Water as the determinant of food engineering properties. A review

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Abstract

Water affects safety, stability, quality and physical properties of food. The influence of water on physical properties of food is dependent on the state of water in food. The state, expressed as water activity, is briefly discussed in the paper. Further, the influence of water on such physical properties as rheological, thermal, mass transfer, electrical, optical and acoustic is presented in details.

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1. State of water in food

Water is a constituent of food, which affects food safety, stability, quality and physical properties. Range of water concentrations in food is very broad and begins with a fraction of a per cent and reaches even more than 98%. Fresh products and liquid food contain usually large amounts of water while baked and dry products are poor in water. In many products the water is constitutive, but there are foods which contain water added during processing.

The state of water in a solution or a solid is expressed by the activity coefficient—a thermodynamic measure of chemical potential of water in the system. Scott (1953, 1957) proposed to express water activity as the ratio of vapour pressure of water in food \( (p) \) to the vapour pressure of pure water \( (p_0) \) at the same temperature and total pressure:

\[
a_w = \frac{p}{p_0}
\]

The above description of water activity assumes that food is in equilibrium with the surrounding atmosphere. Since, most of food processing is done under isobaric conditions, and at moderate temperatures the deviation of water vapour from the ideal gas is small, and water activity calculated from the above equation differs less than 0.5% from the thermodynamic value.

The state of water in food results from the structure of the water molecule and its interactions with remaining food constituents. Spatial configuration of the water molecule is well known. It was proposed by Bjerrum in 1951 (Siniukow, 1994) and is pictured as a regular tetrahedron (Fig. 1). Inside of the solid there is an atom of oxygen, and in corners there are partial charges distant 0.099 nm from the centre of the tetrahedron. The van der Waals diameter of the water molecule is 0.282 nm. According to this model hydrogen atoms are in corners with positive charge and two orbitals of paired electrons are directed to remaining corners.

Partial charges located in the tetrahedron corners lead to interactions between neighbouring molecules. A hydrogen bond is formed, which nature is not strictly electrostatic. Molar energy of hydrogen bond is estimated as 20–35 kJ, and the distance between oxygen atoms is from 0.26 to 0.30 nm (Franks, 1988). Hydrogen bond is linear (Fig. 2) but it can be stretched or bent. In solutions interactions between water and solute molecules also occur. Hence, properties of solution are determined by interactions water–water, water–solute and solute–solute.

Interactions between water and solute molecules are called hydration. In the presence of polar molecules these interactions are dominated by hydrogen bonding. In solutions of small molecules undergoing dissociation interactions between ion and solvent molecules are present. Around ion a hydration shell is formed which density increases with the increase of concentration. Hydration shells are susceptible to deformation (Franks,
1988). It was shown that ions Ca$^{2+}$, Na$^{+}$, Cl$^{-}$ are surrounded by 6 water molecules while ion Li$^+$ is hydrated by 4 water molecules (Franks, 1975). Ordering of water molecules in a hydration shell is dependent on the surface charge density of the ion. Ions with large surface charge density form well ordered hydration shells. These ions are called structure formers. Ions Li$^+$, Mg$^{2+}$, F$^-$, SO$_4^{2-}$, PO$_4^{3-}$ belong to that group. Ions with small surface charge density are not able to overcome interactions between water molecules. In consequence structure of solvent in the vicinity of the ion is distorted. Ions I$^-$, S$^+$, NO$_3^-$, ClO$_4^-$ are considered as structure breakers.

Strong interactions between water and ions orient spatially water molecules in hydration shell. That in turn results in spatial arrangement of neighbouring water molecules. In effect the ions are surrounded by few layers of oriented spatially water molecules. The spherical structure is not compatible with tetrahedral one, and water molecules are strongly distorted as far as their structure and dynamics are concerned.

Hydration of polar molecules cannot be estimated on the number of groups able to form hydrogen bonds. This is because interactions between water and polar molecule can alter spatial conformation of a solute and solvent as well. For example hexoses contain 5 –OH groups and should interact with 5 water molecules. Measurements show that hydration shell contains 3.7 water molecules. This is due to different hydration of optical isomers of hexose. Glucose as the α-isomer interacts with 3 water molecules and as β-pyranose has 4 active groups (Franks, 1988). Moreover, some –OH groups are favoured in comparison with others. In the pyranose ring equatorial groups are preferentially hydrated in comparison with axial groups.

In macromolecules such as proteins or polysaccharides intramolecular interactions deform electron cloud and surplus or deficit of electrons occurs. Hence, hydrogen bonds can be formed and water molecules are built in the structure of biopolymers. Dissociation of some groups leads to ionic interactions. Moreover, polar groups present in macromolecule can form hydrogen bonds and the polymer is surrounded by hydration shell. Two states of water can be considered (Fig. 3). One state, in which water molecules are immobilised in the structure of a macromolecule, is often called the structure water. Another state is the one in which water molecules movement is not completely restricted. Water molecule can reorient in respect to ionic or hydrogen bond. This water is called hydration water. It is, therefore, evident that interactions between water and macromolecules create and stabilise spatial conformation of biopolymers.

Number of water molecules in the hydration shell depends on the nature of macromolecule and its energy and ionisation state. For example phosphatidicholine is surrounded by 10 (Crowe, Clegg, & Crowe, 1998), urea by 7 (Nandel, Verma, Singh, & Jain, 1998) while full hydration of lyzosyme needs 360–400 water molecules. Water is an essential component of starch structure. In a lately proposed model 4 water molecules are present in the A structure unit and 36 water molecules in the B structure (Imberty, Buleon, Tran, & Perez, 1991; Imberty & Perez, 1988).

Apolar compounds and polar compounds containing apolar groups interact with water and reduce its degrees of freedom. It results in a certain stabilisation of water
molecules in space (Fig. 4) and the liquid acquires a structure similar to the structure of a solid. This phenomenon is called hydrophobic hydration, and can be considered as the trial to reject solute molecule by the solvent.

Hydrophobic and hydrophilic interactions lead to formation of structures in which properties of water differ from those of bulk water.

In numerous experiments it was shown that part of water is so strongly bound to food constituents that it is not able to form ice crystals during freezing. Unfreezable water in blood plasma is equal to 0.47 g/g, in collagen 0.26 g/g (Simatos, Faure, Bonjour, & Conach, 1975) in egg albumen 0.55 g/g, in maize starch 0.35 g/g and in cellulose 0.16 g/g (Steinberg & Leung, 1975). Moreover, it was shown that freezing of water in the presence of soy protein occurs at temperatures which span for 40 K (Johari & Sartor, 1998). This is due to interactions between water and proteins, which affect ice crystallisation.

Water is a very good solvent, but its solvent properties depend on the solute and interactions between molecules. In the mixture NaCl-casein absorbing water mobility of salt molecules is observed at w > 0.3 (Gal, 1975; Kinsella & Fox, 1986). Mixture of starch with glucose or sucrose when moistened shows mobility of sugar molecules at \( a_w = 0.8 \) (Duckworth, 1981). Enzymatic hydrolysis of starch with \( \beta \)-amylase is initiated at \( a_w = 0.65 \). Energy of mixing of moistened wheat flour increases at water contents larger than 28% (Daniels, 1975). This is due to interactions between water and protein molecules. At water contents higher than 28% protein chains become mobile, structure of dough is formed and mixing energy increases. Starch and gluten, two main components of wheat flour interact with water to a different degree. In starch, at 2% water content, nuclear magnetic resonans shows no presence of water protons. In gluten this effect occurs until 7.5% water content is reached (Chinachoti, 1998). Protein mobility begins at water content 0.1–0.2 g/g but it does not mean that at higher water contents properties of water are those of bulk water. In collagen water shows latent heat of fusion identical with that of bulk water at water content 0.6 g/g. Full hydration of lysozyme is estimated at 0.45–0.50 g/g but lowering its water content below 0.75 g/g increases temperature of denaturation (Gregory, 1998). These data show that water properties are different from those of bulk water not only in hydration shell but also in the vicinity of that shell.

Numerous literature data and examples presented above picture the state of water in food. At low water activities properties of water differ substantially from those of bulk water. Water molecules are strongly bound by hydrophilic centres, polar groups and charge bearing moieties. This water does not freeze, and its heat of evaporation exceeds that of bulk water. It is not available to chemical reactions and does not serve as a solvent. Moreover, it does not work as a smear, hence mobility of one structures against others is not possible.

Formation of subsequent hydration shells is dependent on surface and spatial conformability of substrates with water molecule structure. Biopolymers induce structuring of water by hydrogen and hydrophobic interactions. Moreover, swelling, rotational and translational mobility of chains, cross-linking and interactions polymer–polymer affects number of molecules hydrating biopolymers. Co-operative binding of water and presence of crystalline and amorphous domains also influence amount of water in hydration shells.

Interactions between biopolymers and water are modified by the presence of small molecules, especially those, which undergo dissociation. Interactions between biopolymers and salts expel water molecules and change spatial conformation of a newly formed structure. Competition for water molecules can lead to redistribution of water in the material. Parts with higher and lower water content can be formed. Effect of small molecules on hydration of polymers is evident. Some salts destabilise and others stabilise structure of biopolymers and affect the extent of hydration shells. The effect of small molecules on hydration of biopolymers is pronounced at water content at which water has solvent properties.

Above presented description of the state of water in food shows that interactions between water molecules and remaining components of the material must affect its properties biological, chemical and physical as well. Water can act as a solvent, it can structure macromolecules by internal bonding and hydrophilic and hydrophobic interactions, and it can act as a plasticizer making possible movement of one structure in respect to others.

2. Effect of water on rheological properties of food

Water influences rheological properties of food in liquid and solid state as well. In liquid state it is
pronounced by changes in viscosity and consistency, while in solid foods water affects their response to force.

Water is a Newtonian liquid and its viscosity is temperature dependent. Small molecules dissolved in water interact with water molecules, hydration shells are formed and some structuring of water surrounding hydrated solutes can occur. This loss of entropy leads to the increased viscosity. Small ions and multivalent ions increase water viscosity due to polarisation, structuring and electrostriction of surrounding water molecules. Ions of Li⁺, Na⁺, H₂O⁺, Ca²⁺, Ba²⁺, Mg²⁺, Al³⁺, OH⁻ and F⁻ show this effect on water viscosity. On the other hand large monovalent ions such as K⁺, NH₄⁺, Cl⁻, Br⁻, J⁻, NO₃⁻, ClO₄⁻ distort water structure and practically increase water flowability.

Increased temperature reduces number of hydrogen bonds and increases vibration of molecules. It results in decreased effect of small molecules and ions on water viscosity. On the other hand increased concentration of solute increases viscosity of solution. Over limited ranges of concentration the effect of solids concentration on viscosity of liquid food can be described by either exponential (Vitali & Rao, 1984), or a power type of relationship (Rao, 1986). The equation of the form:

\[ \mu = \mu_0 \cdot c^a \]

where \( \mu_0 \) is the viscosity of water, Pa·s; \( w \) is water content, %; \( c \) is the solubles concentration, %; \( a \) is constant.

Macromolecules soluble in water affect strongly rheological properties of solution. Solution becomes non-Newtonian and either time independent or time dependent. Macromolecules acquire structure, which in large part is due to interactions with water molecules. The size and shape of hydrated macromolecule influences its behaviour in sheared liquid.

Spherical particles are rotating under the influence of shearing forces. The angular velocity (\( \omega \)) in laminar flow is

\[ \omega = \frac{1}{2} \gamma \]

where \( \gamma \) is shear rate, s⁻¹.

For particles with shape different than sphere the equation is written as

\[ \omega = x \cdot \gamma \]

where \( x \) is dependent on the shape of the hydrated molecule.

Viscosity of a solution of spherical particles can be calculated from the Einstein equation

\[ \mu = \mu_0 (1 + 2.5 \phi) \]

where \( \phi \) is a fraction of volume occupied by spheres.

Translatory and rotational motion of stiff macromolecules results in energy dissipation. Energy lost due to friction is called intrinsic viscosity and is related to molecular weight of the polymer. According to Mark-Houwink equation the intrinsic viscosity is equal to

\[ \mu_{\text{int}} = K \cdot M^b \]

where \( K \) and \( b \) are constants characteristic for the given polymer–solvent system, and \( M \) is molecular mass of polymer.

Chain macromolecules influence solution viscosity even more than the stiff symmetric or asymmetric molecules. Translatory and rotational motion of these macromolecules is accompanied by changes in spatial conformation due to shearing forces. Experimental data shows that intrinsic viscosity of solution of chain macromolecules is proportional to effective hydrodynamic volume and inversely proportional to molecular mass of the polymer. The power \( b \) in the Mark-Houwink equation is in the range \( 0.5 < b < 1 \).

Biopolymers such as proteins, nucleic acids and polysaccharides have spatial conformation much different from the sphere or a chain. Moreover, biopolymers can change the spatial conformation under the influence of temperature or other substances. Nevertheless the Mark-Houwink equation can be used to calculate intrinsic viscosity.

In the Mark-Houwink equation the power value is relevant to solute–solvent interactions in diluted solutions.

Intrinsic viscosity can be calculated from the equation

\[ \mu_{\text{int}} = \beta (v_2 + h_1 v_1) \]

where \( v_1, v_2 \) are the specific volumes of the solvent and solute, \( h_1 \) is the weight of solvent associated with a unit weight of solute, \( \beta \) is the shape factor of the particle.

The volume fraction of the particles is obtained from the equation

\[ \phi = c (v_2 + h_1 v_1) \]

where \( c \) is concentration.

The weight of solvent associated with a unit weight of solute is sometimes called hydrodynamic hydration. It was estimated to be between 0.2 and 0.5 g water/g of different proteins. These values are about the same range as the range of unfreezable water.

The Mark-Houwink equation and intrinsic viscosity apply to diluted solutions in which interactions between polymer molecules can be disregarded. In solution polymer molecules can interact directly or can act one on the other through the solvent molecules. Relationship between viscosity and polymer concentration (\( c \)) was developed by Huggins (Rao, 1986) in the form:

\[ \mu_{\text{red}} = \frac{\mu - \mu_0}{\mu_0 \cdot c} = \mu_{\text{int}} + k_1 \mu_{\text{int}}^2 \cdot c + \cdots \]
where $\mu_{\text{red}}$ is the reduced viscosity, $k_1$ is the interaction coefficient. Generally it is assumed that $k_1$ is not dependent on molecular weight of the polymer. It is a measure of affinity of the polymer to the solvent. However, the interaction coefficient is sensitive to shear rate. The higher the shear rates the shorter the time of contact between interacting molecules. It results in smaller values of $k_1$.

Flow behaviour of the solution is affected by interactions between macromolecules. The larger the macromolecule the lower are the concentrations at which intermolecular interactions affect friction between molecules and solvent. Increase of shear rate affects extent of interactions and the influence of shear rate on shear stress is observed. This influence is the stronger the larger are the molecules. Moreover non-spherical molecules subjected to shearing forces become oriented according to the flow direction. This leads to the dependence of shear force on shear rate. Shear thinning of the liquid is observed and its consistency decreases with increasing shear rate.

Special types of macromolecules are polyelectrolytes. Their size and shape depend on the ionic strength of the solution. When a solution is diluted with water the increase of reduced viscosity is noticed. This is due to swelling of a polymer. At high ionic strength of the solution Debye–Hückel ionic layer reduces electrostatic repulsion of polymer chains and the increase of reduced viscosity is smaller than that observed in solutions with weak ionic strength. For polyelectrolytes, the variation of reduced viscosity with concentration follows the empirical equation (Elfak, Pass, & Phillips, 1978):

$$\frac{\mu - \mu_0}{\mu_0 c} = \frac{A}{1 + B \sqrt{c}} + D$$

where $A$, $B$ and $D$ are constants.

The state of water in solids can be graphically or analytically represented by the so-called sorption isotherms. The sorption isotherm shows relationship between water content and water activity in the material being in the state of equilibrium. At low water activities interactions between water and macromolecules are so strong that water is devoid of solvent properties (Duckworth, 1981). Under these conditions mobility of small molecules as well as macromolecules is very much reduced. Material is regarded as crisp or crunchy.

Increasing water content can lead to plasticizing or antiplasticizing effect. Water acquires properties of solvent and promotes mobility of polymer chains. This plasticization of polymer chains facilitates deformation. Material becomes soft, extensible and flowable and loses crispness, hardness or toughness (Karel, 1985). Numerous authors (Harris & Peleg, 1996; Katz & Labuzza, 1981; Lewicki & Wolf, 1995; Sauvageot & Blond, 1991; Wollny & Peleg, 1994) reported such an effect of water on texture of brittle food. In all these publications it is shown that there is a narrow range of water activities within which there is an abrupt change in mechanical properties of the material. Further increase in water activity leads to little changes in mechanical properties of the material. However, depending on the kind of food, properties of moist food can be appreciated or not accepted by consumers. Moistening of dried fruits or vegetables can lead to properties resembling fresh produce, while sogginess or chewiness of biscuits or snacks means end of acceptability.

In some cases moisture toughening is observed. Increased mobility of macromolecules can expose new centres for interaction with water molecules. This can add some strength to the material and reduce its brittleness. Georget, Parker, and Smith (1995), Nichols, Appelquist, and Davies (1995), Harris and Peleg (1996) and Seow, Chuan, and Chang (1999) reported such antiplasticizing effect of water on food mechanical properties. Our recent work showed that failure stress of flat wheat bread increased as moisture was absorbed (Fig. 5) and reached a peak at an $a_w$ range 0.5–0.6 (Marzec, 2002).

Solvent properties of water can also be manifested by structure collapse. Fast dehydration or freezing of solutions and dispersions can prevent crystallisation and a meta-stable system is formed. Amorphous state is very sensitive to temperature and water (Karel, 1985). In the amorphous state, due to a very high viscosity, material acquires properties of a solid. Increased temperature lowers viscosity and mobility of molecules becomes possible. The same effect is observed when material absorbs water. Phase transition goes through the rubbery state and shrinkage of the material is recorded. At specific water content viscosity of the matrix is too low

![Fig. 5. Influence of water activity on breaking force of flat bread. Breaking means that flat bread is disintegrated into pieces; flow means plastic deformation without disintegration. Points represent replicate experiments.](image-url)
to resist the flow caused by gravity and surface tension forces. For a given material the water content at which phase transition is initiated is strongly dependent on temperature. Further sorption of water leads to crystallisation and material attains stable state.

Collapse of structure and formation of rubbery and crystalline states affects strongly physical properties of the material. The most pronounced effects are stickiness and caking phenomena. Moreover, mechanical properties are much different in comparison to those of the material in the amorphous state.

As it was stated above the amorphous state is metastable. It means that the rate at which the phase transition proceeds is dependent on the increment of temperature or water content. At small increments the rate is low and structure collapse or crystallisation can last for days or even months. Hence, properties of the material become storage time dependent.

3. Influence of water on thermal properties of food

This part of the paper presents the influence of water on those thermal properties of food, which can be directly measured. These include specific heat and thermal conductivity.

Water has a high specific heat in comparison to other food components. Hence, even small amount of water in food affects its specific heat substantially. It is generally accepted that specific heat, as a physical property, obeys the rule of additivity. It means that specific heat of a product is equal to the sum of the fractional specific heats of the main constituents. The simplest models for low-fat foods have a form:

\[ c_p = a + b \cdot w \]

where \( a \) and \( b \) are constants specific for a product, \( w \) is water content in decimal. Such models were proposed by Lamb (1976), Siebel (1982) and reviewed by Sweat (1986) and Miles, van Beek, and Veerkamp (1983). Constants \( a \) and \( b \) are dependent also on the temperature range at which specific heat is calculated. In all these formula when \( w = 1 \) the specific heat is equal to the specific heat of pure water.

Another approach to specific heat calculation assumes that food is composed of two constituents that is water and dry matter. For fruits and vegetables it was proposed to calculate specific heat from the formula (Pijanowski, Mrozewski, Horubala, & Jarczyk, 1973)

\[ c_p = 4.187(1 - 0.0066s) \]

where \( s \) is dry matter content in %.

Using additivity principle specific heat can be calculated from the following equation:

\[ c_p = c_{pw}w + c_{pp}p + c_{pf}f + c_{pc}c \]

where \( c_p \) is specific heat at constant pressure, and \( w, p, f, c \) as well as subscripts \( w, p, f, c \) denote water, protein, fat and carbohydrate content, respectively. Different values are assigned to specific heats of proteins, fat and carbohydrates. Nevertheless all the specific heat models published until now show that water substantially influences specific heat of foods.

Analysis of this type of equations shows that most of them converge on the specific heat of water at \( w = 1 \), but the lower is the water content the more the difference between predictions (Miles et al., 1983).

Calculation of specific heat of frozen food must account for specific heat of ice and specific heat of unfrozen water. Hence, mass fraction of water in food is divided into this portion which crystallises to ice and that which does not undergoes phase change. The fraction of water, which does not freeze out, depends on temperature and interactions between water molecules and food components.

Foods containing large amount of fat have a specific heat which accounts not only for a fraction of fat but includes also term arising from the change of phase of fat.

Thermal conductivity of food depends on structure and chemical composition of the sample (Sweat, 1986). Thermal conductivity increases with increasing water content for all food products at temperatures above freezing. Most of models used to calculate thermal conductivity (\( \lambda \)) of foods with high water content has a form:

\[ \lambda = c_1 + c_2w \]

where \( c_1 \) and \( c_2 \) are constants and \( w \) is water fraction in food.

Similarly as with specific heat most of the equations converge on the thermal conductivity of water at \( w = 1 \). Predictions agree at high water contents, and at low water contents differences are most marked.

Additivity principles are used to calculate thermal conductivity of most of liquid foods and many solid foods. Water, protein, carbohydrate and fat are taken into account. In some calculations ash is also included. As an examples an equation developed by Choi and Okos (Sweat, 1986) can be given:

\[ \lambda = 0.61x_w + 0.20x_p + 0.205x_c + 0.175x_f + 0.135x_a \]

Sweat (1986) presents a modified best-fit equation based on 430 points in the form:

\[ \lambda = 0.58x_w + 0.155x_p + 0.25x_c + 0.16x_f + 0.135x_a \]

where \( x \) is a fraction of a food component and subscripts \( w, p, c, f \) and \( a \) denote water, protein, carbohydrate, fat and ash, respectively.

The above equations are good for non-porous foods. For porous foods they are not accurate and adding air as another component is not satisfactory.
The porosity or volume fraction of air is included in calculation. The parallel model gives
\[ \lambda = \varepsilon_w \lambda_w + \varepsilon_o \lambda_o + \varepsilon_f \lambda_f + \varepsilon_p \lambda_p + \varepsilon_c \lambda_c \]
and for perpendicular model
\[ I = \frac{\varepsilon_w}{\lambda_w} + \frac{\varepsilon_o}{\lambda_o} + \frac{\varepsilon_f}{\lambda_f} + \frac{\varepsilon_p}{\lambda_p} + \frac{\varepsilon_c}{\lambda_c} \]
where \( \varepsilon \) is a volume fraction of food component and subscripts w, p, c, f and o denote water, protein, carbohydrate, fat and air, respectively.

Since some foods have an internal structure or can be described as a dispersed system some structural models for thermal conductivity were developed. The models assume the food consists in two different components physically oriented so that heat travels either in parallel or in perpendicular through each of them.

Assuming that food is composed of dry material and wet material with infinite moisture and that both components are uniformly mixed the parallel model takes the form (Maroulis, Saravacos, Krokida, & Panagiotou, 2002):
\[ \lambda = \frac{1}{\frac{1}{\lambda_d} + \frac{x}{\lambda_w}} \lambda_x \]
and perpendicular model is
\[ \lambda = \left( \frac{1}{\frac{1}{\lambda_d} + \frac{x}{\lambda_w}} + \frac{1}{\lambda_x} \right)^{-1} \]
where \( \lambda_d \) is the thermal conductivity of the dry phase, \( \lambda_x \) is the thermal conductivity of the wet material, \( x \) is the water content, kg/kg d.m.

In dispersed system the volume fraction of dispersed component as well as thermal conductivity of dispersed and continuous component are taken into account (Miles et al., 1983).

In modelling thermal conductivity of frozen foods the presence of unfrozen water complicates calculations. The volume fractions of unfrozen water, ice, fat, protein carbohydrate and air are taken into account and either parallel or perpendicular models are applied (Miles et al., 1983).

Thermal conductivity of binary liquid mixtures is curvilinearly related to mass fraction of water. Usually the relationship between thermal conductivity and mass fraction of water is concave-upwards.

Specific heat and thermal conductivity are intrinsic properties of the material. They represent the ability of the material to accumulate and to transport heat, respectively. It is evident that both properties are strongly related to water content. Moreover, analysis of published data shows that the less water in the material the more discrepancies between predicted and measured values. It seems reasonable to assume that the discrepancies arise from the treatment of whole water in food as bulk water. Interactions between water and food components affect water properties. Hence, it is rather difficult to accept that the interactions do not affect thermal properties.

4. Influence of water on mass transfer properties

Many unit operations in food processing are based on mass transfer. These are drying, extraction, distillation, absorption, crystallisation, salting, candying and many others. Mass transfer can proceed in one phase or can be done through interface between two phases. Two types of mass transfer mechanisms are considered, i.e. molecular and convective.

Molecular mass transfer called diffusion occurs in solids and fluids. Random movement of molecules causes it.

Fick’s first law gives the flux of component A diffusing in a stationary component B:
\[ n_A = D \left( -\frac{dc_A}{dx} \right) \]
where \( c_A \) is the concentration of component A, \( x \) is the diffusion path and \( D \) is the diffusivity or diffusion coefficient. Diffusion coefficient is intrinsic property of the system, hence it is affected by interactions between diffusing substance and the medium.

In liquids the diffusivity can be predicted by empirical relations, like the Wilke-Chang equation (Saravacos, 1986) in which there is an association parameter which accounts for association of solvent molecules. And the association arises from the interactions between molecules. For water it is 2.6 and shows that interactions between water molecules strongly affect diffusion of small molecules.

Solving Fick’s first law is usually done with the assumption that diffusion coefficient is constant and independent of concentration. Experimentally it was shown that this assumption is false, especially at high concentrations of solutes.

Diffusion of macromolecules, even at low concentrations, is more dependent on interactions with solvent than that of small molecules. Einstein related diffusion of macromolecules with their microscopic properties and introduced frictional coefficient. The Einstein equation is
\[ D = \frac{kT \lambda}{RT} \]
where \( N \) is the Avogadro number, \( R \) is gas constant, \( T \) is temperature in K, \( f \) is frictional coefficient and \( k \) is the Boltzmann constant.

The frictional coefficient \( f \) is directly related to size and shape of the macromolecule. Assuming the
macromolecule is a solid sphere the Stokes equation can be applied and diffusion coefficient is

\[ D = \frac{kT}{6\pi\mu r} \]

where \(\mu\) is viscosity of the solvent and \(r\) is radius of a sphere. In most cases the shape of macromolecules differs from the sphere, hence diffusion coefficient is measured experimentally.

The frictional coefficient is affected by intermolecular interactions. At relatively low concentrations it is linearly related to volumetric fraction occupied by macromolecules in the solution:

\[ f = f_0(1 + anv) \]

where \(n\) is the number of macromolecules in a unit volume, \(v\) is the volume of one macromolecule, \(a\) is constant, \(f_0\) is the frictional coefficient of solvent.

Diffusion coefficient is affected by intermolecular interactions and its value is strongly dependent on solution concentration. In real solutions the relationship is

\[ D = \frac{kT}{f} (1 + 2a_2Mc + 3a_3Mc^2 + \cdots) \]

where \(M\) is the molecular weight of macromolecule, \(c\) is concentration, \(a_2, a_3, \ldots\) are viral coefficients. Diffusion coefficient depends on molecular weight, concentration and viral coefficients, which account for intermolecular interactions.

Since both diffusion coefficient and frictional coefficient are influenced by concentration a complex effect of increased concentration (increased intermolecular interactions) on mobility of macromolecules can be observed (Cwietkow, Eskin, & Frenkel, 1968).

The structure, which usually is heterogeneous and interactions with solid matrix affect diffusion of gases, vapours and liquids in solids. Diffusion in solids is an unsteady process. Concentration gradients impose stresses on the material and diffusion can be accompanied by shrinkage, deformation or swelling. In some cases strong interactions between diffusing substance and solid matrix occur and adsorption or chemisorption accompanies diffusion.

Changes in volume and/or sorption processes accompanying diffusion lead to a complex relationship between diffusion coefficient and concentration. In most cases diffusion in solids is interpreted with the help of effective diffusion coefficient. The coefficient accounts for different ways the molecule is transported within the solid and includes porosity (\(\varepsilon\)) and tortuosity (\(\tau\)) of the diffusion path. It is defined as follows:

\[ D_{\text{eff}} = \frac{\varepsilon D}{\tau} \]

The diffusivity of water and other small molecules decreases significantly at low moisture contents. The decrease depends on the kind of diffusing molecule. It was found that diffusion coefficient of water decreases much less with the increased solids content than the diffusion coefficient of other substances. On this basis, in the mid 1960s, Thijssen proposed a selective diffusion mechanism for volatile retention during drying (King, 1988).

At low water contents diffusivity of reactants is strongly solvent and temperature dependent. The way both parameters control the mobility of small molecules and the flexibility of macromolecules is complex and little known.

The Stokes–Einstein relationship describes translational diffusion coefficient of a molecule while the Debye–Stokes–Einstein equation gives the rotational diffusion coefficient:

\[ D_{\text{trans}} = \frac{kT}{6\pi\mu r} \]

\[ D_{\text{rot}} = \frac{kT}{8\pi\mu r^3} \]

Both equations show that the diffusion coefficient is inversely related to viscosity of solvent. Moreover, the influence of the hydrodynamic radius on mobility of the molecule is presented.

In dilute solution individual or local motions of molecules are present and the motion is affected by interactions between molecules and solvent. Activation energy provides information on the number of molecules or the size of the region involved in the motion. At low solvent concentrations motion of one molecule or a polymer segment involves a displacement of the surrounding segments or molecules. A strong cooperativity occurs. Le Meste et al. (1999) measured sucrose diffusion in concentrated solutions at temperatures close to the glass transition temperature. In 90% sucrose solution and at temperatures 60 K above glass transition temperature diffusion coefficient was of the order \(10^{-15} - 10^{-17}\) m²/s while in 30% solution and at room temperature it is of the order of \(10^{-10}\) m²/s.

Mobility of sucrose in starch–sucrose extrudates hydrated with water starts at a moisture content close to 8% (Farhat, Mitchell, Blanshard, & Debyshire, 1996).

5. Effect of water on electrical properties of food

The most intensively investigated electrical properties of foods have been the relative dielectric constant and loss factor. These dielectric properties determine the energy coupling and distribution in a material subjected to dielectric heating.

Primary determinants of electrical properties of food are frequency, temperature, chemical composition and physical structure (Mudgett, 1987). Water as one of the major constituents of foods affects dielectric behaviour
of the material. Dielectric constant and loss factor varies with moisture content. de Loo and Meijboom (1966) and de Loo (1968) showed that high-moisture foods are generally linear dielectrics. On the other hand, data published by Stuchly (1970) showed that the more water contains food the more dielectric properties depend on temperature. Dried solids showed little or no variation of dielectric properties with temperature. Studies done by Kent and Kress-Rogers (1987) and Laursen (1987) showed that dielectric permittivity of sucrose solutions are dependent on concentration. The higher was the sucrose concentration the lower was the dielectric permittivity. It is important to note that interactions of water with other food constituents affect food dielectric properties. Polarity of the water molecules is strengthened by the dissolved ions at high temperatures. The influence of the dissolved ions is even more important at lower frequencies (Ohlsson & Bengtsson, 1975).

Dielectric measurements done on hydrated compressed pellets of lactose and maltose showed that 0.8 water molecules per saccharide molecule are tightly bound (irrotationally). It is reasonable to assume that in both crystals probably only one oxygen atom per molecule is accessible to water. All the water molecules in excess of 0.8 per saccharide molecule are loosely bound (Daoukaki-Diamanti & Pissis, 1987).

Electromagnetic field at radio- and microwave frequencies interacts with food constituents. These interactions result from the dipole rotation of free water and conductive migration of charged molecules. Dipole rotation results in the disruption of tetrahedral hydrogen bonding patterns (Mudgett, 1986).

Salts dissolved in water influence dielectric properties of the solution. Water molecules are bound by counterners of dissolved salts and it results in depression of dielectric constant and increase of loss factor. Sodium chloride binds 5.5 water molecules on average (sodium ion binds 4 and chloride ion binds 7 water molecules). Binding of water by macromolecules leads to low values of dielectric constant. Takashima (1962) investigated hydrated protein crystals and found that dielectric constant increases rapidly when water content increased from 20% to 35%. The moisture content and the state of water influence dielectric properties of foods and that is strongly emphasised in literature (Mudgett, 1986).

Investigation of dielectric properties of freeze-dried potato equilibrated to different water activities (Mudgett, Goldblith, Wang, & Westphal, 1980) showed that the dielectric properties, i.e. dielectric constant and loss factor increase significantly over those of dry solids at water activity close to 0.86. The critical water activity corresponded to moisture content of about 20%.

Electrical conductivity is a food property important in heating and separation processes. It occurs in media that containing electrically charged molecules. Low molecular weight molecules are electrolytes with precisely defined electrical charge. With macromolecules the situation is not as clear and there is still considerable interest in methods for estimating the charge carried by biopolymers.

Law of Coulomb gives the force experienced by a molecule in an electrical field:

\[ F = neE \]

where \( n \) is the number of charges, \( e \) is the magnitude of electronic charge and \( E \) is the electrical field, V/cm. In the steady motion situation the force is equal to the resistance to motion. Hence

\[ fv = neE \]

where \( f \) is the friction factor and \( v \) is the velocity.

The molecule mobility is

\[ v = \frac{neE}{f} \]

and if the particle is spherical then Stokes’ law can be applied:

\[ v = \frac{neE}{6\pi\mu R} \]

where \( R \) is molecule radius and \( \mu \) is the solvent viscosity. From the above equation it is evident that viscosity of liquid food affects pronouncedly mobility of ions, hence it influences electrical conductivity. Moreover, it was found that increased concentration of insoluble particles decreases electrical conductivity (Sastry & Palaniappan, 1992). In general it is accepted that electrical conductivity of liquid foods increases up to about 30% dry matter content. At higher concentrations the viscosity effect prevails and mobility of molecules decreases.

Electrical conductivity of solids, especially of biological origin is dependent on such variables as size and shape and temperature history. Electrical conductivity increases as particles get smaller. Heating of material over 60 °C substantially increases electrical conductivity. Probably it is due to disintegration of cell membranes, which create additional resistance to ion movement. Decrease of water content in the material decreases electrical conductivity. However at water activity lower-than 0.75–0.80 electrical conductivity is small and proves that water–substrate interactions predominate at low material moistness.

6. Effect of water on optical properties of food

Among important physical properties of foods are those properties, which are stimulated thermally. Thermal radiation is released from all bodies and depends on their material properties and temperature.

Thermal radiation is emitted, transferred and absorbed and extends in the electromagnetic spectrum.
from 0.1 to 1000 μm. Between 0.78 and 1000 μm lies infrared radiation, but practical application finds radiation with wavelength below 5.6 μm (Ginzburg, 1969). In food processing near infrared radiation with wavelength around 1 μm is the most important.

Emission of thermal radiation comes normally from molecules in a layer close to the surface. This layer is around 1 μm thick; hence the infrared radiation is a surface process. The emissivity of the material depends on its chemical composition, shape, temperature and the surface texture. Examples of emissivities of materials in food processing are given in Table 1.

Infrared radiation falling on a body is partly absorbed and partly reflected at its surface. According to Kirchhoff’s law a close relationship exists between the emission and absorption capabilities. Since water has a high emissivity foods containing water show significant ability to absorb infrared energy. Absorption of infrared energy by food materials is not a pure surface process. In some products infrared radiation is capable to penetrate the material as deep as 30 mm, and penetration to a depth of 4–5 mm is very common (Ginzburg, 1969).

Water as a constituent of food affects very strongly its capability to absorb infrared energy. Spectral absorption coefficient of water shows three maxima at the following wavelengths: 1.4, 3.0 and 6.0 μm. It means that at those wavelengths water absorbs infrared energy maximally. The wavelength affects the ability of infrared radiation to penetrate the material. Generally the longer the wavelength the more energy is absorbed in surface layers. Hence, in food processing it is recommended to use infrared radiation at wavelength close to the first maximum, i.e. 1.3–1.4 μm.

There is not much research done on relationship between water content of food and its ability to absorb infrared energy. From data published by Ginzburg (1969) it can be inferred that decrease of water content makes material more transparent for infrared radiation. Layer 0.5 mm thick of tomato paste was transparent to infrared radiation in 55.8% and 95% at dry matter contents 15% and 40%, respectively. Similarly wheat dough is much less transparent than bread, however differences in structure must be here taken into account. Drying of potatoes to 42% water content increases their transparency to infrared radiation. According to Asselbergs, Mohr, and Kemp (1960) spectral characteristics of dry matter of apple becomes important in final stages of drying. Nowak (2002) who showed that temperature of apple undergoing drying does not change much until 90% of water is removed (Fig. 6) indirectly proved the major role of water in absorption of infrared energy during drying. Further drying leads to substantial increase of material temperature. It is suggesting that at low moisture contents efficiency of water evaporation decreases and a part of infrared energy is absorbed by the components of dry matter of apple.

Although the data in the literature is scarce it can be concluded that water is responsible, in large degree, for infrared absorptivity of food materials.

Optical properties of food materials are responsible for their colour and appearance. The appearance includes such attributes as translucency, gloss, uniformity and pattern.

There is not much research done on the effect of water on the colour and appearance of food. In liquid foods some information on the effect of water on colour of the product can be extracted from the research considering the colour and pigment concentration. Aqueous solution of red anthocyanin pigment shows maxims for a (redness) and b (yellowness) values in the CIELAB System at pigment concentration of 0.5–2 mg/ml while the L (whiteness) value decreases with increasing antocyanin concentration (Francis, 1987). Kent (1987) and Brimelow (1987) who showed that L value decreases with increased dry matter content in tomato paste report similar results. The a value shows a maximum at concentration close to 20% d.m. while the b value decreases with increasing dry matter content. On the other hand dilution of evaporated milk results in a maximum in the case of L and continuous decrease of a and b (Kent, 1987). Foods such as milk or tomato paste shows internal diffusion of light, which can be observed as translucency and opacity. Research done by MacDou-

### Table 1

Approximate values of emissivities (Fellows, 1988)

<table>
<thead>
<tr>
<th>Material</th>
<th>Emissivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dough</td>
<td>0.85</td>
</tr>
<tr>
<td>Lean beef</td>
<td>0.74</td>
</tr>
<tr>
<td>Beef fat</td>
<td>0.78</td>
</tr>
<tr>
<td>Water</td>
<td>0.955</td>
</tr>
<tr>
<td>Ice</td>
<td>0.97</td>
</tr>
</tbody>
</table>

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Fig. 6. Relationship between temperature of apple slice and water content during infrared drying. Parameter is air velocity.
gall (1987) showed that increasing total solids in the evaporated milk up to about 10% increases the light scatter, which increased reflectance. Further increase in total solids decreases reflectance and product becomes more opaque. For tomato paste the $L$ value showed maximum at total solids concentration close to 10%.

Influence of water on colour and appearance of solid foods is also evident. The appearance of free water on vegetables and fish increase their apparent shininess and increase visual impression of freshness. Blanching of vegetables make them to look more colourful. During this process air in the plant tissue is replaced by water, the refractive index changes and reduces light scattering. In consequence blanched vegetables are perceived more intense in colour (Hutchings, 1994).

Evaporation of water from the material affects colour of material undergoing drying. Results published by Lewicki and Duszczyk (1998) showed that luminance ($Y$ value in the CIE system) of potato, carrot and pumpkin increased linearly with the decrease of water content until the maximum was reached. The maximum occurred in blanched potato at water content 2.18 g/g d.m., while for carrot and pumpkin it was 0.91 and 0.68 g/g d.m., respectively. Chromaticity co-ordinates also changed and the colour moved toward the white point, in the case of carrot and pumpkin. Colour saturation increased at water content below 0.5 g/g d.m. but it was lower than that of raw material.

Changes of colour co-ordinates of material undergoing drying are due mostly to water removal, shrinkage and alterations of the structure of the material surface. Water is replaced by air in porous materials and they appear as pale. Decreased luminance and more saturated colour of the material during final stages of drying are caused probably by the effect of concentration.

7. Effect of water on acoustic emission

Acoustic emission is a significant quality attribute of many food products and is considered as a sign of freshness. Drake (1963) showed that acoustic emission of many foods differs by amplitude, frequency and intensity. Vickers and Bourne (1976) who suggested that frequency of 160 Hz is typical for this type of products investigated crunchiness of food.


Research done by Marzec (2002) showed that acoustic emission of flat bread is strongly related to water activity (Fig. 7). The lower was the water activity the amplitude was the higher and acoustic emission was generated even at very low stress. Increase of water activity to 0.53 reduced the energy of acoustic emission about 4-fold. Most of acoustic emission occurred in two frequency ranges. These are 1–3 kHz and 7–15 kHz. At water activities over 0.53 the acoustic emission was very weak and some sound is present only at frequencies larger than 10 kHz.

8. Conclusions

Water as a component of food affects its physical properties. Practically there is no physical property of food, important from the engineering or consumer point of view, which is not affected by water. The influence of water on food properties arises from interactions between water molecules and other constituents of food. The extent and strength of interactions depends on chemical composition and determines the state of water in food. Hence, many physical properties of food are related to water activity.

At high water contents a rule of additivity is observed and physical properties can be predicted with the use of appropriate equations. The rule of additivity is applicable in those cases in which properties of water are those of bulk water. At low water contents, when interactions between water molecules and food components prevail and water activity is below 1, the influence of water on physical properties is more complicated. It seems that research relating mechanical properties to the state of water in foods gives pretty thorough picture of the effect of water on those properties. However, other properties of food are less elucidated from this point of view. Hence, the influence of the state of water in foods on such properties as thermal, electrical, optical, acoustic and other could be a good topic for a future research.

References
