Agrobiodiversity for Improving Nutrition, Health and Life Quality

Review

Water in biological and food systems

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This article presents data on the physicochemical characteristics of water in biological and food systems such as redox potential, water activity, water potential; and their influence on the processes occurring in plant materials and processed products. According to the laws of thermodynamics, water in biological and food systems is in a stationary state. Entropy changes in biological and food systems do not occur during reversible phase transitions of water. In all studied samples (E >0), despite the rather high content of antioxidants (polyphenols and L-ascorbic acid) in plant raw materials. The only exception was sweet pepper E= -10–+50 mV. The relatively high content of L-ascorbic acid, up to 102 mg.100 g^{-1}, led to a decrease in the redox potential and a shift in redox reactions towards an increase in the reduction potential of the system water – L-ascorbic acid (E ≤0). Bound water has anomalous properties, for example: its density increases, loses the properties of a solvent, fluidity is lost, the boiling point is above 100 °C. In such an environment, biochemical, chemical and biological processes proceed at a low rate, and at a_w ≤0.2 these processes stop completely. Alkaline mineral water belongs to the hydrocarbon group of water obtained from natural sources. The acidity of water exceeds pH 7. Because of the predominance of bicarbonate ions (HCO_3^-), sodium, potassium, magnesium and other minerals in it, the water is conditionally called alkaline, and its beneficial properties are used to treat several diseases. Water has unique properties associated to a certain extent with the polarity of its molecules and their ability to form hydrogen bonds with each other. Therefore, the electrical polarity of liquid water molecules has the property of forming many hydrogen bonds with a total strength between the molecules.

Keywords: water potential, redox potential, water activity, water structure, entropy

Introduction

Water is the main component of most foods. It has a dominant influence on many quality indicators, especially those related to the texture and shelf life of food products. The quality of potable water, including the quality and healing properties of mineral waters, is also of exceptionally great importance. During the processing of vegetable raw materials, various food products containing biologically active substances necessary for the human body can be obtained. In this regard, it is appropriate to consider the role of water in the physicochemical processes occurring in plant materials and food products. Considering that plant raw materials and the assortment of food products are quite diverse, it seems appropriate to consider them as biological and food systems, which are characterized by generalized indicators and their elements, in particular, the state and behaviour of water.

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A set of interrelated and mutually influencing elements with joint action, which are the object of thermodynamic research, is called a thermodynamic system. In particular, fruits, berries, vegetables are complex biological systems of different levels of the organization. Several food products are derivatives of biological systems and our food systems. Previous studies have established that the physical and biological state of fruits, berries, vegetables, obey the fundamental laws of thermodynamics, in particular, they are characterized by a state function – entropy (Opritov, 1999; Masimov, 2018; Etkin, 2019).

The only possible form of functional activity of any system, including biological and food systems, is the life cycle. Biological systems are open non-equilibrium thermodynamic systems, consisting of a set of hierarchically interconnected components, which includes the dynamics of development from inception to the cessation of existence (Ondar, 2011). The life cycle has a beginning and an end; and includes the inception of the system, its formation and continuous development, maturity, reproduction, ageing and cessation of activity. During the life cycle, biochemical reactions constantly and purposefully proceed, aimed at the formation in the structure of fruits and vegetables the embryos, grains, seeds, which contain the genetic codes for the reproduction of the former system. The further existence of the biological system continues due to new generations. A group of systems with approximately the same life cycle in biology is called a species or population (Etkin, 2021; Henry, 2021; Helson and Cox, 2022).

Food products obtained by technological processing of plant raw materials are thermodynamic multicomponent closed systems with a specific life cycle of reproduction, which includes all stages from the idea of obtaining a product, the formation of a product structure, its production technology, transportation, storage time, ageing and its complete degradation after a storage period. The quality, nutritional and biological value of a food product depends on the interaction of all its components (ISO/IEC 15288, 2008; ISO/IEC 42010, 2011).

A special role in the functioning of these systems plays water. Due to its specific chemical structure and its special properties, water has a dominant influence on the vital functions of biological systems and the stability of food systems (Tatarov and Rusu, 2002; Masimov, 2018; Zemskov, 2018).

The mass fraction of water in food products ranges from 2.0 to 97.0%. Typically, water in biological and food systems is in a bound state. The types and state of bound water have different effects on the stability of food systems and the manner in their change over time. Numerous papers published recently are devoted to the study of water and its properties, as well as the influence of water structure and its physical characteristics on the functions of biological systems (Etkin, 2003; Tijskens, 2004; Korotkov, 2019).

From the point of view of theoretical aspects and applied value, it is of interest to consider the physicochemical state of water in certain types of plant raw materials and their processed products. This work presents some considerations about the physical characteristics of water such as redox potential, water activity, as well as indicators of water state in biological and food systems.

Redox potential of water

Water is involved in redox reactions in both food and biological systems. In a living organism during the biological oxidation of food components such as proteins, fats and carbohydrates, through enzymatic redox reactions, chemical bonds are split with the release and accumulation of released energy in molecules of adenosine triphosphate (ATP) (Nelson and Cox, 2022). In food systems, water is the medium in which redox reactions occur, mainly, in the direction of oxidation of phenolic substances, water-soluble vitamins, pigments, etc. (Martinovich and Cherenkevich, 2008; Tatarov, 2017).

Water is a weak electrolyte and is an equilibrium system consisting of water molecules, H^+, HO^- ions. The total reaction of the equilibrium state of system elements is:

$$O_2 + 4H^+ + 4e \rightleftarrows 2\,H_2O \qquad (1)$$

In accordance with equation (1), water molecules are in a reduced state, molecular oxygen and H^+ ions are in an oxidized state. The equilibrium state of water is achieved as a result of the exchange of electrons between the reduced (Red) and oxidized (Ox) components:

$$Ox + ne \rightleftarrows Red$$

Redox potential represents the chemical activity of water components in the oxidation-reduction reaction. This dependence is represented by the Nernst equation (Rubin, 1987; Sandulachi and Tatarov, 2012).

$$E = E^0 + \frac{RT}{nF} Ln \frac{[H^+]^4 [O_2]}{[H_2O]^2} \qquad (2)$$

where: E – redox potential of water, mV; E° – standard value of water redox potential, mV. (E° = 815 mV); R – universal gas constant (R = 8.314 $J.K^{-1}.mol^{-1}$); T – temperature, °K; $[O_2]$ – dissolved oxygen concentration, $mol.dm^{-3}$; $[H^+]$ – hydrogen ion concentration, $mol.dm^{-3}$; $[H_2O]$ – water concentration, $mol.dm^{-3}$; n – number of electrons; F – Faraday constant (F = 96.485 $C.mol^{-1}$)

In accordance with the Nernst equation (2), the redox potential is a generalized index of the state of liquid water, depending on the ratio (Ox/Red):

$$E = E^0 + \frac{RT}{nF} lg \frac{[Ox]}{[Red]} \qquad (3)$$

As a result of experimental data analysis, the redox potential of distilled water corresponds to the following equation:

$$E = E^\circ - 59.16\ pH + 14.79\ lg\ [O_2] \qquad (4)$$

These data indicate the fact that the state of water is shifted to the region of the oxidized state E >0. Thus, pure water is an environment that has oxidizing properties and promotes the oxidation of organic substances and reduces the activity of antioxidants. The experimental data presented in Table 1 indicate different values of the redox potential of water in the studied fruits, vegetables and berries (Tatarov and Rusu, 2002).

A common indicator of the studied fruits, vegetables and berries is the oxidized state. In all studied samples (E >0), despite the rather high content of antioxidants (polyphenols and L-ascorbic acid) in plant raw materials. The only exception was sweet pepper E = -10–+50 mV. The relatively high content of L-ascorbic acid, up to 102 $mg.100\ g^{-1}$, led to a decrease in the redox potential and a shift in redox reactions towards an increase in the reduction potential of the system water – L-ascorbic acid (E ≤0).

The redox potential of the system water – L-ascorbic acid depends on the standard value of the redox potential of water, as well as on the standard value of the redox potential of L-ascorbic acid, the pH of the medium, the concentration of dissolved oxygen. In general, the redox potential of the system water – L-ascorbic acid is determined by the following equation:

$$E^{\circ\circ} = E^\circ_B - E^\circ_{AA} - 59.16\ pH + 44.35\ lg\ [O_2] + 414.40 \qquad (5)$$

where: $E^{\circ\circ}$ – redox potential of the system water – L-ascorbic acid, mV; E°_B – standard value of water redox potential, E°_B = 815 mV; E°_{AA} – standard value of L-ascorbic acid redox potential, mV

The standard value of L-ascorbic acid redox potential depends on the pH value of medium:

$$E^\circ_{AA} = 355 - 25\ pH$$

In the pH range of 3.0 ... 7.0, standard values of redox potential for L-ascorbic acid are:

$$E^\circ_{AA} = 180 \ldots 280\ mV$$

The standard values of redox potential of the system water – L-ascorbic acid in the pH range of 3.0 ... 7.0 are:

$$E^{\circ\circ} = 539 \ldots 553\ mV$$

Table 1 Redox potential of fruits, vegetables and berries (Tatarov and Rusu, 2002)

Species	Redox potential, mV	Water content, %	pH	Antioxidant content, $mg.100\ g^{-1}$	
				L-ascorbic acid	polyphenols
Aronia	220–225	81–82	3.9	42–45	1100
Sea buckthorn	115–136	88–89	2.9	18–21	320
Sweet pepper	-10–+50	92–94	5.6	75–102	–
Tomatoes	190–230	94–95	4.3	5.8–7.1	–
Quince	180–200	96–98	4.2	16.0–17.6	250
Plum	320–340	89–90	3.7	2.3–3.5	200–400
Peach	330–340	90–92	4.1	7.2–8.6	160
Strawberry	128–145	87–93	3.3	32–46	280–360
Raspberry	214–257	84–89	3.6	30–40	235–330

The standard values of redox potential of the system water – L-ascorbic acid ($E^{\circ\circ}$) are higher than the standard values of L-ascorbic acid redox potential (E°_{AA}).

$$E^{\circ\circ} > E^{\circ}_{AA}$$

This ratio once again testifies to the physicochemical properties of water in biological and food systems, in particular, it leads to a decrease in the reduction potential of L-ascorbic acid and other antioxidants. However, it should be noted the special function of water in the process of obtaining energy by living organisms through the biological oxidation of proteins, carbohydrates, and fats and in metabolic processes in biological systems.

Water activity

In biological and food systems, water is one of the key components. Along with the redox potential, the physicochemical properties of water are also determined by an indicator called water activity (a_w) (Smirnov and Trongsawad, 2006; Shishkov, 2009; Masimov, 2018).

Water activity is a thermodynamic indicator of the interaction of water with chemical components in biological and food systems. The activity of biological systems and, in particular, food systems, is determined not by the amount of water in them, but by its thermodynamic state. Water molecules have kinetic energy, which depends on their internal state. Based on the second law of thermodynamics, the internal energy of water is conditionally divided into free (F) and bound (ST) energy. Free energy is characterized by the chemical potential of water (Rubin, 1987).

The chemical potential characterizes the amount of free energy in $J.mol^{-1}$, which 1.0 mol of water has. The chemical potential of water is determined by the equation:

$$\mu = \mu_0 + RT \ln a \qquad (6)$$

where: μ – chemical potential of water; μ_0 – chemical potential of water in standard state (25 °C, 1 atm); R – gas constant; T – absolute temperature; a – thermodynamic activity of water

The decrease in the free energy of water (ΔF) is accompanied by a change in the chemical potential from the value of μ_0 to the value of μ, as a result of energy consumption for desorption processes:

$$\Delta F = \mu - \mu_0 = - RT \ln a = -RT \ln P_m/P_u = -RT \ln \varphi \qquad (7)$$

where: ΔF – value of decreasing in the free energy of water; P_m – partial pressure of moisture vapour on the system surface in equilibrium; P_u – partial pressure of moisture vapour in the environment; φ – relative humidity, %

According to equation (7), the decrease in the free energy of water depends on the value of relative humidity (φ) on the system surface and in the environment. According to the modern concept, water activity is determined by the ratio of the water vapour pressure on the surface of the system (product) to the moisture vapour pressure in the environment at the same temperature in an equilibrium state:

$$a_w = \frac{P_m}{P_u} \qquad (8)$$

The numerical values of a_w vary within 0... 1.0 or 0... 100%. In cases where the partial pressure of moisture vapour on the surface approaches zero ($P_m \to 0$), water is in a bound state with the components located on the product surface. In this case, water does not evaporate $a_w \to 0$.

Water in the liquid state, at $a_w \to 1$, is the medium in which biochemical, chemical and biological processes actively proceed. The decrease in water activity in food and biological systems is a consequence of the transition of water molecules to a bound state. Bound water is a structured medium in the form of ordered layers of molecules, physically and chemically related to macromolecules of carbohydrates, proteins and other chemicals. The more macromolecules with polar groups on the surface, the higher the degree of hydration.

Bound water has anomalous properties, for example: its density increases, loses the properties of a solvent, fluidity is lost, the boiling point is above 100 °C, etc. In such an environment, biochemical, chemical and biological processes proceed at a low rate, and at $a_w \leq 0.2$ these processes stop completely.

At present, the indicator of water activity is widely used in the technology of production and quality control of food products. Depending on the value of water activity a_w, categories of food products with different stability and shelf life are established (Tatarov, 2017).

The shelf life of products at a temperature of 20 °C, depending on the amount of water activity is:

- from 2 to 5 years or more possess dehydrated (dried) food products with a_w = 0.3... 0.6;

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- up to 1 year possess foods with intermediate moisture content and a_w = 0.6… 0.85.

The above products are microbiologically, chemically, physically stable and retain organoleptic properties.

The shelf life of food products with a water content of more than 65%, a_w = 0.97... 1.0 (fruits, berries, milk, meat, etc.) at t = 20 °C ranges from several hours to 2–3 days.

As an example, the stability of the reducing antioxidant activity of vitamin C (L – ascorbic acid) in solutions with different water activities is shown (Figure 1). The system water - vitamin C, with water activity, a_w = 1.0, leads to a complete loss of vitamin C activity within 40 days of storage at t = 20 °C.

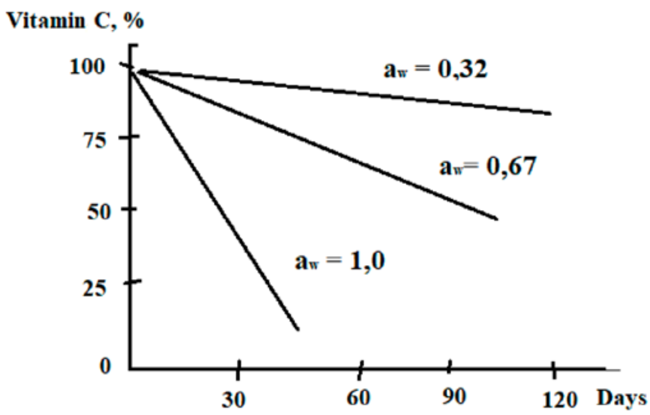

Figure 1 Change in the reducing activity of vitamin C depending on the activity of water at t = 20 °C

Given the importance and great influence of water activity on the stability and shelf life of food products, this indicator (a_w) is included in the system of international standards (ISO 9000, 2015).

Some biological properties of water

In biological systems, liquid water retains the basic physical and chemical properties: structure, boiling and freezing points, density, phase transformations, heat capacity, etc. One of the main elements of biological systems of plant origin is a plant cell. The physiological activity of a cell is determined not by the amount of water, but by its thermodynamic state (Shishkov, 2009). Plants grown at the same humidity and containing almost the same amount of water in the tissues, but at different levels of mineral nutrition, have a different thermodynamic (energy) state. The thermodynamic state of water in biological systems is judged by the magnitude of its chemical potential, water potential, osmotic potential, and pressure potential (Etkin, 2003).

Water potential is a measure of the difference between the free energy of water inside the cell and outside the cell, at the same temperature and pressure. It should also be noted that the difference between the chemical potential of water in a cell (μ) and the chemical potential of pure water (μ_0), the difference $\mu - \mu_0$, referred to the molar volume of water in a cell (v), called water potential (ψ) and used in the study of the water regime of plants (Ondar, 2011).

$$\psi = (\mu - \mu_0)/V \qquad (9)$$

where: ψ – water potential, represents the energy that causes the phenomenon of osmosis in biological systems called pressure deficit or suction force; V – the partial molecular volume of water, $cm^3.mol^{-1}$

The water potential ψ is the algebraic sum of the individual potentials of the system components: osmotic, turgor, matrix and gravitational potentials. If two cells with different potentials ψ are located nearby, water will diffuse between them through the cell wall from a cell with a higher water potential into a cell with a lower potential.

It should be noted that the water entering the root system of plants is not pure (distilled) water, but aqueous solutions containing various mineral substances. In principle, in this situation, one should probably consider a system consisting of water and mineral substances such as: calcium, potassium, sodium, iron, magnesium, aluminium, nitrogen and many others. Depending on the composition and concentration of mineral substances, aqueous solutions will have completely other physicochemical properties and physiological effects compared to pure water (Masimov et al., 2019).

Examples of the influence of the mineral composition on the properties of mineral waters can be given. Alkaline mineral water belongs to the hydrocarbon group of water obtained from natural sources. The acidity of water exceeds pH 7. Because of the predominance of bicarbonate ions (HCO_3^-), sodium, potassium, magnesium and other minerals in it, the water is conditionally called alkaline, and its beneficial properties are used to treat several diseases.

Sulfate-chloride, sodium-calcium mineral water is distinguished by a relatively high content of iodine, bromine and fluorine with a total content of up to

5.0–5.5 $g.dm^{-3}$. It was noted (Masimov, 2018), that the thermodynamic state of intracellular water is significantly affected by ions, increasing, or slowing down the mobility of the water layers adjacent to them. Thus, ions Na^+, Ca^{2+}, Ba^{2+}, Mg^{2+}, Al^{3+}, OH^-, bind water (disrupt the structure of water) and are positively hydrated slowing down the mobility of water molecules. At the same time, K^+, NH^{4+}, Pb^{4+}, CS^+ ions are negatively hydrated and increase water mobility. Ions with negative hydration strongly disrupt the structure of water.

The activity of water in cells depends on temperature, pressure, hydrophobic interaction with non-polar components. The hydrophobic interaction of water with non-polar components is determined by their quantity, composition and conformational changes that affect cell metabolism, the magnitude of the gradient of water activity inside and outside the cell (Mosin and Ignatov, 2011; Zemskov, 2018; Henry, 2021).

Entropy of water

At present, it has been proven that the features of the physical properties of water and numerous short-lived hydrogen bonds in a water molecule create favourable conditions for the formation of special associated molecular structures – clusters (Sidorenko and Ivanova, 2011; Brindza et al., 2014; Horčinova Sedlačkova et al., 2022). Cluster is the structural unit of structured water. Structured water (Smirnov, 2003; Nelson and Cox, 2022), consisting of many clusters of various types, forms a hierarchical spatial liquid crystal structure with special physical properties called activated water. For example, it was developed technology by the "Resonance Effect Technology – MRET", and on its basis, the water activation device was patented in the USA (Patent USA no. 6022479, 1998; Smirnov and Trongsawad, 2006). The activation process consists in changing the structure of water by creating stable dynamic multiple molecular layers of water, similar to the structures of cellular water in living organisms. Activated water retains its basic structure and a significant part of its useful properties for a day at room temperature and at least 45 days at a temperature of +4 °C.

Numerous experimental data affirm the fact that the mechanism of interaction between dissolved substances and water promotes the formation of complex molecular systems that have new physical and chemical parameters and biological activity. However, activated water obtained in various ways is not stable and loses its acquired properties within a short time.

First of all, it should be noted that water has unique properties associated to a certain extent with the polarity of its molecules and their ability to form hydrogen bonds with each other. Therefore, the electrical polarity of liquid water molecules has the property of forming a large number of hydrogen bonds with a total strength between the molecules.

At any moment in time, the vast majority of liquid water molecules are linked by hydrogen bonds. The lifetime or stability of each hydrogen bond is only 10^{-10}… 10^{-11} s. The energy of one hydrogen bond is only about 21 $kJ.mol^{-1}$ (Wernet et al., 2004; Nelson and Cox, 2022). In liquid water, there is a constant formation and destruction of hydrogen bonds between molecules. As a consequence of this phenomenon, the structure of liquid water is dynamic, being fluid and non-fluid at the same time (Pershin, 2006; Nelson and Cox, 2022). However, almost all water molecules are constantly connected by hydrogen bonds. This structure ensures the stability of the branched structure of liquid water, water vapour, as well as frozen crystalline water (Mosin and Ignatov, 2011).

According to the second law of thermodynamics and its statistical nature, the state of various systems, including water, is observed with a high degree of precision. In biological and food systems, water is simultaneously in a macro- and microstate. The microstate is liquid, vaporous and solid (crystalline) water. A microstate is characterized by the arrangement of molecules in a medium at a given point in time. In general, the state of water is determined by the thermodynamic entropy function according to the Boltzmann formula (Rubin, 1987):

$$S = k \ln W \qquad (10)$$

where: S – entropy, $J.mol^{-1}.K^{-1}$; k – Boltzmann constant, represents the ratio between the universal gas constant – R, and the Avogadro number – NAV: $k = R/N_{AV}$; ($R = 8.31$ $J.mol^{-1}.K^{-1}$; $k = 1.38 \times 10^{23}$ $J.K^{-1}$); ln W – logarithm of the probable number of microstates of the system

In this case, the maximum number of microstates through which a given macrostate of water (liquid water) is realized is determined by the thermodynamic probability (W). The Boltzmann formula is applied to estimate the number of water microstates.

Under standard conditions, T = 298 °K, p = 1 atm, n = 1 mol, the value of the entropy of liquid water is: $S(H_2O) = 70$ $J.mol^{-1}.K^{-1}$. At a concentration of water molecules equal to NAV = 1 mol, the Boltzmann constant is: k = R $J.mol^{-1}.K^{-1}$. The number of microstates per 1 mol of water molecules according to formula (10) will be:

$$W = e^{S/R} = e^{70/8.31} = 4537$$

Thus, it turns out that for 6 1023 molecules of liquid water, at a standard temperature of 298 °K (25 °C), there are more than 4500 microstates of water (combinations of water molecules) with an equal probability of realizing one macrostate of liquid water.

Biological systems are open non-equilibrium thermodynamic systems. The change in entropy in biological systems is complex due to the constant exchange of energy and substances with the environment. The change in the entropy of water as an element of these systems is not equal to zero $\Delta S \neq 0$. As a result of these processes, the total change in entropy in biological living systems is always positive.

Food systems, being derivatives of biological systems, as a rule, are irreversible closed systems. Their changes are accompanied by an increase in entropy $\Delta S > 0$. As the entropy in the food system increases, the energy dissipation increases, the entropy increases to a maximum value and the thermodynamic equilibrium of the system is established. However, the change in the entropy of water in food systems is zero $\Delta S = 0$.

In principle, the change in the entropy of water in biological and food does not occur. This is one of the many signs of the unique physical and chemical properties of water. When ice is heated, a phase transition occurs: ice → water; water → vapour; vapour → water; etc. (Carrrasco et al., 2009). The change in entropy during phase transitions of water is equal to the heat of the phase transition. Thus, during the phase transitions of water, an abrupt change in entropy occurs. Under standard conditions, the entropy of ice is 48 $J.mol^{-1}.K^{-1}$, that of water – 70 $J.mol^{-1}.K^{-1}$, and that of vapour – 190 $J.mol^{-1}.K^{-1}$ (Stepanovskikh and Brusniczyna, 2008). In reversible phase transitions of the type: water → vapour → water; water → ice → water; ice → water → vapour, no increase in entropy occurs ($\Delta S = 0$) due to the equality of the expended and released energy.

The transition of water from one state to another takes place not only in biological and food systems but is a well-known natural phenomenon. The uniqueness of this phenomenon lies in the fact that during the phase transitions of water, there are no abrupt changes in the physicochemical properties and, especially, the appearance of an anomaly. Even in biological systems, when water passes from a bound to a free state, water retains its physical and chemical properties. The innumerable number of phase transitions water → vapor → water; water → ice → water did not lead to a change in the structure of unbound water. This indicates a stationary state of unbound water, which is possible with minimal energy consumption. At the same time, liquid water does not reach an equilibrium state with the environment. Nevertheless, it is possible that the study of the structure and function of activated water, methods of obtaining it, will expand our knowledge and present us with new discoveries.

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