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# DIELECTRIC STUDY OF BOUND WATER IN GRAIN AT RADIO AND MICROWAVE FREQUENCIES

**V. M. Serdyuk**

Institute of Applied Physical Problems
Belarusian State University
Kurchatov St., 7, Minsk, 220064, Belarus

**Abstract**—A phenomenological theoretical model of grain dielectric properties is presented for radio and microwave frequencies. On the bases of this model, an inverse problem is solved to determine the dielectric permittivity of bound water inside kernels of winter wheat using results of complex permittivity measurements for bulk grain carried out by other authors. The character of the water complex permittivity dependence on frequency and kernel moisture content is studied. For this, the permittivity was considered as a sum of five different functions, depending on moisture content explicitly, and with coefficients being subject to determination. The frequency dependence of these coefficients was analyzed, and the regions typical for the ionic conductivity and for the dipole-orientational polarization mechanism were detected. For this polarization mechanism, the relaxation frequencies are differ from those of free water. It was concluded that water microparticles inside kernels are formed not by pure water, but by aqueous solution of four different substances coming from the kernel solid phase. It is shown that bound water, for the most part, is in a state that is intermediate between that of free water and that of molecules in the monomolecular water layer on the solid phase boundary.

## 1. INTRODUCTION

Dielectric study of heterogeneous materials in the radio and the microwave ranges provides opportunity to evaluate and control their composition [1–4] and also to detect new physical properties restricted to their constituents. In particular, it was established by this way that water within porous disperse systems is characterized by specific properties differing from the properties of ordinary free water (so-called bound water) [5–11]. It is known that near a solid surface or close to a polymeric macromolecule, water forms the ice-like cluster structure [7, 10, 12]. This feature is revealed to a great extent in a monomoleqular layer, directly bordering to interface boundary, and at moving away from it and going from one molecular layer to another one, local properties of water change continuously, nearing these values of free water [10, 12]. Despite of a great number of publications devoted to this topic, there is no unique opinion about bound water properties up to now. Some researchers regard that the boundary values of its local density and dielectric permittivity in the monomolecular interface layer are identical to the properties of ice [9, 10]. Other authors indicate on differences between these water phases [6, 8], pointing out in particular to the existence of the Debye relaxation frequency for bound water near 100 MHz [8], whereas the similar frequency for ice is about 10 kHz [13, 14]. Probably, the following point of view is correct according to which the properties of bound water are not the same for different heterogeneous systems and are dependent on their composition. Special place among water-containing disperse systems is held by the systems of biological nature (cells, tissues and organisms), for which water is not only one of the constituents but also plays an important active role. In the present work, we investigate the properties of bound water within composition of one of such biological system — in wheat grain. The basic aim of the work is to determine the dependence of the dielectric permittivity of bound water on its moisture content in bulk grain. For this, we use the results of dielectric measurements for bulk grain of winter wheat at various frequencies, presented in [15]. There is a great amount of later experimental data on dielectric properties of bulk grain in modern literature. However, the authors of [15], besides the results on measurement of dielectric permittivity, presented also bona fide the data on measurement of bulk density and kernel density for grain samples under study, which is necessary for electromagnetic simulation.

In order to determine composition of a heterogeneous mixture and to investigate properties of its separate constituents by dielectric measurements, one needs in an adequate theoretical model. It should establish connection between physical parameters of mixture constituents and parameters of a system as a whole, which are measured by experiment. Various methods are used for determination of such connection: scattering methods taking into account statistical distributions for location and properties of particles formed by mixture constituents [16–23], and phenomenological approach based on some simple self-empirical laws [24–28]. This approach was used for simulation of dielectric properties of bulk grain at microwave frequencies [29]. However, the theoretical model [29] does not consider absorbed water inside kernels as specific bound water and ascribes to it the same properties as free water [30, 31]. That is why the theory [29] needs certain corrections for the study of bound water.

## 2. THEORETICAL MODEL OF BULK GRAIN DIELECTRIC PERMITTIVITY

From the physical point of view, a bulk grain represents a disperse system formed by separate kernels (disperse particles) and air spaces between them (continuous disperse medium). But, this system is more complex than some other disperse systems like clouds [20] or rain medium [21–23]. Every separate kernel has developed porous structure and also can be considered as a complex disperse system of the next level. It is formed by organic substance of inhomogeneous composition and density, with air microcapillaries in it and with microparticles of absorbed water [32]. For such complex systems a rigorous microscopic approach is very difficult for construction of a dielectric response theory. However, we shall take an interest in grain dielectric properties at the radio and the microwave range with frequencies not more than 12 GHz. Here, a wavelength exceeds grain kernel dimensions not less then by a factor of 10. Under this condition, radiation recognizes the dielectric parameters of material as averaged over its whole volume. This circumstance gives possibility to use a phenomenological approach for theoretical modeling of grain dielectric properties, which does not deal with local physical parameters in every point of a mixture, but employs their values averaged over sufficiently great volumes [24–27].

For bulk grain as a two-component disperse system, the mean dielectric permittivity $\varepsilon_g$ can be determined using the known Reynolds-Hough formula [24–27]

$$\varepsilon_g = 1 + (\varepsilon_k - 1)vK \tag{1}$$

where $\varepsilon_g = \mathrm{Re}\varepsilon_g + i\mathrm{Im}\varepsilon_g$ is the complex dielectric permittivity of a system as a whole, $i = \sqrt{-1}$ is the imaginary unit, $\varepsilon_k$ is the mean dielectric permittivity of separate kernels, $v$ is their volume fraction in bulk material, $K$ is the ratio of the mean electric field strength inside kernels and the field strength in the whole volume of bulk grain. The dielectric permittivity of continuous disperse medium (air) is assumed here to be equal to the unit.

The volume fraction of kernels $v$ is calculated as the ratio of bulk density of the whole material $\rho_g$ to the mean density of disperse particles (kernels) $\rho_k$: $v = \rho_g/\rho_k$. For grain of hard winter wheat at the temperature $t = 24°\text{C}$ the moisture dependence of these values was studied experimentally in [15] (see Fig. 1). This dependence is well approximated by the following function

$$\rho_{g,k} = A_{g,k} - \frac{B_{g,k} u_{g,k}}{(1 + P_{g,k} u_{g,k}) \sqrt{1 + u_{g,k}^2}} \tag{2}$$

where $u_{g,k} = (M - M_{g,k})/\Delta_{g,k}$; $A_g = 0.695$; $B_g = 0.145$; $P_g = 0.35$; $M_g = 0.192$; $\Delta_g = 0.115$; $A_k = 1.363$; $B_k = 0.099$; $P_k = 0.32$; $M_k = 0.18$; $\Delta_k = 0.11$. These numerical values were determined by ordinary choice under the condition of a close approximation to the experimental data. Further, $M$ is the moisture content, which is determined by the ratio of the mass of absorbed water, $m_w$, to the mass of the whole material, $m_k = m_{dk} + m_w$,

$$M = m_w/m_k \tag{3}$$

where $m_{dk}$ is the mass of absolutely dry kernels. Here and everywhere below, additional index "*d*" at every symbol denotes the value of a corresponding parameter in the limiting case of $M \to 0$. Note also that in all formulas of this article, the moisture content $M$ is measured in absolute units or in percent if the appropriate symbol is present.

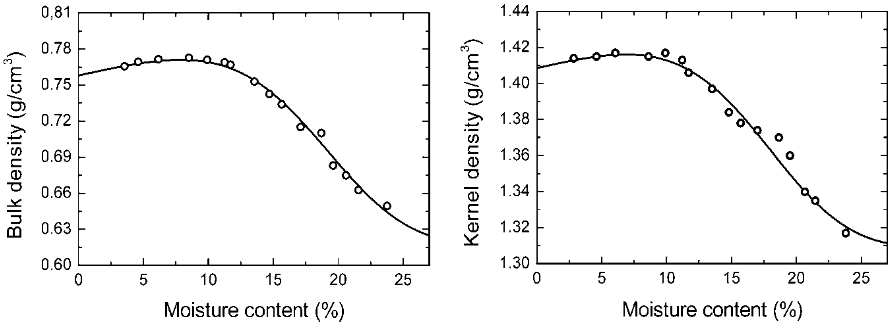


**Figure 1.** Dependence of the bulk density (left) and the kernel density (right) of hard red winter wheat on moisture content at 24°C: the experimental data [15] (points) and their theoretical approximation by Equation (2) (lines).

The ratio $K$ is usually determined under the assumption that each disperse particle is embedded into an equivalent continuous medium with some effective dielectric permittivity [24–27]. For bulk grain as a system having relatively high concentration of disperse particles, it is natural to suppose that this effective permittivity is equal to the mean dielectric permittivity $\varepsilon_g$ of the whole system. Then for the value K we can write the general expression [29]

$$K = \frac{D}{1 + [(\varepsilon_k/\varepsilon_g) - 1]\, S} \tag{4}$$

where $D$ and $S$ are the complex parameters, which have the sense of coefficients that take into account the dimensions and the shape of disperse particles. In the absence of external actions inducing predominant spatial orientation of kernels in a sample (pressure, long-duration shaking), one can assume that kernels are orientated chaotically in a material. In this case, the mean kernel shape may be considered as close to spherical. At very low frequencies of propagated electromagnetic radiation, the wavelength $\lambda$ exceeds the kernel dimensions by many orders. For this case, one can assume that $D = 1$ and $S = 1/3$ [29, 33]. However, at higher frequencies, corrections to these magnitudes should be introduced [29]. They are proportional to the ratio of the disperse particle mean dimension $d$ to the wavelength $\lambda$

$$D = 1 + C_D(d/\lambda) \quad S = (1/3) + C_S(d/\lambda) \tag{5}$$

where $C_D$ and $C_S$ are the complex coefficients. The method of their determination is presented below.

Substitution of expression (4) into (1) yields a quadratic equation in the grain dielectric permittivity $\varepsilon_g$, if the kernel permittivity $\varepsilon_k$ is known [29]. And inversely, this equation provides the possibility to calculate the appropriate value of the mean kernel permittivity according to the measured value of bulk grain permittivity.

In contrast to the primary disperse system, every kernel as a next-level disperse subsystem is characterized by considerably more complex structure. Here, the determination of the shape of disperse particles and of their spatial arrangement is a difficult problem. Dielectric properties of such systems are described usually by the Lichtenecker's power law of mixing [26, 28]

$$\varepsilon_k^{\theta} = \varepsilon_{ks}^{\theta} v_{ks} + \varepsilon_w^{\theta} v_{kw} \tag{6a}$$

or

$$\ln \varepsilon_k = \theta^{-1} \ln[(1 - v_{kw}) \exp(\theta \ln \varepsilon_{ks}) + v_{kw} \exp(\theta \ln \varepsilon_w)] \tag{6b}$$

where $\theta$ is a real index of power, $\varepsilon_w$ is the dielectric permittivity of water, $v_{kw}$ is its volume fraction inside kernels, $\varepsilon_{ks}$ and $v_{ks} = 1 - v_{kw}$ are the dielectric permittivity and the volume fraction of the remaining kernel material, accordingly. The last is solid organic substance filled in by developed network of air microcapillaries. For them we also can write:

$$\varepsilon_{ks}^{\chi} = \varepsilon_{sm}^{\chi} v_{sm} + \varepsilon_{a}^{\chi} v_{sa} \tag{7a}$$

or

$$\ln\varepsilon_{ks} = \chi^{-1} \ln\left[v_{sm} \exp\left(\chi \ln \varepsilon_{sm}\right) + v_{sa}\right] \tag{7b}$$

where $\chi$ is another real index of power, $\varepsilon_a = 1$ and $v_{sa}$ are the dielectric permittivity and the volume fraction of air in the kernel volume with no water, $\varepsilon_{sm}$ and $v_{sm}$ are the dielectric permittivity and the volume fraction of solid substance in this volume, accordingly.

The value of the index $\theta$ or $\chi$ can vary over a limited range, $-1$ to $+1$, and is usually determined by a mutual location of components in a disperse system [26, 28]. In order to refine this statement, the following supposition has been put forward in [29], that this value is connected with the spatial arrangement order of such location. It is known, that $\theta = \pm 1$ or $\theta = 0$ for the cases when different components of a heterogeneous system are separated as plane alternated layers or, on the contrary, are rather well mixed as small-disperse phases [26, 28]. These limiting cases may be considered as corresponding to the greatest spatial order and disorder of a disperse system. For intermediate cases $(0 < \theta < 1)$ the supposition [29] leads to the assumption that decrease of confusion and elevation of spatial order in location of components results in a rise of the value of the index $\theta$ or $\chi$. Thereby, the notion of dielectric order has been introduced for disperse systems, and this notion was related directly with the value of the index of power law (6) or (7) for dielectric permittivity of the considered system [29].

It will be assumed that the indexes $\theta$ and $\chi$ in (6) and (7) are not equal one to the other. It may correspond to a heterogeneous distribution of water particles inside air microcapillaries of kernels, when the spatial structure of water particle distribution differs from the spatial structure of the air microcapillary system. Moreover, small particles of water absorbed by kernels can embed directly into solid organic substance of a kernel increasing their volume and avoiding available air micropores [29]. This phenomenon can be explained as the formation of new microcracks inside a solid substance under the process of moisture absorption by kernels [32] and immediate filling in of them by absorbed water.

It will be also assumed below, that volume, density and dielectric properties of the solid organic substance of a kernel are unchanged at various moisture contents, if this substance does not contain air microcapillaries and microcracks which can be filled in by water. Of course, it is an approximation, because bulk grain is an active biological system. However, this assumption is necessary to remain within the framework of phenomenological treatment and to role out of it parameters, which are difficult to determine and to measure.

According to Equation (6), in the limiting case of moisture absence in kernels ($M \to 0$), their dielectric permittivity $\varepsilon_k$ ($\varepsilon_k \to \varepsilon_{dk}$) should coincide with the permittivity $\varepsilon_{ks}$: $\varepsilon_{ks} = \varepsilon_{dk}$. Then in this case for the dielectric permittivity of the solid substance $\varepsilon_{sm}$ from (7) we obtain

$$\ln \varepsilon_{sm} = \chi^{-1} \ln \left[ v_{dsm}^{-1} \exp \left( \chi \ln \varepsilon_{dk} \right) - v_{dsa} v_{dsm}^{-1} \right]$$

In view of the last relationship, Equation (7b) at any $M$ takes the form

$$\ln\varepsilon_{ks} = \frac{1}{\chi} \ln \left( \frac{v_{sm}}{v_{dsm}} \exp(\chi \ln \varepsilon_{dk}) + v_{sa} - \frac{v_{dsa}}{v_{dsm}} \right) \tag{8}$$

Definition (3) provides the possibility to establish that the dry kernel mass is proportional to the mass of moist kernels: $m_{dk} = m_k(1 - M)$. From here, taking into consideration the relationship between mass, density and volume ($m = \rho V$), we can write

$$V_{dk}/V_k = (\rho_k/\rho_{dk})(1 - M) \tag{9}$$

Besides, directly from definition (3) we receive the following equation for the volume fraction of water in kernels $v_{kw} = V_{kw}/V_k$

$$v_{kw} = M\rho_k/\rho_w \tag{10}$$

Let us assume that the mean water density $\rho_w$ coincides with the density of free water: $\rho_w = 1\,\mathrm{g/cm^3}$. Although the structure of bound water is considered usually as similar to the structure of ice, its density (near $0.92\,\mathrm{g/cm^3}$) does not much differ from the density of free water. Such distinction is not essential in comparison with the distinction of dielectric properties between these water phases.

Volume of kernels is combined by the volume of solid substance, the volume of air microcapillaries and the volume of water. Hence, the following relationship takes place for the volume fractions $v_{ks}$, $v_{ka}$ and $v_{kw}$ of these phases in kernels

$$v_{ks} + v_{ka} + v_{kw} = 1 \tag{11}$$

Let the volume of air micropores vanish at some value $M_0$ of moisture content. Then the volume of solid substance $V_{ks}$ will be equal to the kernel volume $V_k$ except for the water volume $V_{w0}$: $V_{ks} = V_{k0} - V_{w0}$, or $V_{ks} = V_{k0}[1 - M_0(\rho_{k0}/\rho_w)]$. Here, additional lower index "0" denotes the value of a parameter at $M = M_0$. Since volume $V_{ks}$ is considered as unchanged, then for any moisture content $M$

$$v_{ks} = V_{ks}/V_k = V_{k0} V_k^{-1} [1 - (\rho_{k0}/\rho_w)]$$

The ratio $V_{k0}/V_k$ of kernel volumes can be expressed in terms of their densities using Equation (9) at two different moisture contents $M$ and $M_0$. Then

$$v_{ks} = \frac{\rho_k(1-M)}{\rho_{k0}(1-M_0)}\left(1 - M_0\frac{\rho_{k0}}{\rho_w}\right) \tag{12}$$

In that way, two among three volume fractions in Equation (11) have been determined using (10) and (12). Therefore, the remaining third fraction of air capillaries in kernels can be calculated from the equation: $v_{ka} = 1 - v_{ks} - v_{kw}$. The other volume parameters in Equations (7) and (8) are determined by the simple relationships: $v_{sa} = v_{ka}/v_{ks}$; $v_{sm} = 1 - v_{sa}$, and similarly for the case when $M \to 0$: $v_{dsa} = v_{dka}/v_{dks}$; $v_{dsm} = 1 - v_{dsa}$.

For the value of moisture content $M_0$, corresponding to zero-value of air volume inside kernels, one can take the value $M$, for which air volume fraction is minimal. It can be easily established by means of test calculations using density dependencies (2) and Equations (10)–(12). For bulk grain of hard winter wheat, it will be the value of $M_0 = 13.8\%$. Then Equations (10)–(12) determine unambiguously the volume fractions of all three phases inside kernels at various values of moisture content $M$, if the dependence (2) of the kernel density on $M$ is taken into account. Corresponding plots are presented in Fig. 2. The graph for relative value $\Delta V_k/V_{dk} = (V_k - V_{dk})/V_{dk}$ which was calculated by means of Equation (9), is also displayed here. It shows clearly, how much the kernel volume $V_k$ is changed in the process of water absorption, relative to its volume $V_{dk}$ in the absolutely dry condition.

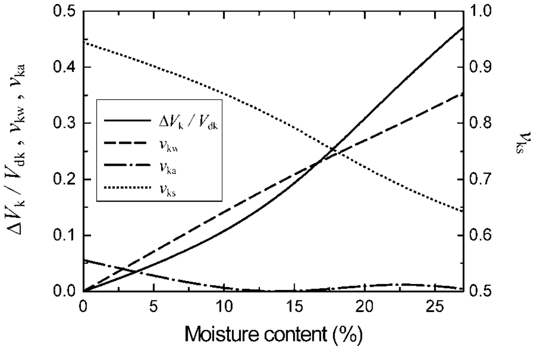


**Figure 2.** Volume fractions of water $v_{kw}$, of air $v_{ka}$ and of solid substance $v_{ks}$ in kernels of hard red winter wheat and the relative change of kernel volume $\Delta V_k$ in comparison with the volume of dry kernels $V_{dk}$ as functions of moisture content at 24°C.

The fact that air volume inside kernels at $M = M_0$ was supposed to be equal to zero, does not signify full filling of all air microcapillaries by water at this value of moisture content. It is enough to regard that for this case, remaining air micropores in kernels are never filled in by moisture. Then their influence on the kernel dielectric permittivity in (7) will be included into the solid substance permittivity $\varepsilon_{ks}$, because the latter is expressed in terms of the dielectric permittivity $\varepsilon_{dk}$ of absolutely dry kernels via relationship (8).

So, if the complex dielectric permittivity of dry kernels $\varepsilon_{dk}$, the dielectric permittivity of water $\varepsilon_w$ and also values of the indexes $\theta$ and $\chi$ in the power mixing rules are known, then we can calculate the complex dielectric permittivity of bulk grain depending on its moisture content by Equations (1), (2), (4)–(8), (10)–(12). Besides, one should know the coefficients $C_D$ and $C_S$, which determine the frequency dependence of the kernel dimension and shape parameters $D$ and $S$ (5). However, the influence of these coefficients will be appreciable only at relatively high frequencies above 1 GHz.

The proposed model also provides the possibility to solve the inverse problem of bound water permittivity evaluation using measured values of the bulk grain dielectric permittivity at various moisture contents. In the next part of this article the solution of this problem is considered.

## 3. DIELECTRIC PROPERTIES OF BOUND WATER

The data on complex permittivity measurements for bulk grain of hard winter wheat at various frequencies and at the temperature $t = 24°\mathrm{C}$ are presented in [15]. These data were digitized from the plots of [15] and are reproduced in Fig. 3 for some frequencies. In the process of their analysis, one immediately pays attention to some generalities. Firstly, the permittivity is decreased with increasing frequency, and this rule is satisfied strongly for the real part (dielectric constant) and approximately for the imaginary part (dielectric loss factor) of the bulk grain dielectric permittivity [15]. Secondly, both the real and the imaginary parts of it are increased monotonically with increasing the moisture content $M$. In the cases of high frequencies, the most quick growth of their values takes place in the range from 5% to 15% moisture content, and then at $M > 15\%$ it becomes slower. However, at low frequencies the reverse dependence exists: at first one observes slow rise of the dielectric constant and the loss factor with increasing $M$, but then at $M > 18\%$ these values display the fast-moving growth. For this, the absolute value of $\varepsilon_g$ can reach a magnitude more than 700 relative units (at the frequency of 250 Hz), that is nearly by an

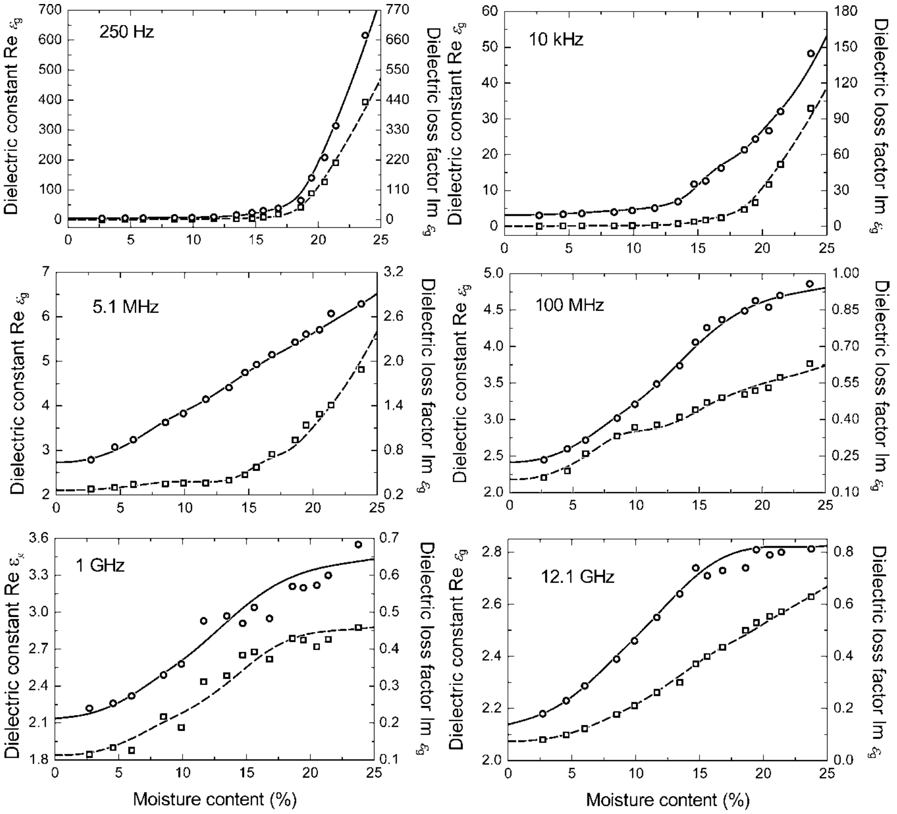


**Figure 3.** Dependence of complex dielectric permittivity $\varepsilon_g$ of hard red winter wheat on moisture content at 24°C and at various frequencies: the experimental data [15] (points) and results of theoretical computation (curves). The circles and the solid lines show the dielectric constant Re$\varepsilon_g$, the squares and the dashed curves indicate the dielectric loss factor Im$\varepsilon_g$.

order of magnitude greater than that of free water and ice at the same frequency [30]. But, according to the mixing laws (1) and (6), the permittivity of a mixture is smaller in magnitude than permittivities of its constituents. Hence, the magnitude of water dielectric permittivity should more exceed the said value. Therefore, at low frequencies bound water inside kernels reveals properties, which essentially differ from the properties of free water and ice. Probably, the simplest explanation of this fact is following: kernels accumulate not pure water but aqueous solution of different substances, which come here from solid phase. However, Equations (8)–(12) for the dielectric permittivity of solid substance in kernels have been obtained under supposition, that its volume, density and dielectric properties remain constant independently on moisture content. Both these suppositions will be not in contradiction, if one assumes that the quantity of substance dissolved in water is negligible in comparison with the total mass of solid substance, and its loss does not have an appreciable effect on volume, density and dielectric permittivity of remaining solid mass of kernels. Otherwise, the theoretical determination of volume fractions and permittivities of different phases inside kernels will be extremely complicated.

Let us consider the following relationship describing the functional dependence of the dielectric permittivity $\varepsilon_w$ of aqueous solutions on frequency $\omega$ [31]

$$\begin{aligned}\varepsilon_w(\omega) \;=\; & \varepsilon(\infty)+\frac{\varepsilon(0)-\varepsilon(\infty)}{1-i\omega\tau_w}+\sum_m \frac{P_m}{1-i\omega\tau_m}+\frac{i}{\omega}\sum_n Q_n\sigma_n \\ & +\sum_k R_k\frac{\omega_k\Gamma_k}{\omega_k^2-\omega^2-i\omega\Gamma_k} \qquad (13)\end{aligned}$$

where $P_m$, $Q_n$ and $R_k$ are the amplitude factors which are frequency-independent. The first two addends in the right-hand side of (13) describe the dipole relaxation of pure water under the Debye approximation (here $\varepsilon(0)$ and $\varepsilon(\infty)$ are the limiting values of its dielectric permittivity $\varepsilon$ at $\omega \to 0$ and at $\omega \to \infty$ accordingly, $\tau_w$ is the relaxation time). The next two addends characterize the contribution of solutes to the resulting dielectric permittivity due to dipole relaxation and ionic conductivity. Here, the possibility of presence of different substances with various relaxation times $\tau_m$ and with various ionic conductivities $\sigma_n$ is taken into account. Besides, the last addend was introduced into the right-hand side in order to describe the resonance processes [34] at the frequencies $\omega_k$ with the dissipation coefficients $\Gamma_k$. Usually, such processes are connected with electronic polarization and are observed at optical frequencies. But, they can be caused by the intramolecular oscillations of mobile fragments of complex molecules, as occurs in liquid crystals under the influence of electromagnetic field [35]. In this case, the resonance frequencies are within the microwave range, and resonant amplitudes are not relatively great here. These two special features of microwave resonances for complex molecules can be conditioned by small mobility and large mass of oscillating molecular fragments.

The monotonic decrease of the real part of the resulting permittivity (dielectric constant) (13) with increasing frequency is connected with the Debye law of dipole relaxation of water as itself and of solutes, whereas for the imaginary part (dielectric loss factor), this law causes the presence of local peaks. The monotonic decrease of the last value is maintained by another mechanism — ionic conductivity of a solution. It is necessary to add that every resonance of intramolecular oscillations determines local rise of the real and the imaginary parts of the permittivity (13) on isolated frequency ranges.

The amplitude coefficients $P_m$, $Q_n$ and $R_k$ in (13) are dependent on the concentrations of corresponding solutes. But, character of these dependences is unknown, and it is unknown how the concentrations of different substances in water are changed under the change of its mass content in kernels. That is why Equation (13) will be considered only as an illustration, and more rigorous study of bound water dielectric properties will be carried out by using the expansion of its dielectric permittivity in functions explicitly depending on grain moisture content.

Usually, in similar cases, one applies a resolution of unknown function into an infinite system of orthogonal functions (sines, cosines or the Legendre polynomials). But, we shall attempt to apply a system of basic functions, which is not orthogonal one to another, in order to have a possibility of confining their number to a minimum. With that end in view, we need a special choice of basic functions, being close to the initial unknown function. In this case, it is a complicated problem. On the one hand, the exact solution for the bound water permittivity at various frequencies should be known for their determination, on the other hand, from the beginning, such a solution should be considered as an expansion in given functions. However, it appeared in the calculation process that the general view of the bound water functional dependence on moisture content is insignificantly dependent on the initial parameters. Therefore, the choice of basic functions and the determination of water permittivity can be developed under the method of successive approximations.

In Fig. 4, there are shown the values of complex dielectric permittivity of bound water in kernels, which where calculated through the use of Equations (1), (2), (4)–(8), (10)–(12) for experimental values of bulk grain permittivity [15] (Fig. 3) at the following magnitudes of parameters

$$C_D = 0.08 + 0.25i; \quad C_S = 1 \tag{14}$$

$\chi = 0.25$; $\theta$ is about 0.5, and the dielectric permittivity of absolutely dry kernels $\varepsilon_{dk}$ corresponds to the values shown in Fig. 5. At small variations of the said parameters, the general view of the functional dependences shown in Fig. 4 remains almost the same. For specific statement of the problem, it is enough to evaluate roughly the behavior of the bound water permittivity dependence on moisture content.

The first basic function is chosen in order to be close to the dependence of the water dielectric constant at the highest frequency (12.1 GHz; Fig. 4), because the influence of solutes on its permittivity should be minimal here. We shall use the function

$$w_1(M) = 2.65\frac{\sqrt{(4M)^2 + 0.09} - 0.3}{(4M)^3 + 1} \tag{15a}$$

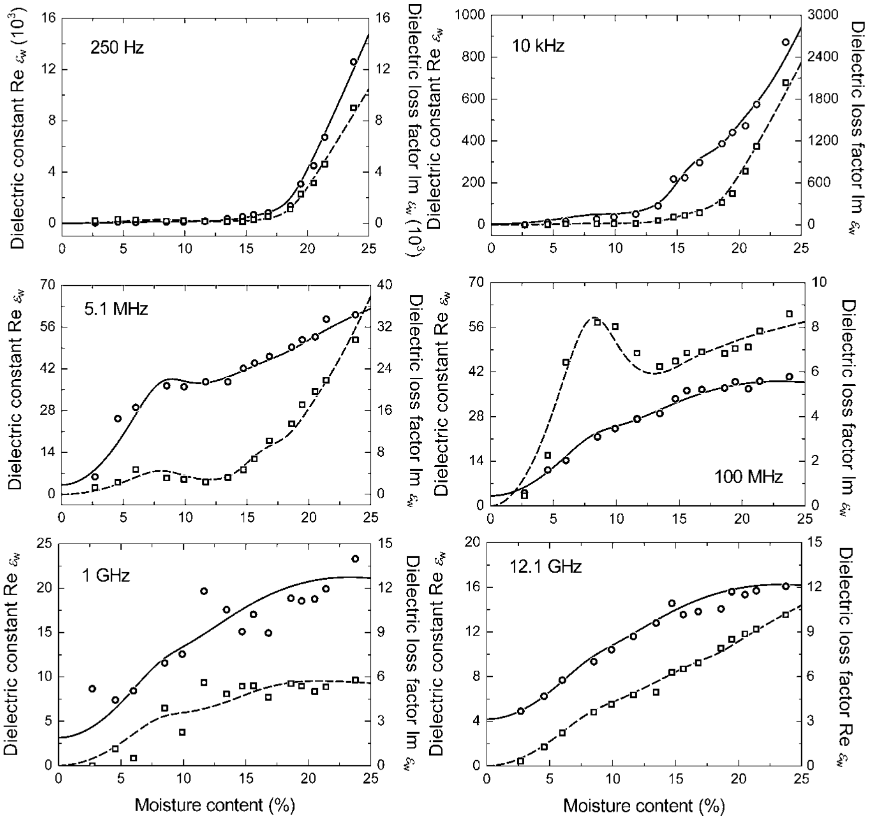


**Figure 4.** Dependence of complex dielectric permittivity $\varepsilon_w$ of bound water inside kernels of hard red winter wheat on moisture content at 24°C and at various frequencies: the results calculated for the experimental data [15] (points) and the results of calculations according to the present theoretical model (curves). The circles and the solid lines show the dielectric constant Re$\varepsilon_w$, the squares and the dashed curves indicate the dielectric loss factor Im$\varepsilon_w$.

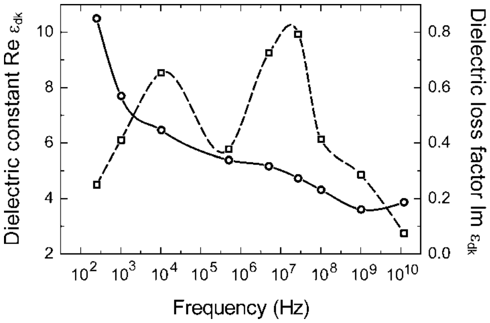


**Figure 5.** Complex dielectric permittivity $\varepsilon_{dk}$ of dry kernels of hard red winter wheat as a function of frequency at 24°C: computed values (points) and their mathematical interpolation (curves). The circles and the solid lines show the dielectric constant Re$\varepsilon_{dk}$; the squares and the dashed curves indicate the dielectric loss factor Im$\varepsilon_{dk}$.

When frequency is decreased, the plots in Fig. 4 demonstrate appearance of humps with the maximums at $M = 0.09$ and at $M = 0.17$. These additional humps can be described by functions

$$w_2(M) = 1.75\frac{(M/0.09)^2}{1+(M/0.09)^8} \tag{15b}$$

$$w_3(M) = \begin{cases} 0; & M \le 0.03 \\ 0.65\left(\dfrac{u_1}{\sqrt{1+u_1^2}} - \dfrac{u_2}{\sqrt{1+u_2^2}}\right); & M > 0.03 \end{cases} \tag{15c}$$

where $u_1 = (M - 0.15)/0.02$ and $u_2 = (M - 0.21)/0.03$. Finally, one should take into account the possibility of rapid increase of the permittivity with moisture content increase beginning from $M = 0.18$ and up to $M = 0.25$ at low frequencies. Such an increase can be simulated additionally by the following function

$$w_4(M) = 0.4\left\{20M + \sqrt{[20(M-0.185)]^2 + 0.08} - 3.7108\right\} \tag{15d}$$

The numerical parameters of the functions (15a)–(15d) were selected by fitting to the above mentioned dependence at the highest frequency, and to the mentioned above additives appearing at low frequencies, to within a constant addend and a multiplier.

The dielectric permittivity of bound water in kernels will be sought in the form of the following decomposition

$$\varepsilon_w(M) = a_{w0} + a_{w1}w_1(M) + a_{w2}w_2(M) + a_{w3}w_3(M) + a_{w4}w_4(M) \tag{16}$$

where $a_{wm}$ $(m = 0, 1, 2, 3, 4)$ are the complex coefficients, which are independent of grain moisture content and having the dimensions of $\varepsilon$, $w_n(M)$ $(n = 1, 2, 3, 4)$ are the real dimensionless functions (15), which are shown graphically in Fig. 6. These functions are normalized in such a way that at a maximum they reach values approximately equal to unity.

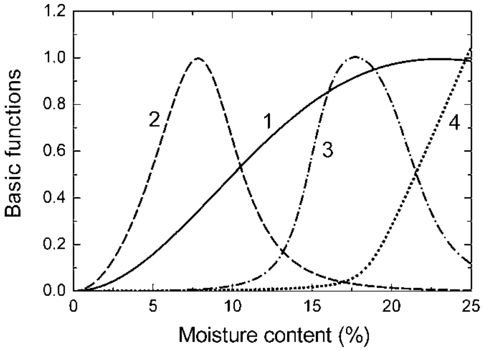


**Figure 6.** Basic functions of moisture content used for the simulation of bound water permittivity.

At $M \to 0$, the functions $w_1$, $w_2$, $w_3$ and $w_4$ tend to zero, hence in this case $\varepsilon_w \to a_{w0}$. Let us consider the physical sense of this result. Every separate kernel as a porous disperse system is characterized by strong hydrophilic properties. If the moisture absorbed by dry grain at first it tends to form a monomolecular layer on walls of air microcapillaries, because the water molecules of this layer interact with active sorption centers the most actively [32]. And inversely, in the process of grain drying the moisture from this layer is extracted at the last moment. Hence, it follows that the coefficient $a_{w0}$ describes the dielectric permittivity of bound water in the monomolecular interfaces layer.

However, here the idea is rather about general tendency than about strict law. When the quantity of absorbed water is increased, air microcapillaries are filled in by water nonuniformly: somewhere the monomolecular layer only arises, and somewhere else the layers of two and three water molecules appeared, for which the permittivity is increased and approaches the permittivity of free water. Rather fast growth of the function $w_1$ (15a) at moisture content over 3% shows it (see Fig. 6). But, after reaching the value of the moisture content $M = 15\%$, this growth is decelerated, and then, at $M = 22\%$, it is ended entirely. Such behavior of the functional dependence $w_1$ can be explained by the increase of bound water fraction in the interfaces layer or directly near it. Indeed, in the process of filling in of kernels by moisture at reaching the moisture content value more than 15%, the solid substance of kernel endosperm is partially damaged with the formation of thick network of microcracks [32], which surface causes extension of the interfaces layer. This fact is verified also by the calculation of volume fractions of different phases in kernels based on the density measurements (see Fig. 2). At moisture content $M$ more than 15%, the value $\Delta V_k/V_{dk}$ of relative increase of kernel volume begins to increase more rapidly than the volume fraction of water $v_{kw}$, and the air volume fraction $v_{ka}$ is increased again after reaching the minimum at $M \approx 14\%$. Such behavior is possible, if the volume of air microcavities inside kernels is increased more rapidly than the volume of sorbed water, with the increase of moisture content.

The function $w_2$ (15b) is characterized by more rapid increase than $w_1$, but after reaching the maximum at $M = 9\%$ it decreases rapidly. Probably, this function, as other functions (15c), (15d), describes the contribution of some dissolved substances to the bound water dielectric permittivity (16), and their dependencies on moisture content can be explained by the change of concentrations of these substances in bound water. From this point of view, the substance corresponding to the function (15b) is well entrained by moisture to the surface of the interface monomolecular layer. But, with the increase of absorbed water mass and with the approach of its properties to the properties of free water, this substance is precipitated from the solution. Similar behavior is typical also for another dissolved substance, which contribution is described by the function $w_3$ (15c). Probably, the increase of this substance concentration in the bound water solution causes precipitation of the previous substance from the solution. And the fourth function $w_4$ (15d) can describe contribution of one more substance, which starts to dissolve only at the presence of sufficient quantity of water with properties approaching the properties of free water. Therefore, we can conclude that the functions (15) characterize the change of concentration of solutes in bound water inside kernels due to the change of their moisture content.

It should not be regarded that the function $w_1$ describes the dielectric permittivity of pure water, and only $w_2$, $w_3$ and $w_4$ characterize the presence of solutes. This function also can correspond to an aqueous solution of one or even several substances, if their concentrations in bound water are constant and are independent of grain moisture content. In the same way, each of the functions $w_2$, $w_3$ and $w_4$ can describe contributions of several various substances simultaneously, if their concentrations in water change equally with the change of moisture content.

In order to determine the unknown coefficients $a_{wm}$ ($m = 0, 1, 2, 3, 4$), let us set up the following functional

$$F = \sum_{j=1}^{N} \left| \varepsilon_{gj}^{(\exp)} - \varepsilon_g(M_j) \right|^2 \tag{17}$$

where $\varepsilon_{gj}^{(\exp)}$ are the values of bulk grain dielectric permittivity which were measured in experiment [15] for one frequency and $N$ various values of moisture content $M_j$ ($N = 15$), $\varepsilon_g(M_j)$ are the values of the same quantity, which are calculated theoretically for the same values of moisture content $M_j$ through the use of Equations (1), (2), (4)–(8), (10)–(12) after substitution of relations (15), (16) into (6). The minimum of the functional (17) will be sought by varying coefficients $a_{wm}$ and calculating the sums over all measured values of moisture content [15] for every frequency. In addition to these five coefficients, we should take into consideration the presence of the following unknown values: the coefficients $C_D$ and $C_S$ of the kernel dimension and shape parameters $D$ and $S$ (5), the indexes $\theta$ and $\chi$ of the power mixing laws (6) and (7), and also the dielectric permittivity $\varepsilon_{dk}$ of dry kernels. In the general statement, the problem for minimization of the functional (17) with such a large number of unknowns becomes ambiguous and allows a lot of different solutions. In order to remove this ambiguity, a series of obvious conditions are imposed, which permit selection of the unique solution of the minimization problem for the functional (17).

- For the coefficients $a_{wm}$ determining the dielectric permittivity (16) of bound water, we seek the solutions, which should provide predominant decrease of their imaginary and especially of their real parts with frequency increase. We start with the statement, that the main mechanisms of polarization of an aqueous solution are dipole-orientational and ionic ones. As far as it is known for us, for bound water within most of disperse systems, the resonance mechanism was not detected. Hence, for the coefficients $a_{wm}$ solutions are sought which have a minimal number of resonances, corresponding to the regions of local increase for the real parts of these coefficients with increasing frequency. The same conditions will be also imposed on the dielectric permittivity $\varepsilon_{dk}$ of dry kernels.
- A solution for the complex coefficient $a_{w0}$ is sought being the closest to the dielectric permittivity of ice [13, 14, 30] (at least, over a certain frequency range it should be real value 3.16).
- As supposed above, the concentrations of substances in the aqueous solution can change under moisture content change, and it causes the different behavior of the functions $w_m$ ($m = 1, 2, 3, 4$) (15)

(Fig. 6) with moisture content. Therefore, molecules and ions of these substances within the aqueous solution are in the state allowing free transition from kernel solid phase to the solution and inversely. Apparently, the bond energy for ions or molecules of the substances corresponding to the functions $w_2$, $w_3$ and $w_4$ in the solute, is about the same or even less than the bound energy for them within the solid phase. Thus, one more limiting condition is deduced in the application of the minimization problem for the functional (17): a solution should be sought having a minimal value of the coefficients $a_{w2}$, $a_{w3}$ and $a_{w4}$ which will describe a minimal concentration of corresponding substances in the aqueous solution.

- Dielectric permittivity $\varepsilon_{dk}$ of dry kernels can be approximately evaluated by Equations (1), (2), (4), if one uses the limiting value of the dielectric permittivity $\varepsilon_g$ of bulk grain at zero moisture content. The last value can be determined by polynomial extrapolation of the measured values of $\varepsilon_g$ [15] for the samples with small moisture content $M$ into the point $M \to 0$. The approximate value of dry kernel dielectric permittivity $(\varepsilon_{dk})_{ref}$, found in this way, can be used as the initial approximation for calculation of exact value $\varepsilon_{dk}$, and then we can introduce the additional condition enforcing the minimum for the value of $|(\varepsilon_{dk})_{ref} - \varepsilon_{dk}|^2$.
- The real and the imaginary parts of the bound water dielectric permittivity $\varepsilon_w$ obtained as intermediate results in the calculation process of the functional (17), should be positive values at any moisture content and frequency.
- The minimal value should be selected among all possible values of the indexes $\theta$ and $\chi$ for the power mixing laws (6) and (7), which are in conformity with all previous conditions. These minimal values should correspond in the best way to the rather disordered location of different phases inside kernels, which are characterized by extremely developed porous structure.

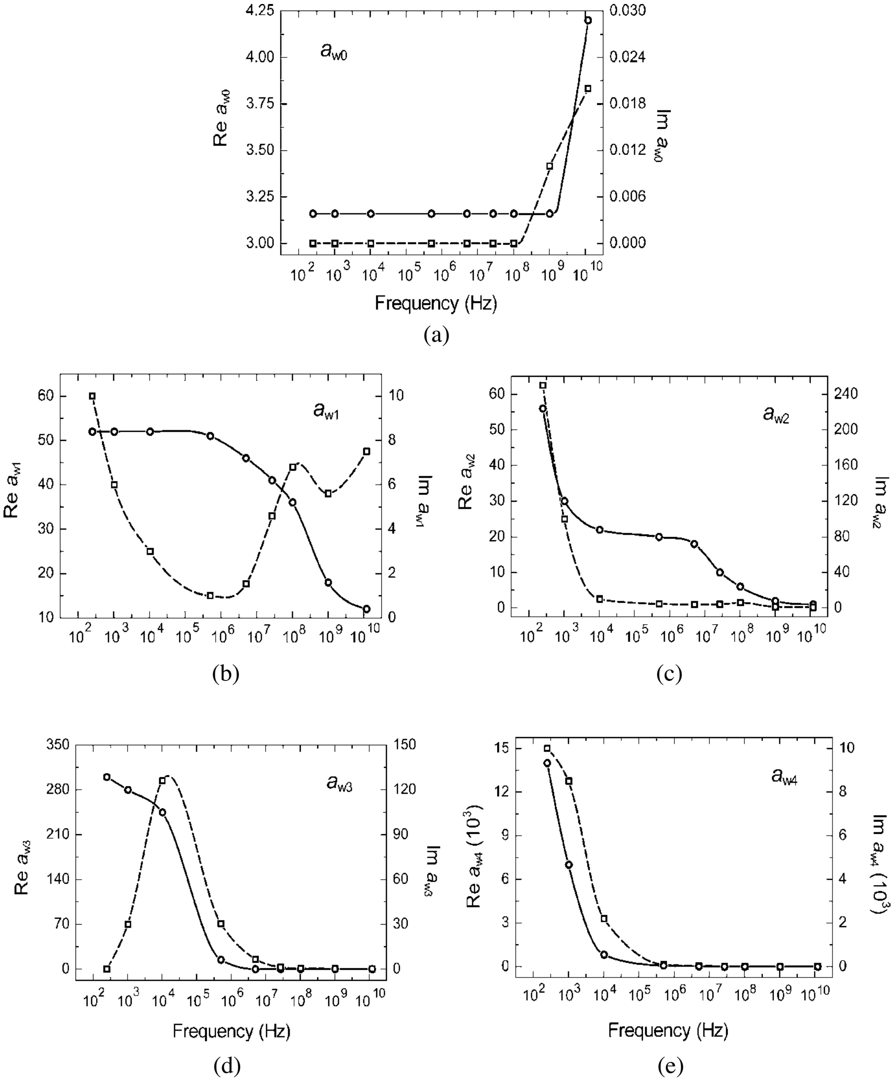
In order to solve the minimization problem for the functional (17), the numerical method of descent done in turn of coordinates was used taking into consideration the above pointed conditions. This solution for the coefficients $a_{wm}$ $(m = 0, 1, 2, 3, 4)$ and for the dielectric permittivity $\varepsilon_{dk}$ of dry kernels at various frequencies is presented graphically in Figs. 5 and 7. The points in these figures show the found values of parameters for every frequency, specifying the experimental data in [15], and the lines connecting these points were obtained by the method of spline interpolation for intermediate frequency ranges. If was assumed that the mean kernel dimension is $d \approx 3\,\text{mm}$, and that the solutions for the coefficients $C_D$ and $C_S$ determining the dimension and shape parameters (5), correspond to the values (14). Here, for the index $\chi$ of the power mixing law, the constant value of 0.25 was used. It is a minimal value providing positivity of the dielectric constant and of the loss factor of bound water. But for the index $\theta$, we proposed the following dependence on moisture content $M$

$$\theta = \frac{1}{4}\frac{u}{\sqrt{1+u^2}} + \frac{1}{2}; \quad u = 2(10M - 1) \tag{18}$$

It increases with increasing moisture content from 0.25 at $M \to 0$ to 0.75 at $M = 0.25$ (Fig. 8). This dependence was selected under the following considerations. At low moisture contents, the value of $\theta$ should be as minimal as possible, taking into account the condition of positivity for values of the bound water dielectric constant and its loss factor. But calculations show, that at $M > 10\%$, such small value as 0.25, can not provide sufficiently fast growth of the real and the imaginary parts of grain dielectric permittivity with increasing moisture content $M$, as observed for experimental data [15] (see Fig. 3). So, we should ensure the possibility for value $\theta$ to increase continuously with increasing $M$, when the latter approaches 10%.

Let us consider the diagrams in Fig. 7 showing the frequency dependence of the coefficients representing the bound water permittivity decomposition in the basic functions $w_n$ (15). Over the wide frequency range, the coefficient $a_{w0}$ is the constant real value of 3.16, and only at the frequencies more than 100 MHz, the growth of the real and imaginary parts of this coefficient is observed (Fig. 7(a)). Probably, at the frequency slightly exceeding the maximal experimental frequency [15] of 12.1 GHz, there is a resonant peak of molecular oscillations. In this frequency range near 20 GHz, there is a location of the Debye dipole-orientational relaxation frequency of free water [30, 31], which is caused by the heat motion of weekly bound dipole-molecules. However, the appearing of resonance polarization mechanism is possible only for strong bond [34]. Probably, such bond arises between water molecules and the surface of solid kernel substance, on which these molecules locate as a thin monomolecular layer.

The frequency dependence of the real and the imaginary parts of the coefficient $a_{w1}$ (Fig. 7(b)) are typical for aqueous solutions [31]. Decrease of the imaginary part with increasing frequency at low frequencies displays the presence of the ionic polarization mechanism. The real part of this coefficient is constant here, and only at frequencies over 1 MHz its value is decreased monotonically. Such behavior displays also the presence of the dipole-orientational polarization mechanism. It should cause existence of local maxima of the imaginary part, and two such maxima are present on the plot: one at the frequency about 140 MHz and the other possible one at the frequency



(a)

(b) (c)

(d) (e)

**Figure 7.** Decomposition coefficients for the complex dielectric permittivity of bound water inside kernels of hard red winter wheat versus frequency at 24°C: computed values (points) and their mathematical interpolation (curves). The circles and the solid lines show the real parts of these coefficients, the squares and the dashed curves indicate their imaginary parts.

more than 10 GHz. Perhaps, the first maximum is caused by the presence of dipole-molecules of a certain solute in water, and the second one more likely corresponds to the relaxation frequency of water itself ($\approx$ 19 GHz, [30, 31]).

The plots for the coefficient $a_{w2}$ (Fig. 7(c)) are similar, but the conductivity value for ions in a solute is more significant here. The relaxation mechanism of polarization for this solute determines decrease of the real part of $a_{w2}$ at the frequencies less than 10 kHz and more than 1 MHz, as well as the presence of one peak of the imaginary part at the frequency about 100 MHz (the contribution of free water in the polarization is not taken into account by this coefficient). Probably, the other possible maximum of the imaginary part at low frequencies is completely concealed by the presence of strong ionic conductivity.

The frequency dependence of the imaginary part of the coefficient $a_{w3}$ is presented graphically as the wide peak located at the frequency $f_{rel} \approx 15$ kHz (Fig. 7(d)). The ionic mechanism does not occur just here, hence, one can conclude that molecules of the solute corresponding to this coefficient remain as electroneutral in the solution. Perhaps, such low relaxation frequency $f_{rel}$, as it takes place for the coefficient $a_{w3}$, is provided by relatively large relaxation time $\tau_{rel} = 1/(2\pi f_{rel}) \approx 10^{-5}$ s, which can correspond to large-scale torsion oscillations of some polymeric macromolecules or of their fragments.

At last, the plots of the real and the imaginary parts of the coefficient $a_{w4}$ (Fig. 7(e)) demonstrate rather giant dispersion with very large relaxation time and with so small relaxation frequency, that the peak of the imaginary part is almost invisible against a background of the contribution of ionic conductivity. These two graphs are like the spectral dependence of the dielectric permittivity for an aqueous suspension of erythrocytes [31], which are conditioned by the specific display of the ionic conductivity mechanism under the presence of polymeric macromolecules.

The graphs, demonstrating the frequency dependences of the dielectric constant and the dielectric loss factor of dry kernels (Fig. 5), show the possible presence of two relaxation regions for solid kernel phase, nearly 10 kHz and 20 MHz. They have not quite proper appearance for dielectric relaxation plots [31, 34]. Perhaps, it is caused by the fact that the spline interpolation on too thin a grid of experimental frequencies can not reflect the typical form of dielectric relaxation plots. Otherwise, it can be explained by the presence of two relaxation bands but not of two separate lines. These bands may be conditioned by superposition of a set of closely spaced frequencies for the dipole-orientational mechanism of different substances in solid phase.

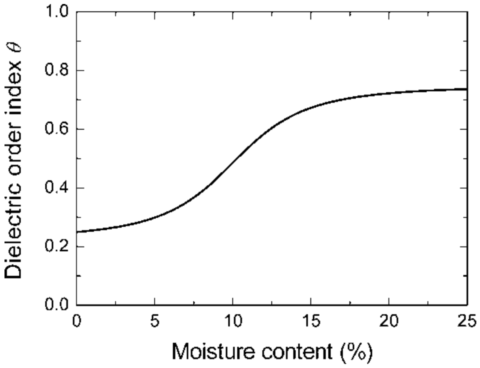


**Figure 8.** Dielectric order index $\theta$ as a function of moisture content in kernels of winter wheat.

In order to show a relationship between the obtained solutions and the experimental data [15], the calculated plots for dependence of the dielectric permittivity of bulk grain and the permittivity of bound water on moisture content are shown in Figs. 3 and 4. They were computed according to Equations (1), (2), (4)–(8), (10)–(12) taking into account the obtained solution (14)–(16), (18) and the numerical data presented in Figs. 5 and 7. It should be noted that similar solutions can be constructed with constant values of the index $\theta$ of the power mixing law (6), but only with values of $\theta$ which are appreciably more than zero, for instance with $\theta = 0.5$. Calculations verify, that such a solution corresponds to experimental data not worse than the former solution having varying index $\theta$, but with more great coefficients $a_{w3}$, $a_{w4}$ and with slightly changed values of some other parameters. So, the effect of continuous modification of dielectric order in grain [29], connected with varying values of $\theta$ under change of its moisture content, can be completely concealed by the effect of inconstancy of the bound water dielectric permittivity. But we still are convinced of the existence of this effect. It is difficult to believe that such a great value as 0.5 for the dielectric order index $\theta$ can exist at small moisture contents, because such value corresponds to rather high spatial order in location of water microparticles inside kernels. They have very developed porous structure, and their substance is in sufficiently disordered state, which should correspond to rather small values of the order index $\theta$. However, such values can not provide sufficiently great values of grain dielectric constant and its loss factor at high moisture contents, as was pointed out above. In this region, for constant values $\theta < 0.3$ one can not achieve a good agreement with experimental data for

$\mathrm{Re}\varepsilon_g$ and $\mathrm{Im}\varepsilon_g$ taking into consideration all necessary conditions. Therefore, the value of the dielectric order index $\theta$ should not be a constant. In addition, we cite one more circumstance based on the independent consideration. According to the thermodynamical approach, in kernels "decreasing of entropy occurs under development of the moisture transport process, and it points out the rise of ordering of the structure (system) grain-water. It is just what is expected, if one proceeds from the notion of diffusion mechanism of moisture transport (high level of chaotic character of water) and from formation of clusters (like bunches of grapes) of its molecules in the region of energetic influence of active sorption centers" [32]. Therefore, increase in absorbed water quantity, causing the rise of intensity of moisture transport process inside kernels, is accompanied by the rise of the order in spatial location of water particles after transition to a steady state. And change of order in spatial location of different components of a disperse system should influence the value of the index of the power mixing law (6) for water inside kernels.

## 4. CONCLUSION

In the present work, some specific properties of bound water in composition of winter wheat kernels have been detected. It is established that water microparticles inside kernels are formed not by reagent-grade water but by an aqueous solution of a number of substances, which come into this solution from kernel solid substance. Five different constituents of bound water dielectric permittivity were separated. As we supposed, the existence of moisture content dependencies for these constituents is due to the presence of four or more various substances within the solution besides water and due to the possibility for the concentration to be changeable under the moisture content change, i.e., the change of total water content inside kernels. Analysis of separated contributions to the total dielectric permittivity of the aqueous solution at various frequencies shows the presence of a dipole-orientational polarization mechanism and ionic conductivity of the substances in the solution. In addition, it appears that the water monomolecular layer located on the surface of kernel microcapillaries has specific physical properties. Over the wide frequency range, its dielectric permittivity is equal to the real value of 3.16 (the dielectric permittivity of ice), but at high frequencies more than 1 GHz, the dielectric constant of water in monomolecular layer begins to increase. We connected this effect with the presence of the resonance peak of molecular oscillations in this layer, which is observed hypothetically at the frequency more than 12 GHz, which is the location of the Debye dipole-orientational relaxation frequency of free water. The possible transformation of the Debye relaxation into the molecular resonance is apparently caused by the existence of strong bonds between water molecules in this layer and the surface of solid kernel substance.

Identification of the substances dissolved in bound water, is a special and rather difficult problem. The available experimental data are not enough to determine relaxation and resonant frequencies of solution components. For example, we can not determine exactly the resonant frequency of water molecules in the monomolecular interface layer, because it is located at higher frequencies than the highest frequency of available experimental data. However, the following circumstance is of more vital importance. Besides relaxation and resonant frequencies, one should know the concentrations of components in a solution, for which determination by the dielectric method is difficult. The contribution of one or another solute to the solution permittivity (16) are determined by the non-dimensional functions $w_n(M)$ $(n = 1, 2, 3, 4)$ (15) with the corresponding coefficients $a_{wn}$. But we do not know to what concentration such a contribution corresponds. Let us say, for namely water it is determined by the function $w_1$ (15a) with the coefficient $a_{w1}$ plus the constant value $a_{w0}$. But this is the contribution averaged over the whole volume of water inside kernels, including both the interface monomolecular layer adjoining to solid walls of microcapillaries, and transition layers having properties which are intermediate between the properties of this layer and of free water. It is known that the dimensions of microcapillaries inside kernels are of the order of $10^{-7}$–$10^{-8}$ cm, or smaller than 1 nm [32]. As it follows from here, the presence of actually separate monomolecular layers, having properties of free water inside kernels, is improbable [12]. In any case, it is clear that even at high values of moisture content, the main mass of absorbed water is in the state, which is intermediate between that of the interface layer and that of free water. For such a state, it is quite possible that the contribution of dipole-orientational polarization mechanism for dissolved organic molecules will be rather different from the similar contribution for the same molecules in the solution of free water.

The described above methodology can be used for study of bound water in composition of other moisture containing disperse systems. For this, one should dispose of experimental data on their complex dielectric permittivity over a broad moisture content range at various frequency or (and) temperature. Also one needs measured values of bulk density and particle density over the corresponding moisture content (and temperature) range.

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