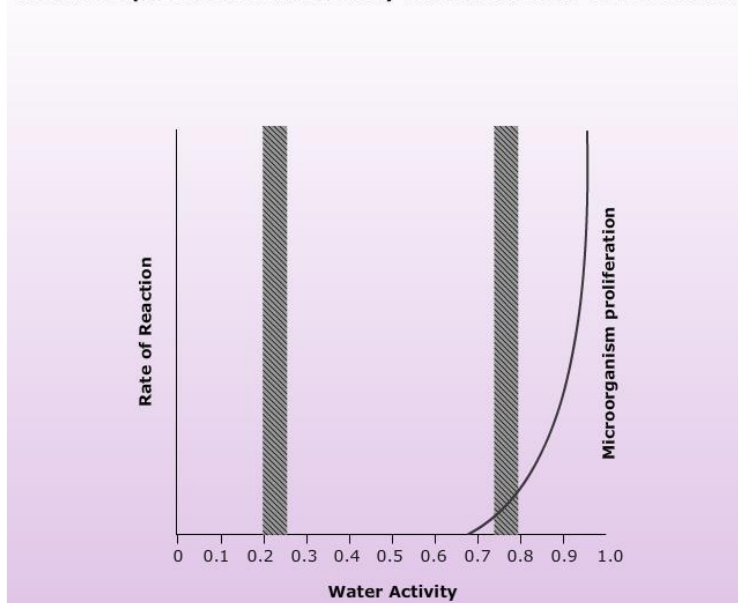
However yeast and mold are usually inhibited between 0.8-0.88. Enzyme activity increases gradually between water activity of 0.3-0.6 and then rapidly increases in the loosely bound water range i.e. water activity of about 0.8.

Relationship Between Water Activity and a Number of Reaction Rates



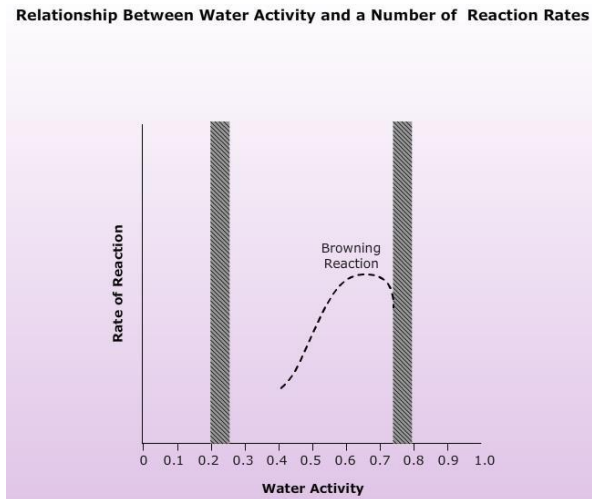
Water activity and a number of reaction rates-enzyme activity

Relationship Between Water Activity and a Number of Reaction Rates



Water activity and a number of reaction rates-microorganism proliferation

Maillard reaction strongly depends on water activity and reaches a maximum rate at a value of 0.6 to 0.7. Beyond this range the rate of reaction decreases. The explanation for such behaviour is that in intermediate water activity range, the reactants are all dissolved and further increase in a_w leads to dilution of reactants, which adversely affects the reaction rate.



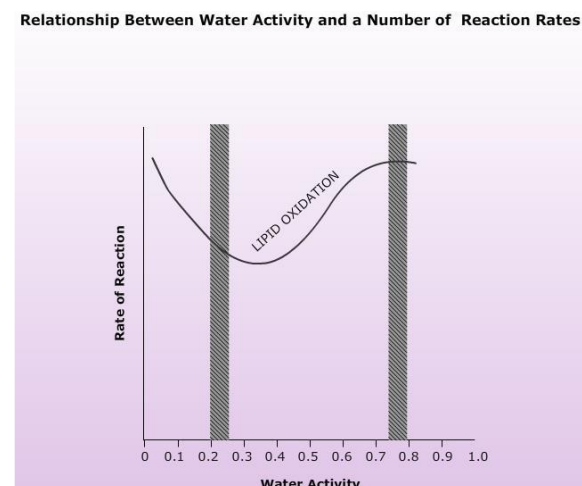
The effect of water activity on oxidation of lipids is complex. Lipid oxidation rates are at a high in the monolayer water range of water activity, reach a minimum at water activity of 0.3-0.4 and then increases to a maximum at 0.8. If we start at very low water activity value, it is apparent that rate of oxidation decreases as water is added. Further addition results in increased rate of reaction followed by another reduction. The interpretation for such a behaviour is that first addition interferes with oxidation probably by—

1. Binding hydroperoxides and thereby interfering with their decomposition which hinders the progress of oxidation.
2. Hydration of metallic ions thereby reducing their effectiveness as catalyst of oxidation
3. Quenching free radicals and by preventing access of O₂ to the lipid which further provides protection against oxidation.

The increases observed by further addition of H₂O maybe due to--

1. Increased solubility of O₂, thereby increasing the mobilization of O₂ as well as catalysts
2. The swelling of macromolecules which exposes more catalytic sites

The second decrease observed at a_w 0.8 may probably be due to dilution of the catalysts that decreases their effectiveness.



Therefore, the storage stability of foods is highest when the a_w lies between 0.2-0.4. Food must be prevented against microbial spoilage when a_w is between 0.6-0.8.
