7 Water in milk and dairy products

7.1 Introduction

The water content of dairy products ranges from around 2.5 to 94% (w/w) (Table 7.1) and is the principal component by weight in most dairy products, including milk, cream, ice-cream, yogurt and most cheeses. The moisture content of foods (or more correctly their water activity, section 7.3), together with temperature and pH, are of great importance to food technology. As described in section 7.8, water plays an extremely important role even in relatively low-moisture products such as butter (*c.* 16% moisture) or dehydrated milk powders (*c.* 2.5–4% moisture). Water is the most important diluent in foodstuffs and has an important influence on the physical, chemical and microbiological changes which occur in dairy products. Water is an important plasticizer of non-fat milk solids.

7.2 General properties of water

Some physical properties of water are shown in Table 7.2. Water has higher melting and boiling temperatures, surface tension, dielectric constant, heat capacity, thermal conductivity and heats of phase transition than similar molecules (Table 7.3). Water has a lower density than would be expected from comparison with the above molecules and has the unusual property of expansion on solidification. The thermal conductivity of ice is approximately four times greater than that of water at the same temperature and is high compared with other non-metallic solids. Likewise, the thermal diffusivity of ice is about nine times greater than that of water.

The water molecule (HOH) is formed by covalent (σ) bonds between two of the four sp^3 bonding orbitals of oxygen (formed by the hybridization of the 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals) and two hydrogen atoms (Figure 7.1a). The remaining two sp^3 orbitals of oxygen contain non-bonding electrons. The overall arrangement of the orbitals around the central oxygen atom is tetrahedral and this shape is almost perfectly retained in the water molecule. Due to electronegativity differences between oxygen and hydrogen, the O-H bond in water is polar (a vapour state dipole moment of 1.84 D). This results in a partial negative charge on the oxygen and a partial positive charge on each hydrogen (Figure 7.1b). Hydrogen bonding can occur between the two lone electron pairs in the oxygen atom and the hydrogen atoms of other

Table 7.1 Approximate water content of some dairy products (modified from Holland *et al.*, 1991)

Product	Water (g/100 g)
Skimmed milk, average	91
pasteurized	91
fortified plus SMP	89
UHT, fortified	91
Whole milk, average	88
pasteurized[a]	88
summer	88
winter	88
sterilized	88
Channel Island milk, whole, pasteurized	86
summer	86
winter	86
semi-skimmed, UHT	89
Dried skimmed milk	3.0
with vegetable fat	2.0
Evaporated milk, whole	69
Flavoured milk	85
Goats' milk, pasteurized	89
Human milk, colostrum	88
mature	87
Sheep's milk, raw	83
Fresh cream, whipping	55
Cheeses	
Brie	49
Camembert	51
Cheddar, average	36
vegetarian	34
Cheddar-type, reduced fat	47
Cheese spread, plain	53
Cottage cheese, plain	79
with additions	77
reduced fat	80
Cream cheese	46
Danish blue	45
Edam	44
Feta	57
Fromage frais, fruit	72
plain	78
very low fat	84
Full-fat soft cheese	58
Gouda	40
Hard cheese, average	37
Lymeswold	41
Medium-fat soft cheese	70
Parmesan	18
Processed cheese, plain	46
Stilton, blue	39
White cheese, average	41
Whey	94
Drinking yogurt	84
Low-fat plain yogurt	85
Whole-milk yogurt, plain	82
fruit	73
Ice-cream, dairy, vanilla	62
non-dairy, vanilla	65

[a] The value for pasteurized milk is similar to that for unpasteurized milk.

Table 7.2 Physical constants of water and ice (from Fennema, 1985)

Molecular weight	18.01534
Phase transition properties	
Melting point at 101.3 kPa (1 atm)	0.000°C
Boiling point at 101.3 kPa (1 atm)	100.00°C
Critical temperature	374.15°C
Critical pressure	22.14 MPa (218.6 atm)
Triple point	0.0099°C and 610.4 kPa (4.579 mmHg)
Heat of fusion at 0°C	6.012 kJ (1.436 kcal) $\mathrm{mol^{-1}}$
Heat of vaporization at 100°C	40.63 kJ (9.705 kcal) $\mathrm{mol^{-1}}$
Heat of sublimation at 0°C	50.91 kJ (12.16 kcal) $\mathrm{mol^{-1}}$

Other properties at	20°C	0°C	0°C (ice)	−20°C (ice)
Density ($\mathrm{kg\,l^{-1}}$)	0.9998203	0.999841	0.9168	0.9193
Viscosity (Pa s)	1.002×10^{-3}	1.787×10^{-3}	–	–
Surface tension against air ($\mathrm{N\,m^{-1}}$)	72.75×10^{-3}	75.6×10^{-3}	–	–
Vapor pressure (Pa)	2.337×10^{3}	6.104×10^{2}	6.104×10^{2}	1.034×10^{2}
Specific heat ($\mathrm{J\,kg^{-1}\,K^{-1}}$)	4.1819	4.2177	2.1009	1.9544
Thermal conductivity ($\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}$)	5.983×10^{2}	5.644×10^{2}	22.40×10^{2}	24.33×10^{2}
Thermal diffusivity ($\mathrm{m^2\,s^{-1}}$)	1.4×10^{-5}	1.3×10^{-5}	$\sim 1.1 \times 10^{-4}$	$\sim 1.1 \times 10^{-4}$
Dielectric constant,				
static[a]	80.36	80.00	91[b]	98[b]
at 3×10^9 Hz	76.7	80.5	–	3.2
	(25°C)	(1.5°C)	(−12°C)	–

[a]Limiting value at low frequencies.

[b]Parallel to *c*-axis of ice; values about 15% larger if perpendicular to *c*-axis.

Table 7.3 Properties of water and other compounds (from Roos, 1997)

Property	Ammonia (NH_3)	Hydrofluoric acid (HF)	Hydrogen sulphide (H_2S)	Methane (CH_4)	Water (H_2O)
Molecular weight	17.03	20.02	34.08	16.04	18.015
Melting point (°C)	−77.7	−83.1	−85.5	−182.6	0.00
Boiling point (°C)	−33.35	19.54	−60.7	−161.4	100.00
Critical T (°C)	132.5	188.0	100.4	−82.1	374.15
Critical P (bar)	114.0	64.8	90.1	46.4	221.5

molecules which, due to the above-mentioned differences in electronegativity, have some of the characteristics of bare protons. Thus, each water molecule can form four hydrogen bonds arranged in a tetrahedral fashion around the oxygen (Figure 7.1d). The structure of water has been described as a continuous three-dimensional network of hydrogen-bonded molecules, with a local preference for tetrahedral geometry but with a large number of strained or broken hydrogen bonds. This tetrahedral geometry is usually

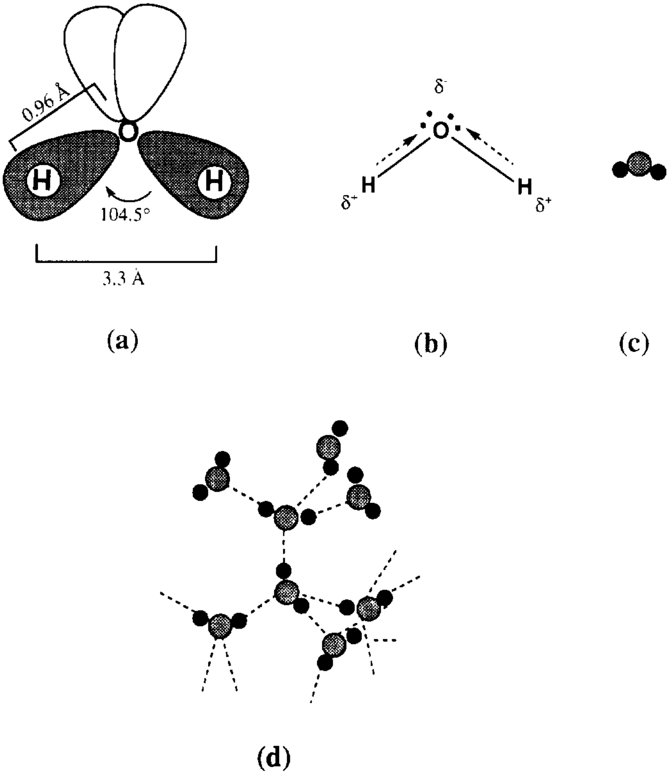

Figure 7.1 Schematic representations (a–c) of a water molecule and hydrogen bonding between water molecules (d).

maintained only over short distances. The structure is dynamic; molecules can rapidly exchange one hydrogen bonding partner for another and there may be some unbonded water molecules.

Water crystallizes to form ice. Each water molecule associates with four others in a tetrahedral fashion as is apparent from the unit cell of an ice crystal (Figure 7.2). The combination of a number of unit cells, when viewed from the top, results in a hexagonal symmetry (Figure 7.3). Because of the tetrahedral arrangement around each molecule, the three-dimensional structure of ice (Figure 7.4) consists of two parallel planes of molecules lying close to each other ('basal planes'). Basal planes of ice move as a unit under pressure. The extended structure of ice is formed by stacking of several basal planes. This is the only crystalline form of ice that is stable at a pressure of 1 atm at 0°C, although ice can exist in a number of other crystalline forms, as well as in an amorphous state. The above description of ice is somewhat simplified; in practice the system is not perfect due to the presence of ionized

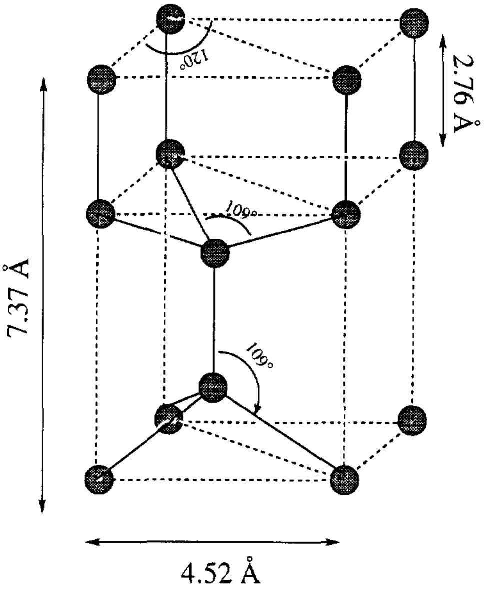

Figure 7.2 Unit cell of an ice crystal at 0°C. Circles represent the oxygen atoms of water molecules, — indicates hydrogen bonding. (Modified from Fennema, 1985.)

water (H_3O^+, OH^-), isotopic variants, solutes and vibrations within the water molecules.

With the exceptions of water vapour and ice, water in dairy products contains numerous solutes. Thus, the interactions of water with solutes is of great importance. Hydrophilic compounds interact strongly with water by ion–dipole or dipole–dipole interactions while hydrophobic substances interact poorly with water and prefer to interact with each other ('hydrophobic interaction').

Water in food products can be described as being free or bound. The definition of what consitiutes 'bound' water is far from clear (see Fennema, 1985) but it can be considered as that part of the water in a food which does not freeze at −40°C and exists in the vicinity of solutes and other non-aqueous constituents, has reduced molecular mobility and other significantly altered properties compared with the 'bulk water' of the same system (Fennema, 1985). The actual amount of bound water varies in different products and the amount measured is often a function of the assay technique. Bound water is not permanently immobilized since interchange of bound water molecules occurs frequently.

There are a number of types of bound water. Constitutional water is the most strongly bound and is an integral part of another molecule (e.g. within the structure of a globular protein). Constitutional water represents only a

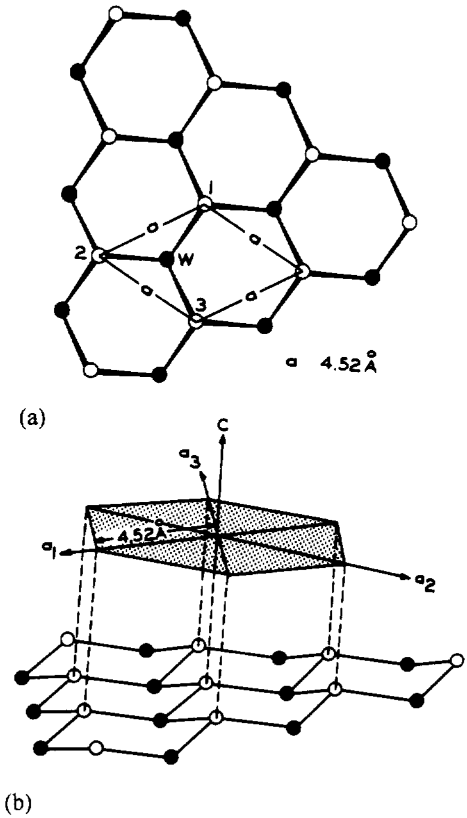

Figure 7.3 The 'basal plane' of ice (combinations of two planes of slightly different elevations) viewed from above. The closed circles represent oxygen atoms of water molecules in the lower plane and the open circles oxygen atoms in the upper plane, (a) seen from above and (b) from the side (from Fennema, 1985).

small fraction of the water in high-moisture foods. 'Vicinal' or monolayer water is bound to the first layer sites of the most hydrophilic groups. Multilayer water occupies the remaining hydrophilic sites and forms a number of layers beyond the monolayer water. There is often no clear distinction between constitutional, monolayer and multilayer water since they differ only in the length of time a water molecule remains associated with the food.

The addition of dissociable solutes to water disrupts its normal tetrahedral structure. Many simple inorganic solutes do not possess hydrogen bond donors or acceptors and therefore can interact with water only by dipole interactions (e.g. Figure 7.5 for NaCl). Multilayer water exists in a structurally disrupted state while bulk-phase water has properties similar to

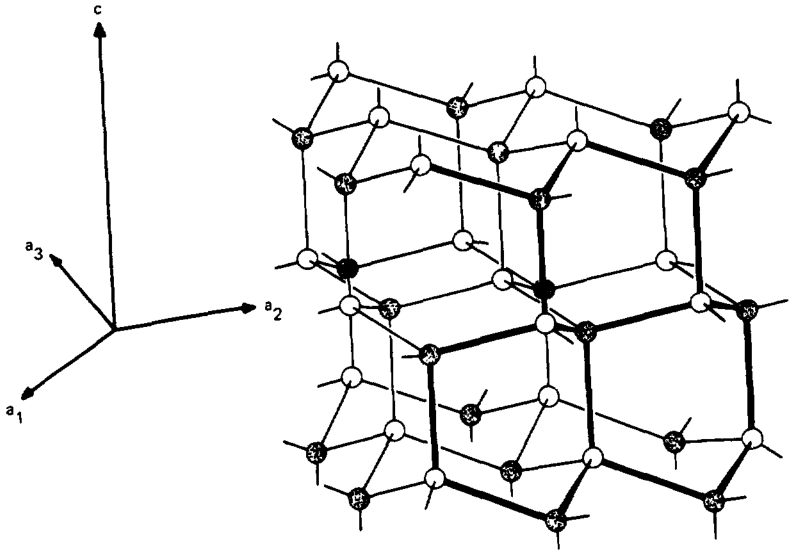

Figure 7.4 The extended structure of ice. Open and shaded circles represent oxygen atoms of water molecules in the upper and lower layers, respectively, of a basal plane (from Fennema, 1985).

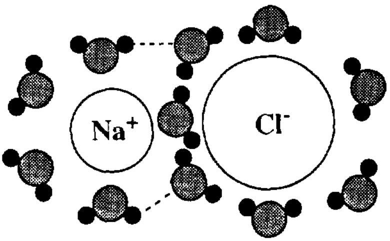

Figure 7.5 Arrangement of water molecules in the vicinity of sodium and chloride ions (modified from Fennema, 1985).

those of water in a dilute aqueous salt solution. Ions in solution impose structure on the water but disrupt its normal tetrahedral structure. Concentrated solutions probably do not contain much bulk-phase water and structures caused by the ions predominate. The ability of an ion to influence the structure of water is influenced by its electric field. Some ions (principally small and/or multivalent) have strong electric fields and loss of the inherent structure of the water is more than compensated for by the new structure resulting from the presence of the ions. However, large, monovalent ions have weak electric fields and thus have a net disruptive effect on the structure of water.

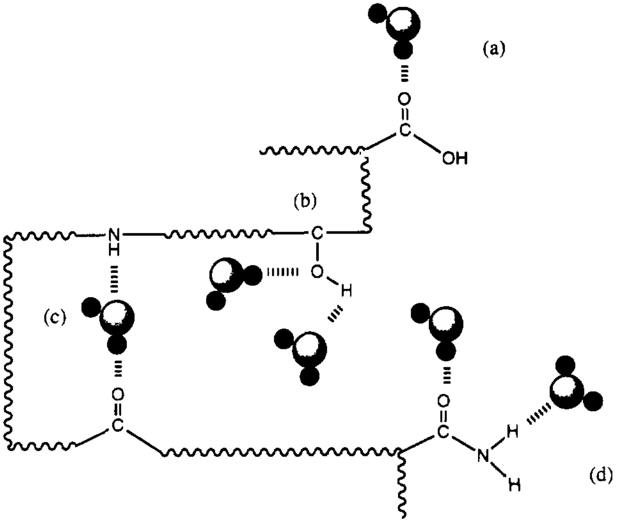

Figure 7.6 Schematic representation of the interaction of water molecules with carboxylic acid (a), alcohol (b), -NH and carbonyl groups (c) and amide groups (d).

In addition to hydrogen bonding with itself, water may also form such bonds with suitable donor or acceptor groups on other molecules. Water–solute hydrogen bonds are normally weaker than water–water interactions. By interacting through hydrogen bonds with polar groups of solutes, the mobility of water is reduced and, therefore, is classified as either constitutional or monolayer. Some solutes which are capable of hydrogen bonding with water do so in a manner that is incompatible with the normal structure of water and therefore have a disruptive effect on this structure. For this reason, solutes depress the freezing point of water (Chapter 11). Water can potentially hydrogen bond with lactose or a number of groups on proteins (e.g. hydroxyl, amino, carboxylic acid, amide or imino; Figure 7.6) in dairy products.

Milk contains a considerable amount of hydrophobic material, especially lipids and hydrophobic amino acid side chains. The interaction of water with such groups is thermodynamically unfavourable due to a decrease in entropy caused by increased water–water hydrogen bonding (and thus an increase in structure) adjacent to the non-polar groups.

7.3 Water activity

Water activity (a_w) is defined as the ratio between the water vapour pressure exerted by the water in a food system (p) and that of pure water (p_0) at the same temperature:

$$a_w = \frac{p}{p_0}. \tag{7.1}$$

Due to the presence of various solutes, the vapour pressure exerted by water in a food system is always less than that of pure water (unity). Water activity is a temperature-dependent property of water which may be used to characterize the equilibrium or steady state of water in a food system (Roos, 1997).

For a food system in equilibrium with a gaseous atmosphere (i.e. no net gain or loss of moisture to or from the system caused by differences in the vapour pressure of water), the equilibrium relative humidity (ERH) is related to a_w by:

$$\text{ERH}(\%) = a_w \times 100. \tag{7.2}$$

Thus, under ideal conditions, ERH is the % relative humidity of an atmosphere in which a foodstuff may be stored without a net loss or gain of moisture. Water activity, together with temperature and pH, is one of the most important parameters which determine the rates of chemical, biochemical and microbiological changes which occur in foods. However, since a_w presupposes equilibrium conditions, its usefulness is limited to foods in which these conditions exist.

Water activity is influenced by temperature and therefore the assay temperature must be specified. The temperature dependence of a_w is described by the Clausius–Clapeyron equation in modified form:

$$\frac{\mathrm{d}\ln(a_w)}{\mathrm{d}(1/T)} = \frac{-\Delta H}{R} \tag{7.3}$$

where T is temperature (K), R is the universal gas constant and ΔH is the change in enthalpy. Thus, at a constant water content, there is a linear relationship between $\log a_w$ and $1/T$ (Figure 7.7). This linear relationship is not obeyed at extremes of temperature or at the onset of ice formation.

The concept of a_w can be extended to cover sub-freezing temperatures. In these cases, a_w is defined (Fennema, 1985) relative to the vapour pressure of supercooled water ($p_{o(SCW)}$) rather than to that of ice:

$$a_w = \frac{p_{ff}}{p_{o(SCW)}} = \frac{p_{ice}}{p_{o(SCW)}} \tag{7.4}$$

where p_{ff} is the vapour pressure of water in the partially frozen food and p_{ice} that of pure ice. There is a linear relationship between $\log a_w$ and $1/T$ at sub-freezing temperatures (Figure 7.8). The influence of temperature on a_w is greater below the freezing point of the sample and there is normally a pronounced break at the freezing point. Unlike the situation above freezing

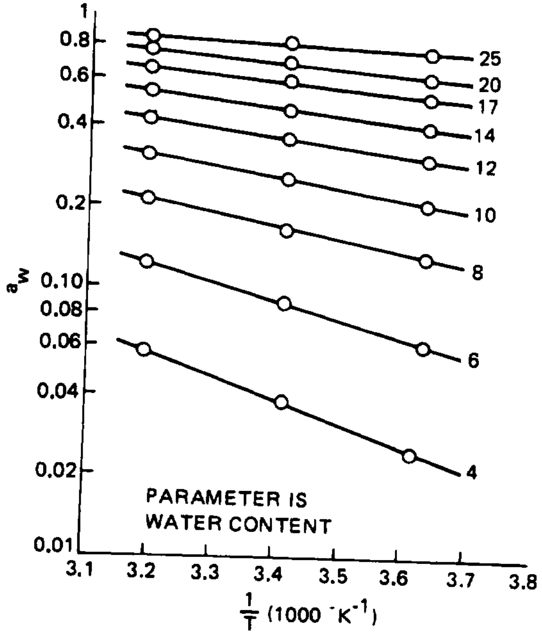

Figure 7.7 Clausius-Clapeyron relationship between water activity and temperature for native potato starch. Numbers on curves indicate water content, in g per g dry starch (from Fennema, 1985).

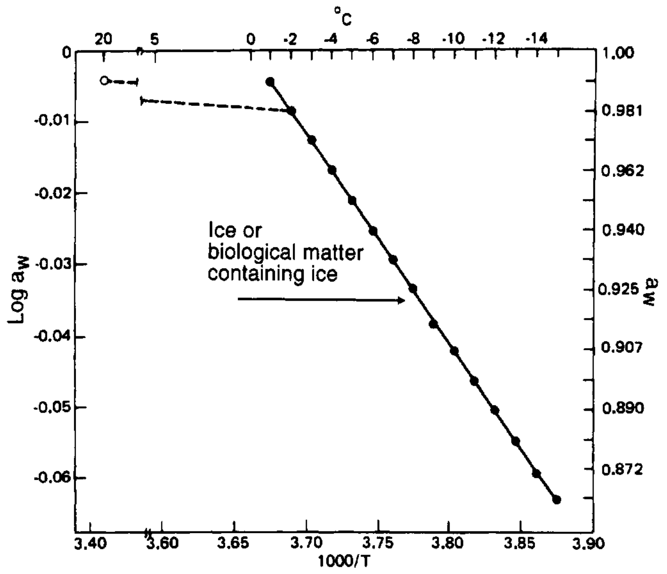

Figure 7.8 Relationship between water activity and temperature for samples above and below freezing (from Fennema, 1985).

(where a_w is a function of composition and temperature), a_w below freezing is independent of sample composition and is influenced only by temperature. Thus, a_w values of foods at sub-freezing temperatures cannot be used to predict the a_w of foods above freezing. Sub-freezing a_w values are far less useful indicators of potential changes in foods than a_w values determined above the freezing point.

Water activity may be measured by a number of techniques (Marcos, 1993). Comparison of manometric readings taken simultaneously on a food system and on pure water is the most direct technique. a_w can also be measured in dilute solutions and liquid foods with low solute concentrations by cryoscopy, since under certain conditions a_w can be considered as a colligative property. In these cases, the Clausius–Clapeyron equation is valid:

$$a_w = \gamma[n_2/(n_1 + n_2)] \tag{7.5}$$

where n_1 and n_2 are the number of moles of solute and water, respectively, and γ is the activity coefficient (approximately one for dilute solutions); n_2 can be determined by measuring the freezing point from the relation:

$$n_2 = \frac{G\Delta T_f}{1000K_f} \tag{7.6}$$

where G is the grams of solvent in the sample, ΔT_f is the freezing point depression (°C) and K_f is the molal freezing point depression constant for water, i.e. 1.86.

Water activity may also be measured by determining the ERH for a food sample, using equation 7.2.

ERH may be estimated by measuring the relative humidity of the headspace over a food in a small, sealed container hygrometrically, psychrometrically or directly by measuring the moisture content of the air by gas chromatography. ERH can be estimated by moisture-related colour changes in paper impregnated with cobalt thiocyanate ($Co(SCN)_2$) and compared to standards of known a_w.

Differences in the hygroscopicity of various salts may also be used to estimate a_w. Samples of the food are exposed to a range of crystals of known a_w; if the a_w of the sample is greater than that of a given crystal, the crystal will absorb water from the food.

Alternatively, a_w may be measured by isopiestic equilibration. In this method, a dehydrated sorbent (e.g. microcrystalline cellulose) with a known moisture sorption isotherm (section 7.4) is exposed to the atmosphere in contact with the sample in an enclosed vessel. After the sample and sorbent have reached equilibrium, the moisture content of the sorbent can be measured gravimetrically and related to the a_w of the sample.

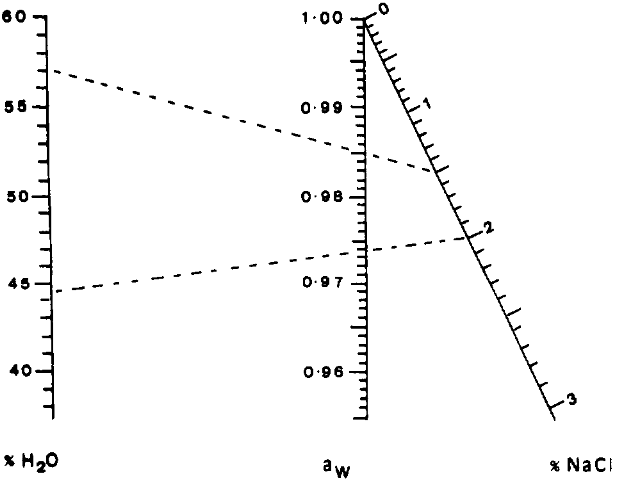

Figure 7.9 Nomograph for direct estimation of water activity (a_w) of unripe cheeses from % H_2O and % NaCl. Examples: If % H_2O = 57.0, and % NaCl = 1.5, then a_w = 0.985; if % H_2O = 44, % NaCl = 2.0, then a_w = 0.974 (from Marcos, 1993).

The a_w of a sample can also be estimated by exposing it to atmospheres with a range of known and constant relative humidities (RH). Moisture gains or losses to or from the sample may then be determined gravimetrically after equilibration. If the weight of the sample remains constant, the RH of the environment is equal to the ERH of the sample. The a_w of the food may be estimated by interpolation of data for RH values greater and less than the ERH of the sample.

For certain foodstuffs, a_w may be estimated from chemical compostion. A nomograph relating the a_w of freshly made cheese to its content of moisture and NaCl is shown in Figure 7.9. Likewise, various equations relating the a_w of cheese to [NaCl], [ash], [12% trichloroacetic acid-soluble N] and pH have been developed (see Marcos, 1993).

7.4 Water sorption

Sorption of water vapour to or from a food depends on the vapour pressure exerted by the water in the food. If this vapour pressure is lower than that of the atmosphere, **absorption** occurs until vapour pressure equilibrium is reached. Conversely, **desorption** of water vapour results if the vapour pressure exerted by water in the food is greater than that of the atmosphere. **Adsorption** is regarded as sorption of water at a physical interface between a solid and its environment. Absorption is regarded as a process in which adsorption occurs in the interior of the substance (Kinsella and Fox, 1986).

The water sorption characteristics of dairy products (like those of most other foodstuffs) are governed by their non-fat constituents (principally lactose and proteins). However, in many milk and whey products, the situation is complicated by structural transformations and/or solute crystallization.

The relationship between the water content of a food (g H_2O per g dry matter) and a_w at a constant temperature is known as a **sorption isotherm**. Sorption isotherms are prepared by exposing a set of previously dried samples to atmospheres of high RH; desorption isotherms can also be determined by a similar technique. Isotherms provide important information regarding the difficulty of removing water from a food during dehydration and on its stability, since both ease of dehydration and stability are related to a_w. A typical sorption isotherm is shown in Figure 7.10. Most sorption isotherms are sigmoidal in shape, although foods which contain large amounts of low molecular weight solutes and relatively little polymeric material generally exhibit J-shaped isotherms. The rate of water sorption is temperature dependent and for a given vapour pressure, the amount of water lost by desorption or gained by resorption may not be equal and therefore sorption hysteresis may occur (Figure 7.11).

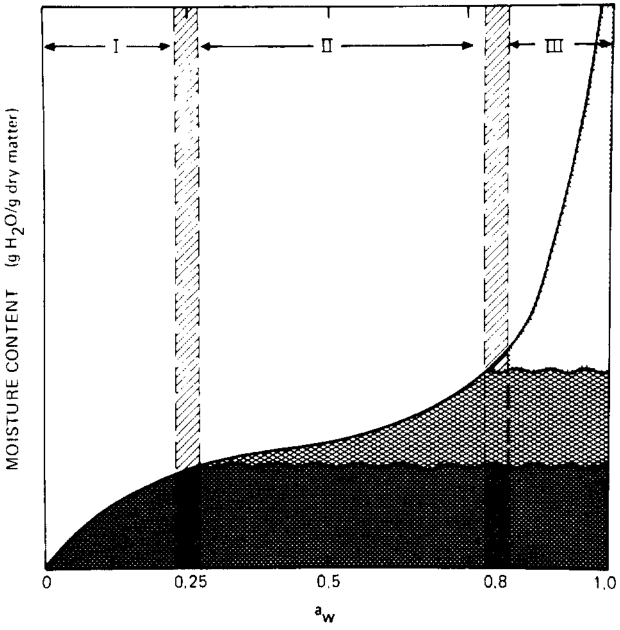

Figure 7.10 Generalized moisture sorption isotherm for a food (from Fennema, 1985).

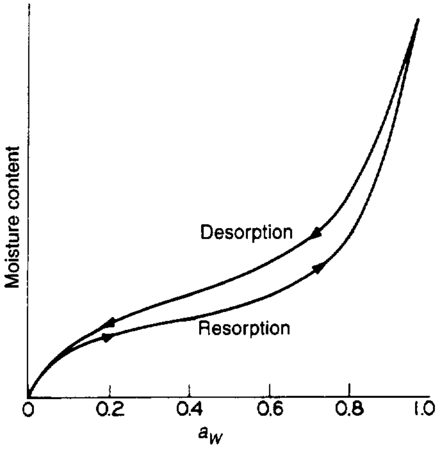

Figure 7.11 Hysteresis of a moisture sorption isotherm (from Fennema, 1985).

The moisture present in zone I (Figure 7.10) is the most tightly bound and represents the monolayer water bound to accessible, highly polar groups of the dry food. The boundary between zones I and II represents the monolayer moisture content of the food. The moisture in zone II consists of multilayer water in addition to the monolayer water, while the extra water added in zone III consists of the bulk-phase water.

Water sorption isotherms may be determined experimentally by gravimetric determination of the moisture content of a food product after it has reached equilibrium in sealed, evacuated desiccators containing saturated solutions of different salts. Data obtained in this manner may be compared with a number of theoretical models (including the Braunauer–Emmett–Teller model, the Kühn model and the Gruggenheim–Andersson–De Boer model; see Roos, 1997) to predict the sorption behaviour of foods. Examples of sorption isotherms predicted for skim milk by three such models are shown in Figure 7.12.

The sorption behaviour of a number of dairy products is known (Kinsella and Fox, 1986). Generally, whey powders exhibit sigmoidal sorption isotherms, although the characteristics of the isotherm are influenced by the composition and history of the sample. Examples of sorption isotherms for whey protein concentrate (WPC), dialysed WPC and its dialysate (principally lactose) are shown in Figure 7.13. At low a_w values, sorption is due mainly to the proteins present. A sharp decrease is observed in the sorption isotherm of lactose at a_w values between 0.35 and 0.50 (e.g. Figure 7.13). This sudden decrease in water sorption can be explained by the crystallization of amorphous lactose in the α-form, which contains one mole of water of crystallization per mole. Above a_w values of about 0.6, water sorption is principally influenced by small molecular weight components (Figure 7.13).

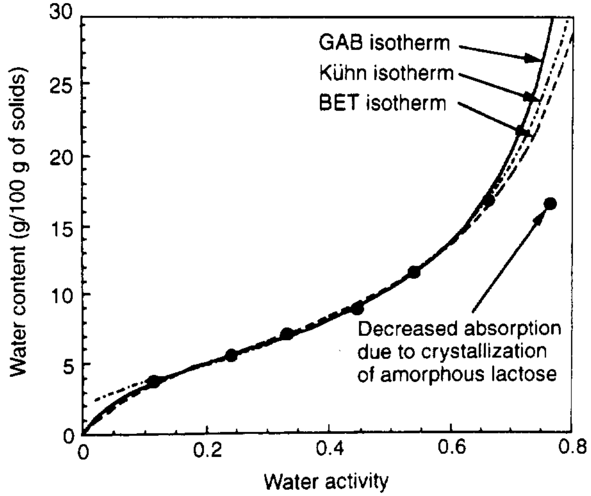

Figure 7.12 Adsorption of water by skim milk and sorption isotherms predicted by the Braunauer-Emmett-Teller (BET), Kühn and Guggenheim-Andersson-De Boer (GAB) sorption models (from Roos, 1997).

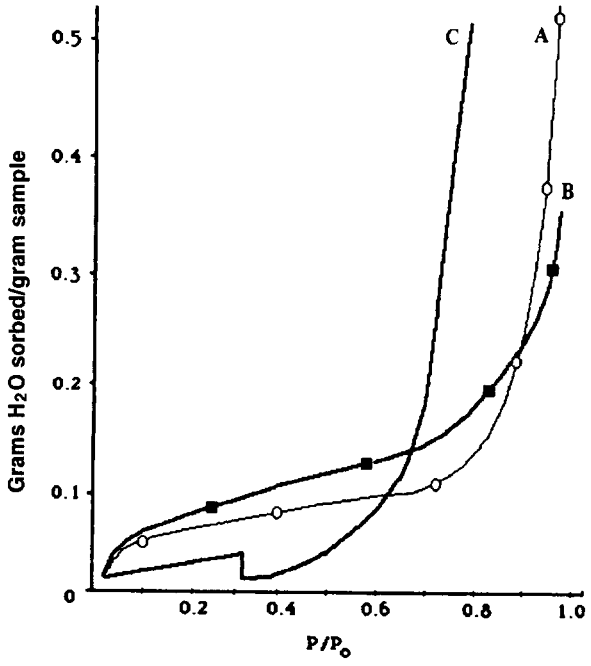

Figure 7.13 Water vapour sorption by whey protein concentrate (A), dialysed whey protein concentrate (B) and dialysate (lactose) from whey protein concentrate (C) (from Kinsella and Fox, 1986).

Despite some conflicting evidence (Kinsella and Fox, 1986), it appears that denaturation has little influence on the amount of water bound by whey proteins. However, other factors which may accompany denaturation (e.g. Maillard browning, association or aggregation of proteins) may alter protein sorption behaviour. Drying technique affects the water sorption characteristics of WPC. Freeze-dried and spray-dried WPC preparations bind more water at the monolayer level than do roller-, air- or vacuum-dried samples, apparently due to larger surface areas in the former. As discussed above, temperature also influences water sorption by whey protein preparations. The sorption isotherm for β-lactoglobulin is typical of many globular proteins.

In milk powders, the caseins are the principal water sorbants at low and intermediate values of a_w. The water sorption characteristics of the caseins are influenced by their micellar state, their tendency towards self-association, their degree of phosphorylation and their ability to swell. Sorption isotherms for casein micelles and sodium caseinate (Figure 7.14) are generally sigmoidal. However, isotherms of sodium caseinate show a marked increase at a_w between 0.75 and 0.95. This has been attributed to the

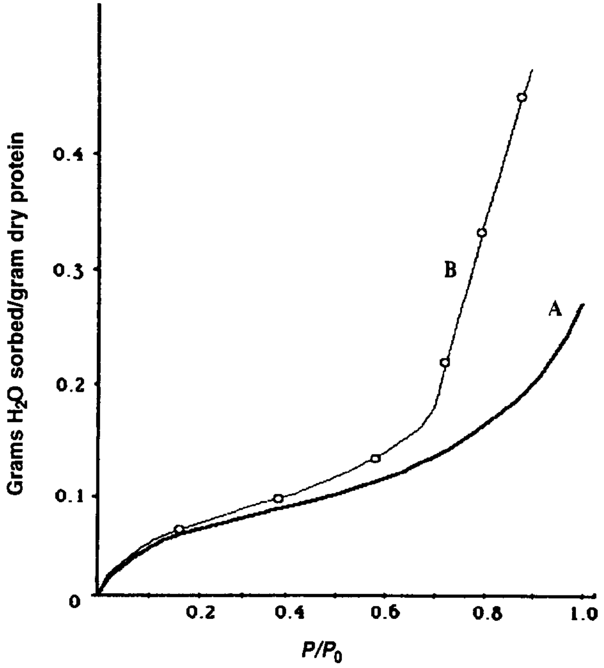

Figure 7.14 Sorption isotherm for casein micelles (A) and sodium caseinate (B) at 24°C, pH 7 (from Kinsella and Fox, 1986).

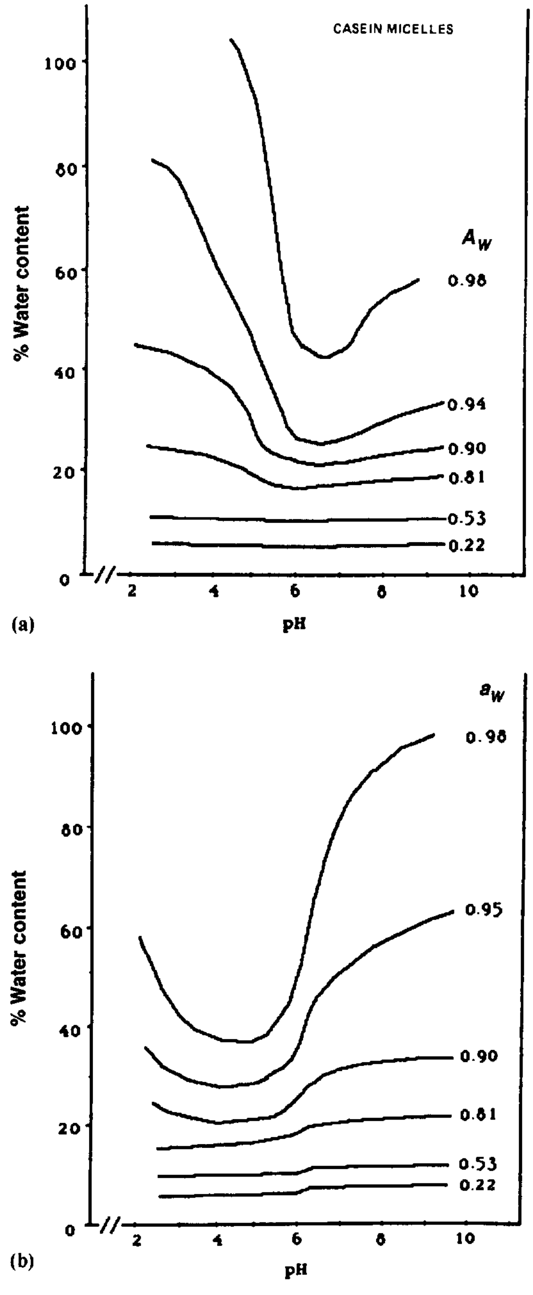

Figure 7.15 Equilibrium water content of (a) casein micelles and (b) sodium caseinate and casein hydrochloride as a function of pH and changing water activities (isopsychric curves) (from Kinsella and Fox, 1986).

presence of certain ionic groups, bound Na^+ or the increased ability of sodium caseinate to swell.

Heating of casein influences its water sorption characteristics, as does pH. With some exceptions at low pH, the hydration of sodium caseinate increases with pH (Figure 7.15b). Minimum water sorption occurs around the isoelectric pH (4.6). At low and intermediate values of a_w, increasing pH, and thus $[Na^+]$, has little influence on water sorption. At low a_w values, water is bound strongly to binding sites on the protein while at higher a_w both protein and NaCl sorb available water in multilayer form. Water sorption by casein micelles (Figure 7.15a) has a minimum at about pH 6–7 at high a_w. This difference in sorption minima between caseinate and casein micelles is because hydration of caseinate is due mainly to ion effects (Na^+ being more effective in this respect than Cl^-). Hydration behaviour of casein micelles, on the other hand, reflects effects of pH on micelle integrity. Hydrolysis of κ-casein by rennet appears to have only a small influence on its ability to bind water, although the chemical modification of amino groups has a greater effect. Genetic variation in the amino acid sequences of the caseins caused by genetic polymorphism also influences water sorption. The addition of NaCl to isoelectric casein greatly increases water sorption.

The greatest consequences of water sorption are in the context of dehydrated dairy products. In addition to being influenced by relative humidity, temperature and the relative amounts and intrinsic sorption properties of its constituents, the amount of water sorbed by milk powders is influenced by the method of preparation, the state of lactose, induced changes in protein conformation and swelling and dissolution of solutes such as salts. As discussed in Chapter 2, amorphous lactose is hygroscopic and may absorb large amounts of water at low relative humidities, while water sorption by crystalline lactose is significant only at higher relative humidities and thus water sorption by milk products containing crystallized lactose is due mainly to their protein fraction.

7.5 Glass transition and the role of water in plasticization

The non-fat solids in low-moisture dairy products (e.g. milk powders) or frozen milk products (since dehydration occurs on freezing) are amorphous in most dairy products (except those containing pre-crystallized lactose). The non-fat solids exist in a metastable, non-equilibrium state as a solid glass or a supercooled liquid. Phase changes can occur between these states with a phase transition temperature range called the glass transition (T_g; Roos, 1997). Changes in heat capacity, dielectric properties, volume, molecular mobility and various mechanical properties occur on glass transition. The temperature of onset of the glass transition of amorphous water (i.e. the transformation of a solid, amorphous glass into a supercooled liquid and

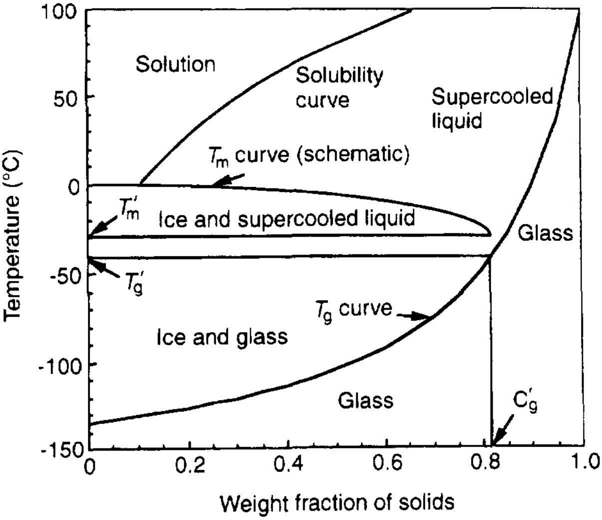

Figure 7.16 State diagram of lactose (from Roos, 1997).

vice versa) is about −135°C. T_g increases with increasing weight fraction of solids (Figure 7.16). The addition of water causes a sharp decrease in T_g.

The stability of dairy products decreases sharply above a critical water activity (section 7.8). This decrease in stability is related to the influence of water on the glass transition and the role of water as a plasticizer of amorphous milk constituents (Roos, 1997).

7.6 Non-equilibrium ice formation

Cooling solutions to below their freezing point results in the formation of ice. If solutions of sugars are cooled rapidly, non-equilibrium ice formation occurs. This is the most common form of ice in frozen dairy products (e.g. ice-cream). Rapid freezing of ice-cream mixes results in the freeze concentration of lactose and other sugars, resulting in supersaturated solutions if the temperature is too low to permit crystallization. The rapid cooling of lactose results in the formation of a supersaturated, freeze-concentrated amorphous matrix.

Various thermal transitions can occur in rapidly cooled solutions, including glass transition, devitrification (ice formation on warming a rapidly-frozen solution) and melting of ice. The relationship between temperature, weight fraction of solids, solubility and glass transition of lactose is shown in Figure 7.16.

7.7 Role of water in stickiness and caking of powders and crystallization of lactose

As discussed in section 2.2.7, drying of whey or other solutions containing a high concentration of lactose is difficult since the semi-dry powder may stick to the metal surfaces of the dryer. The influence of dryer temperature and other process parameters on stickiness during the drying of whey are discussed in Chapter 2. The role of agglomeration on the wetting and reconsitiution of dairy powders was also discussed in Chapter 2.

The principal cause of sticking and caking is the plasticization of amorphous powders by heating or by exposure to high relative humidities. As discussed by Roos (1997), heating or the addition of water reduces surface viscosity (thus permitting adhesion) by creating an incipient liquid state of lower viscosity at the surface of the particle. If sufficient liquid is present and flowing by capillary action, it may form bridges between particles strong enough to cause adhesion. Factors that affect liquid bridging include water sorption, melting of components (e.g. lipids), the production of H_2O by chemical reactions (e.g. Maillard browning), the release of water of crystallization and the direct addition of water.

The viscosity of lactose in the glassy state is extremely high and thus a long contact time is necessary to cause sticking. However, above T_g, viscosity decreases markedly and thus the contact time for sticking is reduced. Since T_g is related to sticking point, it may be used as an indicator of stability. Caking of powders at high RH results when the addition of water plasticizes the components of the powder and reduces T_g to below the ambient temperature.

The crystallization of amorphous lactose was discussed in Chapter 2.

7.8 Water and the stability of dairy products

The most important practical aspect of water in dairy products is its effect on their chemical, physical and microbiological stability. Chemical changes which are influenced by a_w include Maillard browning (including loss of lysine), lipid oxidation, loss of certain vitamins, pigment stability and the denaturation of proteins. Physical changes involve crystallization of lactose. Control of the growth of micro-organisms by reduction in a_w is of great significance for the stability of a number of dairy products. The relationship between the stability of foods and a_w is summarized in Figure 7.17.

Milk is the only naturally occurring protein-rich food which contains a large amount of a reducing sugar. Maillard browning is undesirable in the context of nearly all dairy foods. Since lactose is a reducing sugar, it can participate in these browning reactions and essentially all dairy products (with the exceptions of butter oil, butter and dairy spreads) have sufficient

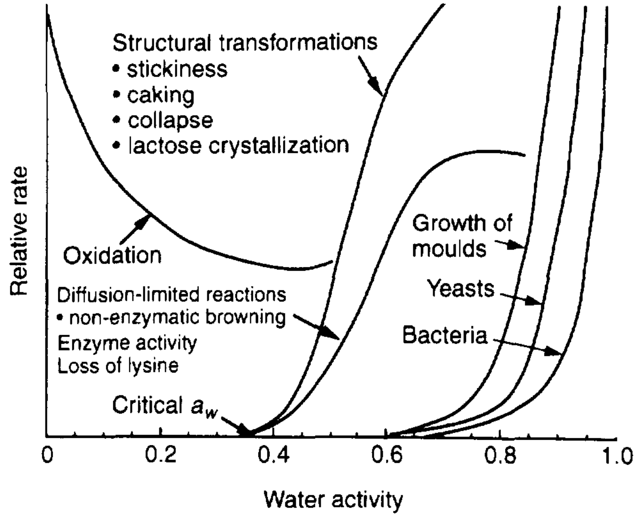

Figure 7.17 Stability map for non-fat milk solids showing schematic rates of various deteriorative changes and growth of micro-organisms as a function of water activity (from Roos, 1997).

protein to supply the necessary amino groups. Many of the stages of Maillard browning (Chapter 2) have high activation energies and thus the process is accelerated at high temperatures. The combination of the presence of lactose and high temperatures occurs during the production of many milk and whey powders, processed cheese and when dairy products are heated during cooking (e.g. the browning of Mozzarella cheese during baking of pizzas). The loss of lysine accompanies the early stages of the Maillard reaction in which its ε-amino group participates. Loss of lysine is significant from a nutritional standpoint since it is an essential amino acid. Loss of lysine may occur without visible browning.

For a given product composition and temperature, the rate of browning is affected by a_w. The influence of water on the rate of Maillard browning depends on the relative importance of a number of factors. Water imparts mobility to reacting species (thus increasing the rate of browning) but may also dilute reactants (thus reducing the rate of browning). At low values of a_w, the increase in molecular mobility is most significant, while at higher values of a_w, the dilution effect predominates. At lower a_w values, water can also dissolve new reacting species. The presence of water can retard certain steps in browning in which water is released as a product (product inhibition, e.g. the initial glycosylamine reaction) or enhance other reactions (e.g. deamination). For many foods, the rate of Maillard browning usually reaches a maximum at intermediate moisture levels ($a_w \approx$ 0.40–0.80). However, the maximum rate is greatly influenced by the presence of other constituents in the food, such as glycerol or other liquid humectants which can shift the maximum to lower a_w values. The rate of browning of milk powders is also accelerated by the crystallization of lactose.

Lipid oxidation can cause defects in high-fat dairy products. The mechanism of lipid oxidation is discussed in Chapter 3. At low a_w, the rate of oxidation decreases with increasing a_w and reaches a minimum around the monolayer value and then increases at higher a_w. The antioxidant effect of water at low values of a_w has been attributed to bonding of hydroperoxide intermediates and the hydration of metal ions, which act as catalysts. The increased rate of oxidation at higher a_w is a consequence of increased mobility of reactants. In general, water may influence the rate of lipid oxidation by affecting the concentration of initiating radicals, the degree of contact, the mobility of reacting species and the relative importance of radical transfer versus recombination events. Side reactions associated with lipid oxidation (e.g. cross-linking of proteins, enzyme inactivation by peroxidation products, degradation of amino acids) are also influenced by a_w.

The stability of some vitamins is influenced by a_w. In general, the stability of retinol (vitamin A), thiamin (vitamin B_1) and riboflavin (vitamin B_2) decreases with increasing a_w. At low a_w (below 0.40), metal ions do not have a catalytic effect on the destruction of ascorbic acid. The rate of loss of ascorbic acid increases exponentially as a_w increases. The photodegradation of riboflavin (Chapter 6) is also accelerated by increasing a_w.

Water activity influences the rate of thermal denaturation of proteins, including enzymes. Generally, the denaturation temperature increases with decreasing a_w. The rate of nearly all enzyme-catalyzed reactions increases with increasing a_w, as a consequence of increased molecular mobility.

The emulsification state of water in butter (i.e. the water droplet size) is very important for the quality of the product. Bacteria in butter can grow only in the aqueous emulsified phase. A finely divided aqueous phase restricts bacterial growth since the nutrients available in small droplets will quickly become limiting. Also, unless bacterial contamination is high, it is likely that most small water droplets in butter are sterile.

Together with pH and temperature, a_w has a major influence on the rate of growth of micro-organisms. Indeed, reduction of a_w by drying or the addition of salt or sugars is one of the principal traditional techniques used to preserve food. The minimum a_w required for microbial growth is about 0.62, which permits the growth of xerophilic yeasts. As a_w increases, moulds and other yeasts can grow and, finally, bacteria (above about 0.80). a_w also controls the growth of pathogenic micro-organisms; *Staphylococcus aureus* will not grow below $a_w \sim 0.86$ while the growth of *Listeria monocytogenes* does not occur below $a_w \sim 0.92$.

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