0 Water

0.1 Foreword

Water (moisture) is the predominant constituent in many foods (Table 0.1). As a medium water supports chemical reactions, and it is a direct reactant in hydrolytic processes. Therefore, removal of water from food or binding it by increasing the concentration of common salt or sugar retards many reactions and inhibits the growth of microorganisms, thus improving the shelf lives of a number of foods. Through physical interaction with proteins, polysaccharides, lipids and salts, water contributes significantly to the texture of food.

Table 0.1. Moisture content of some foods

Food	Moisture content (weight-%)	Food	Moisture content (weight-%)
Meat	65–75	Cereal flour	12–14
Milk	87	Coffee beans, roasted	5
Fruits, vegetables	70–90	Milk powder	4
Bread	35	Edible oil	0
Honey	20		
Butter, margarine	16–18		

The function of water is better understood when its structure and its state in a food system are clarified. Special aspects of binding of water by individual food constituents (cf. 1.4.3.3, 3.5.2 and 4.4.3) and meat (cf. 12.5) are discussed in the indicated sections.

0.2 Structure

0.2.1 Water Molecule

The six valence electrons of oxygen in a water molecule are hybridized to four sp^3 orbitals that are elongated to the corners of a somewhat deformed, imaginary tetrahedron (Fig. 0.1). Two hybrid orbitals form O–H covalent bonds with a bond angle of 105° for H–O–H, whereas the other 2 orbitals hold the nonbonding electron pairs (n-electrons). The O–H covalent bonds, due to the highly electronegative oxygen, have a partial (40%) ionic character.

Each water molecule is tetrahedrally coordinated with four other water molecules through hydrogen bonds. The two unshared electron pairs (n-electrons or sp^3 orbitals) of oxygen act as H-bond acceptor sites and the H–O bonding orbitals act as hydrogen bond donor sites (Fig. 0.2). The dissociation energy of this hydrogen bond is about 25 kJ mole^{-1}.

The simultaneous presence of two acceptor sites and two donor sites in water permits association in a three-dimensional network stabilized by

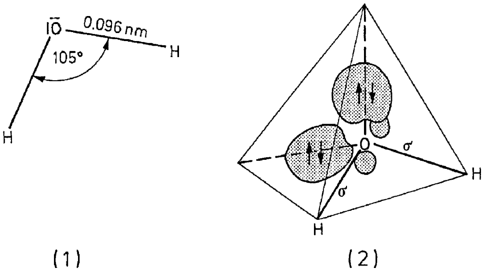

Fig. 0.1. Water. (**1**) Molecular geometry, (**2**) orbital model

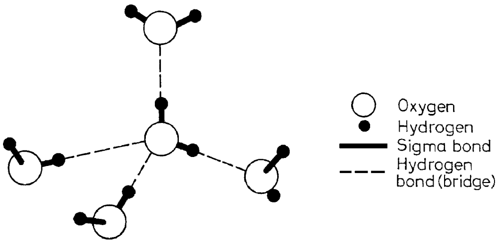

Fig. 0.2. Tetrahedral coordination of water molecules

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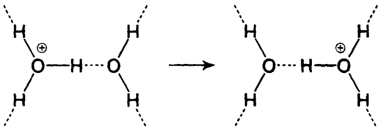
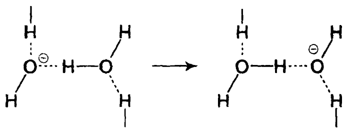
H-bridges. This structure which explains the special physical properties of water is unusual for other small molecules. For example, alcohols and compounds with iso-electric dipoles similar to those of water, such as HF or NH_3, form only linear or two-dimensional associations.

The above mentioned polarization of H–O bonds is transferred via hydrogen bonds and extends over several bonds. Therefore, the dipole moment of a complex consisting of increasing numbers of water molecules (multi-molecular dipole) is higher as more molecules become associated and is certainly much higher than the dipole moment of a single molecule. Thus, the dielectric constant of water is high and surpasses the value, which can be calculated on the basis of the dipole moment of a single molecule. Proton transport takes place along the H-bridges. It is actually the jump of a proton from one water molecule to a neighboring water molecule. Regardless of whether the proton is derived from dissociation of water or originates from an acid, it will sink into the unshared electron pair orbitals of water:



(0.1)

In this way a hydrated $H_3O^{\oplus}$ ion is formed with an exceptionally strong hydrogen bond (dissociation energy about 100 kJ mol^{-1}). A similar mechanism is valid in transport of $OH^{\ominus}$ ions, which also occurs along the hydrogen bridges:



(0.2)

Since the transition of a proton from one oxygen to the next occurs extremely rapidly ($\nu > 10^{12}\ s^{-1}$), proton mobility surpasses the mobilities of all other ions by a factor of 4–5, except for the stepwise movement of $OH^{\ominus}$ within the structure; its rate of exchange is only 40% less than that of a proton.

H-bridges in ice extend to a larger sphere than in water (see the following section). The mobility of protons in ice is higher than in water by a factor of 100.

0.2.2 Liquid Water and Ice

The arrangements of water molecules in “liquid water” and in ice are still under intensive investigation. The outlined hypotheses agree with existing data and are generally accepted.

Due to the pronounced tendency of water molecules to associate through H-bridges, liquid water and ice are highly structured. They differ in the distance between molecules, coordination number and time-range order (duration of stability). Stable ice-I is formed at 0 °C and 1 atm pressure. It is one of nine known crystalline polymorphic structures, each of which is stable in a certain temperature and pressure range. The coordination number in ice-I is four, the O–H$\cdots$O (nearest neighbor) distance is 0.276 nm (0 °C) and the H-atom between neighboring oxygens is 0.101 nm from the oxygen to which it is bound covalently and 0.175 nm from the oxygen to which it is bound by a hydrogen bridge. Five water molecules, forming a tetrahedron, are loosely packed and kept together mostly through H-bridges.

Table 0.2. Coordination number and distance between two water molecules

	Coordination number	O–H$\cdots$O Distance
Ice (0 °C)	4	0.276 nm
Water (1.5 °C)	4.4	0.290 nm
Water (83 °C)	4.9	0.305 nm

When ice melts and the resultant water is heated (Table 0.2), both the coordination number and the distance between the nearest neighbors increase. These changes have opposite influences on the density. An increase in coordination number (i.e. the number of water molecules arranged in an orderly fashion around each water molecule) increases the density, whereas an increase in distance between nearest neighbors decreases the density. The effect of increasing coordination number is predominant during a temperature increase from 0 to 4 °C. As a consequence, water has an unusual property: its density in the liquid state at 0 °C (0.9998 g cm^{-3}) is higher than in the solid state (ice-I, $\rho = 0.9168$ g cm^{-3}). Water is a structured liquid with a short time-range order. The water molecules, through H-bridges, form short-lived polygonal structures which are rapidly cleaved and then reestablished giving a dynamic equilibrium. Such fluctuations explain the lower viscosity of water, which otherwise could not be explained if H-bridges were rigid.

The hydrogen-bound water structure is changed by solubilization of salts or molecules with polar and/or hydrophobic groups. In salt solutions the n-electrons occupy the free orbitals of the cations, forming "aqua complexes". Other water molecules then coordinate through H-bridges, forming a hydration shell around the cation and disrupting the natural structure of water.

Hydration shells are formed by anions through ion-dipole interaction and by polar groups through dipole-dipole interaction or H-bridges, again contributing to the disruption of the structured state of water.

Aliphatic groups which can fix the water molecules by dispersion forces are no less disruptive. A minimum of free enthalpy will be attained when an ice-like water structure is arranged around a hydrophobic group (tetrahedral-four-coordination). Such ice-like hydration shells around aliphatic groups contribute, for example, to stabilization of a protein, helping the protein to acquire its most thermodynamically favorable conformation in water.

The highly structured, three-dimensional hydrogen bonding state of ice and water is reflected in many of their unusual properties.

Additional energy is required to break the structured state. This accounts for water having substantially higher melting and boiling points and heats of fusion and vaporization than methanol or dimethyl ether (cf. Table 0.3). Methanol has only one hydrogen donor site, while dimethyl ether has none but does have a hydrogen bond acceptor site; neither is sufficient to form a structured network as found in water.

Table 0.3. Some physical constants of water, methanol and dimethyl ether

	F_p (°C)	K_p (°C)
H_2O	0.0	100.0
CH_3OH	−98	64.7
CH_3OCH_3	−138	−23

0.3 Effect on Storage Life

Drying and/or storage at low temperatures are among the oldest methods for the preservation of food with high water contents. Modern food technology tries to optimize these methods. A product should be dried and/or frozen only long enough to ensure wholesome quality for a certain period of time.

Naturally, drying and/or freezing must be optimized for each product individually. It is therefore necessary to know the effect of water on storage life before suitable conditions can be selected.

0.3.1 Water Activity

In 1952, Scott came to the conclusion that the storage quality of food does not depend on the water content, but on water activity (a_w), which is defined as follows:

$$a_w = P/P_0 = ERH/100 \tag{0.3}$$

P = partial vapor pressure of food moisture at temperature T
P_0 = saturation vapor pressure of pure water at T
ERH = equilibrium relative humidity at T.

The relationship between water content and water activity is indicated by the sorption isotherm of a food (Fig. 0.3).

At a low water content (<50%), even minor changes in this parameter lead to major changes in water activity. For that reason, the sorption isotherm of a food with lower water content is shown with an expanded ordinate in Fig. 0.3b, as compared with Fig. 0.3a.

Figure 0.3b shows that the desorption isotherm, indicating the course of a drying process, lies slightly above the adsorption isotherm pertaining to the storage of moisture-sensitive food. As a rule, the position of the hysteresis loop changes when adsorption and desorption are repeated with the same sample. The effect of water activity on processes that can influence food quality is presented in Fig. 0.4. Decreased water activity retards the growth of microorganisms, slows enzyme catalyzed reactions (particularly involving hydrolases; cf. 2.2.2.1) and, lastly,

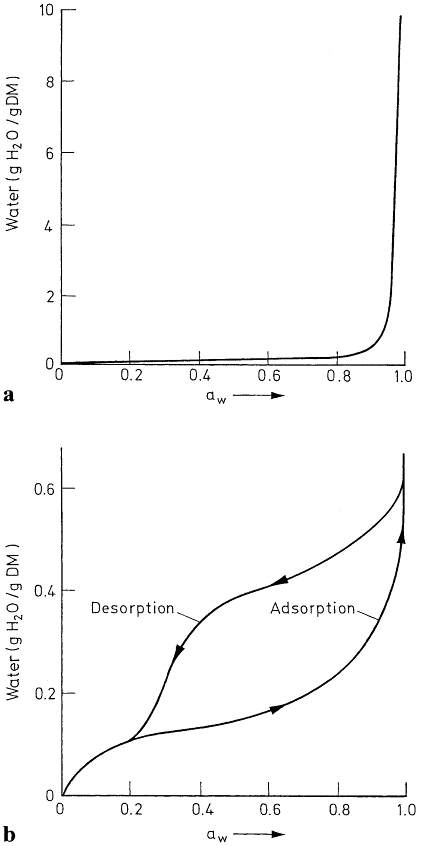


Fig. 0.3. Moisture sorption isotherm (according to *Labuza et al.*, 1970). **a** Food with high moisture content; **b** Food with low moisture content (DM: Dry matter)

Table 0.4. Water activity of some food

Food	a_w	Food	a_w
Leberwurst	0.96	Marmalades	0.82–0.94
Salami	0.82–0.85	Honey	0.75
Dried fruits	0.72–0.80		

retards non-enzymatic browning. In contrast, the rate of lipid autoxidation increases in dried food systems (cf. 3.7.2.1.4).

Foods with a_w values between 0.6 and 0.9 (examples in Table 0.4) are known as “intermediate moisture foods” (IMF). These foods are largely protected against microbial spoilage.

One of the options for decreasing water activity and thus improving the shelf life of food is to use additives with high water binding capacities (humectants). Table 0.5 shows that in addition to common salt, glycerol, sorbitol and sucrose

Table 0.5. Moisture content of some food or food ingredients at a water activity of 0.8

	Moisture content (%)		Moisture content (%)
Peas	16	Glycerol	108
Casein	19	Sorbitol	67
Starch (potato)	20	Saccharose	56
		Sodium chloride	332

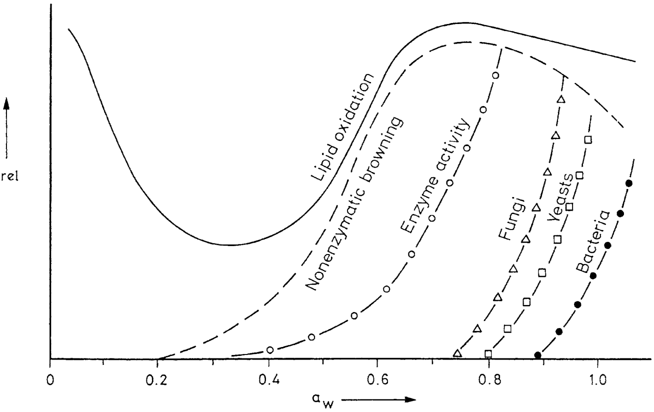


Fig. 0.4. Food shelf life (storage stability) as a function of water activity (according to *Labuza*, 1971)

have potential as humectants. However, they are also sweeteners and would be objectionable from a consumer standpoint in many foods in the concentrations required to regulate water activity.

0.3.2 Water Activity as an Indicator

Water activity is only of limited use as an indicator for the storage life of foods with a low water content, since water activity indicates a state that applies only to ideal, i.e. very dilute solutions that are at a thermodynamic equilibrium. However, foods with a low water content are non-ideal systems whose metastable (fresh) state should be preserved for as long as possible. During storage, such foods do not change thermodynamically, but according to kinetic principles. A new concept based on phase transition, which takes into account the change in physical properties of foods during contact between water and hydrophilic ingredients, is better suited to the prediction of storage life. This will be briefly discussed in the following sections (0.3.3–0.3.5).

0.3.3 Phase Transition of Foods Containing Water

The physical state of metastable foods depends on their composition, on temperature and on storage time. For example, depending on the temperature, the phases could be glassy, rubbery or highly viscous. The kinetics of phase transitions can be measured by means of differential scanning calorimetry (DSC), producing a thermogram that shows temperature T_g as the characteristic value for the transition from glassy to rubbery (plastic). Foods become plastic when their hydrophilic components are hydrated. Thus the water content affects the temperature T_g, for example in the case of gelatinized starch (Fig. 0.5).

Table 0.6 shows the T_g of some mono- and oligosaccharides and the difference between melting points T_m.

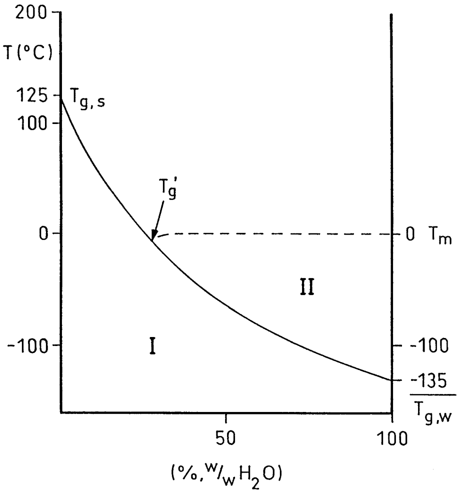


Fig. 0.5. State diagram, showing the approximate T_g temperatures as a function of mass fraction, for a gelatinized starch-water system (according to *Van den Berg*, 1986).
States: I = glassy; II = rubbery;
$T_{g,s}$ and $T_{g,w}$ = phase transition temperatures of dehydrated starch and water; T_m = melting point (ice)

Table 0.6. Phase transition temperature T_g and melting point T_m of mono- and oligosaccharides

Compound	T_g [°C]	T_m
Glycerol	−93	18
Xylose	9.5	153
Ribose	−10	87
Xylitol	− 18.5	94
Glucose	31	158
Fructose	100	124
Galactose	110	170
Mannose	30	139.5
Sorbitol	−2	111
Sucrose	52	192
Maltose	43	129
Maltotriose	76	133.5

During the cooling of an aqueous solution below the freezing point, part of the water crystallizes, causing the dissolved substance to become enriched in the remaining fluid phase (unfrozen water). In the thermogram, temperature T_g' appears, at which the glassy phase of the concentrated solution turns into a rubber-like state. The position of T_g' (−5 °C) on the T_g curve is shown by the example of gelatinized starch (Fig. 0.5); the quantity of unfrozen water W_g' at this temperature is 27% by weight. Table 0.7 lists the temperatures T_g' for aqueous solutions (20% by weight) of carbohydrates and proteins. In the case of oligosaccharides composed of three glucose molecules,

Table 0.7. T'_g and W'_g of aqueous solutions (20% by weight) of carbohydrates and proteins[a]

Substance	T'_g	W'_g
Glycerol	−65	0.85
Xylose	−48	0.45
Ribose	−47	0.49
Ribitol	−47	0.82
Glucose	−43	0.41
Fructose	−42	0.96
Galactose	−41.5	0.77
Sorbitol	−43.5	0.23
Sucrose	−32	0.56
Lactose	−28	0.69
Trehalose	−29.5	0.20
Raffinose	−26.5	0.70
Maltotriose	−23.5	0.45
Panose	−28	0.59
Isomaltotriose	−30.5	0.50
Potato starch (DE 10)	−8	
Potato starch (DE 2)	−5	
Hydroxyethylcellulose	−6.5	
Tapioca (DE 5)	−6	
Waxy corn (DE 0.5)	−4	
Gelatin	−13.5	0.46
Collagen, soluble	−15	0.71
Bovine serum albumin	−13	0.44
α-Casein	−12.5	0.61
Sodium caseinate	−10	0.64
Gluten	−5 to −10	0.07 to 0.41

[a] Phase transition temperature T'_g (°C) and water content W'_g (g per g of substance) of maximum freeze-concentrated glassy structure.

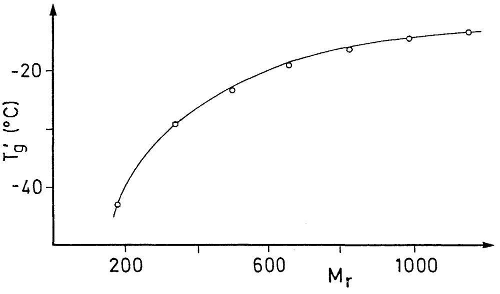


Fig. 0.6. Phase transition temperatures T'_g (aqueous solution, 20% by weight) of the homologous series glucose to maltoheptaose as a function of molecular weight M_r

maltotriose has the lowest T'_g value in comparison with panose and isomaltotriose. The reason is probably that in aqueous solution, the effective chain length of linear oligosaccharides is greater than that of branched compounds of the same molecular weight.

In the case of homologous series of oligo- and polysaccharides, T_g and T'_g increase with the molecular weight up to a certain limit (Fig. 0.6). Table 0.8 lists the phase transition temperatures T'_g of some fruits and vegetables.

Table 0.8. Phase transition temperature T'_g of some fruits and vegetables

Fruit/vegetable	T'_g(°C)
Strawberries	−33 to −41
Peaches	−36.5
Bananas	−35
Apples	−42
Tomatoes	−41.5
Peas (blanched, frozen)	−25
Carrots	−25.5
Broccoli, stalks	−26.5
Broccoli, flower buds	−11.5
Spinach (blanched, frozen)	−17
Potatoes	−11

0.3.4 WLF Equation

The viscosity of a food is extremely high at temperature T_g or T'_g (about 10^{13} Pa.s). As the temperature rises, the viscosity decreases, which means that processes leading to a drop in quality will accelerate. In the temperature range of T_g to about ($T_g + 100\,°C$), the change in viscosity does not follow the equation of *Arrhenius* (cf. 2.5.4.2), but a relationship formulated by *Williams, Landel* and *Ferry* (the WLF equation):

$$\log \frac{\eta}{\rho T} \Big/ \frac{\eta_g}{\rho_t T_g} = -\frac{C_1(T-T_g)}{C_2+(T-T_g)} \qquad (0.4)$$

Viscosity (η) and density (ρ) at temperature T; viscosity (η_g) and density (ρ_g) at phase transition temperature T_g; C_1 and C_2: constants.

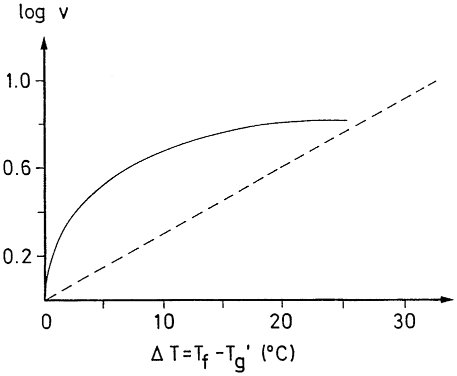


Fig. 0.7. Crystallization of water in ice cream (according to *Levine* and *Slade*, 1990).
v: crystallization velocity;
T_f: temperature in the freezer compartment;
T'_g: phase transition temperature.
The *Arrhenius* kinetics (– – –) is shown for comparison

According to the WLF equation, the rate of which in our example water crystallizes in ice cream at temperatures slightly above T'_g rises exponentially (Fig. 0.7). If the *Arrhenius* equation were to be valid, crystallization would accelerate linearly at a considerably slower rate after exceeding T'_g (Fig. 0.7).

0.3.5 Conclusion

In summary, we find that the rate of a food's chemical and enzymatic reactions as well as that of its physical processes becomes almost zero when the food is stored at the phase transition temperature of T_g or T'_g. Measures to improve storage life by increasing T_g or T'_g can include the extraction of water through drying and/or an immobilization of water by means of freezing, or by adding polysaccharides. Table 0.9 shows examples of how the drop in quality of certain foods can be considerably delayed when T_g or T'_g are increased by the addition of polysaccharides and approximated to the storage temperature.

Table 0.9. Unwanted chemical, enzymatic and physical processes in the production and storage of foods, depending on phase transition temperature T_g or T'_g and delayed by the addition of starch partial hydrolysates (lower DE value)

Process
1. Agglomeration and lumping of foods in the amorphous state
2. Recrystallization
3. Enzymatic reaction
4. Collapse of structure in case of freeze-dried products
5. Non-enzymatic browning

0.4 References

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