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SUBSTANTIATION OF THE MECHANISM OF INTERACTION BETWEEN BIOPOLYMERS OF RYE-AND-WHEAT FLOUR AND THE NANOPARTICLES OF THE MAGNETOFOOD FOOD ADDITIVE IN ORDER TO IMPROVE MOISTURE-RETAINING CAPACITY OF DOUGH

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Обґрунтовано механізми вологоутримуючої здатності наночастинок (НЧ) поліфункціональної харчової добавки «Магнетофуд» в житньо-пшеничному тісті. Розглянуто механізми взаємодії НЧ харчової добавки «Магнетофуд» з водою у середовищах з різним Rh , а також механізми взаємодії НЧ «Магнетофуд» з іоногенними групами білків, ліпідів, вуглеводів житньо-пшеничного борошна. Запропонована «кластерно-петельно-ланцюгова» модель взаємодії харчової добавки «Магнетофуд» з біополімерами житньо-пшеничного борошна

Ключові слова: поліфункціональна харчова добавка, борошно житньо-пшеничне, механізм взаємодії, «кластерно-петельно-ланцюгова» модель

Обоснованы механизмы влагоудерживающей способности наночастиц (НЧ) полифункциональной пищевой добавки «Магнетофуд» в ржано-пшеничном тесте. Рассмотрены механизмы взаимодействия НЧ пищевой добавки «Магнетофуд» с водой в средах с различным Rh , а также механизмы взаимодействия НЧ «Магнетофуд» с ионногенными группами белков, липидов, углеводов ржано-пшеничной муки. Предложенная «кластерно-петельно-цепочечная» модель взаимодействия пищевой добавки «Магнетофуд» с биополимерами ржано-пшеничной муки

Ключевые слова: полифункциональная пищевая добавка, мука ржано-пшеничная, механизм взаимодействия, «кластерно-петельно-цепочечная» модель

1. Introduction

Dough and ready-made bread are complex hydrophilic colloidal systems. Their state depends on properties of the raw materials used for their preparation, parameters of the

technological process, changes occurring during baking and storage of bread [1, 2]. Therefore, moisture state in dough and bread represents not only theoretical but also practical interest. The following is of great importance for improvement and control of the technological process:

- knowledge of the mechanisms of hydration of main food system components (proteins, fats, carbohydrates);
- control of the processes of sorption-desorption of moisture using technological parameters of the medium (temperature, acidity, etc.);
- control of moisture sorption-desorption processes using manufacturing methods, in particular, introduction of biologically active and food additives.

Magnetofood is a polyfunctional food additive of a complex action. It is a fine-dispersed powder with a particle size of ~78 nm [3]. The nanoobjects that include the Magnetofood have an enormous potential and carry a lot of important fundamental discoveries, new functional and technological properties and promising production applications [4]. It should be noted that most nanomaterials used in food products occupy an intermediate position between nanoscale and microscopic structures. For example, diameter of DNA is 12 nm. Corresponding dimensions are 30...10,000 nm for liposomes, 44...200 nm for amylopectin, 500 nm for cubosomes, <1,000 nm for nanosensors [5].

Nanobiotechnologies form one of the branches of current nano-science that is most actively developing and attracting more and more attention from researchers in various fields of chemistry, physics, biology, biochemistry, medicine and engineering in recent years. Nanobiotechnology can potentially affect many aspects of food technology. Safety and quality of food products, means of delivery of biologically active components, new materials for detecting pathogens and protecting the environment are the main fields of use of nanomaterials in food products [4, 5].

Interaction of the Magnetofood with biopolymers (proteins, proteids, carbohydrates, lipids) is a system of complex chemical reactions. Nucleation of a new, stable phase from an initial metastable phase occurs in this process. An important role is played by supramolecular organization of the Magnetofood nanoparticles and the structure of the organic matrix. This results in formation of spatial nanostructures which significantly affect functional and technological properties of raw materials and semi-finished products.

To explain the mechanism of moisture-retaining power of the Magnetofood food additive nanoparticles and the mechanism of interaction of the Magnetofood nanoparticles with polymers of dough systems, it is necessary to, understand the nature and strength of the interaction of the Magnetofood nanoparticles with water and corresponding substrates [6, 7].

2. Literature review and problem statement

Analysis of literature data [3–11] has shown that various food additives are widely used for adjusting flour properties. Nanoparticles have unusual physical and chemical properties associated with manifestation of so-called “quantum dimensional effects” [8, 9]. These effects are brought about by physical and chemical properties caused by behavior of electrons, namely: size decreases with transition from a macroscopic body to a scale of several hundred or several thousand atoms; density of states of electrons in the valence band and in the conduction band changes sharply. In the first place, “quantum dimensional effects” influence magnetic, electrical, and chemical properties. “Continuous” density of states in macro-objects is replaced in nanoobjects by discrete levels with distances between them depending on the size of particles [10]. Therefore, nanoparticles cease

to demonstrate physical-chemical, biochemical and other properties inherent in the substance macrostate or show them in a modified form. Nanoparticles belong to a separate, intermediate group and are called “artificial atoms”. This is associated with the dimensionally dependent behavior of the nanoparticle properties and atypicality compared with the properties of atoms on the one hand and macroscopic bodies on the other hand [10].

Another major factor affecting physical and chemical properties of nanoparticles is the increase in their relative fraction of “surface” atoms that are in different conditions (coordination number, symmetry of the local environment, etc.) than the spatial phase atoms. That is why a serious change in properties of “surface” atoms occurs which also changes the nature of interaction between the atoms on the surface and those inside the particle which can result in a fundamental alteration of physical and chemical properties. For example, it was proved both theoretically and experimentally that magnetism of surface atoms completely disappears in the “cluster formations” of ferromagnets when applying coating of carbonyl ligands while the magnetic behavior of atoms remains unchanged within the “cluster” [10]. Unique physical-chemical properties (PCP) of nanoparticles are intensively investigated. PCP are determined by many factors: chemical composition; type of lattice, degree of imperfection, size and shape of particles, morphology of particles, especially for particles with a complex structure; interaction of particles with the surrounding matrix and adjacent particles. By changing size, shape, composition, and structure of nanoparticles, it is possible to control physical and chemical characteristics of biomaterials within certain limits [4, 5, 8–11].

The presence of these heterogeneities does not allow us to consider nanoparticles homogeneous in the literal sense because properties of surface and internal regions differ. From the energy point of view, reduction of the particle size results in an increase in the portion of surface energy in the chemical potential which enables an effective interaction with any chemical compounds. The depth of interaction with medium (in particular with biopolymers such as proteins, lipids, carbohydrates) is determined by two main factors: surface energy and nature of the nanoparticle chemical substance [11].

Water-absorbing power of flour and visco-elastic properties of dough are closely related to the ratio of gluten-forming fractions: gliadin and glutenin. Moreover, while ω -, α - and γ -gliadins are present in gluten in a monomeric form, glutenins are preferably aggregated through hydrogen, hydrophobic and ionic interactions and disulphide covalent bonds [12]. It is (–S–S–) bonds that have a major influence on the gluten protein macromolecules forming a kind of spatial grid of parallel or folded chains of protein molecules which determines rheological properties of dough. Strong flour in which gluten fraction prevails is characterized by a longer duration of dough formation and its higher stability. Weak flour in which functional properties of gliadin prevail binds water quickly but in small quantities, that is, it quickly forms dough but its viscosity drops rapidly. By changing molecular-mass distribution and structure of proteins, biochemically or thermally affecting the dough, its moisture-retaining power and visco-elastic properties may be changed [2, 12, 13].

It was noted that with a decrease in the size of flour particles, its functional and technological characteristics improve due to a growing number of hydrophilic and hydrophobic centers of protein. As studies have shown, optimal particle size for gluten is 20 μm [2, 13].

The rye proteins have specific hydrophilic properties. They swell rapidly when mixing flour with water and their substantial portion swells (is peptized) infinitely turning into a colloidal solution [2].

Wheat proteins have a high moisture-absorbing and moisture-retaining power as they contain a large number of hydrophilic centers. These are the following groups: *anionic*: COO⁻ (glutamine and aspartic acids); *cationic*: NH₃⁺, =NH⁺-, NH₂-C=NH₂⁺ (lysine, histidine, arginine); *polar uncharged* functional groups: OH, -CONH₂, -SH (serine, threonine, tyrosine, glutamine, asparagine, and cysteine); high-polar *amidogroup* of glutamine and asparagine. At the same time, a small number of non-amidated residues of glutamine and aspartic acids as well as residues of lysine and histidine give respectively negatively and positively charged groups able to draw water dipoles. However, residues of such amino acids as glycine, leucine, isoleucine, alanine, valine, phenylalanine and proline in a quantity of 40–50 % of all amino acids of wheat protein give its molecule hydrophobic properties which determines good fat-absorbing and fat-retaining power [2, 14].

One of the main directions of present-day solutions is getting smaller amount of fat and higher moisture-retaining power in the modified products (ice cream, mayonnaise, etc.). According to developers, such products will not differ in their type and taste from “fat” products since insoluble substances are not used. Mayonnaise consisting of the emulsion with nanodroplets of water inside it is closest to the introduction to the market [3, 4, 7, 8, 15].

Mineral compounds (ammonium salts of orthophosphate acid, sodium, and potassium orthophosphates) are used in bakery to increase moisture-retaining power of flour and dough [16, 17]. Disadvantages of these additives are lack of functionality regarding specific volume, porosity, and shape-keeping of bread.

To improve moisture-retaining power and actual yield of bakery products, special compositions of DSM enzymes for non-starch flour polysaccharides [18, 19] can be effectively used. Disadvantage of these additives is their narrow applicability and lack of integrated action.

Food additives, such as sodium sulphite, cysteine and special bioproducts (Bakezyme®) are food additives of recovering action. They act on gluten by destroying disulphide (-S-S-) cross-links of the secondary protein structure thereby providing greater mobility to the dough layers, smaller resilience of gluten and higher elasticity, up to a complete liquefaction and decrease in flour moisture-retaining power is observed [18, 19].

A variety of polysaccharides have found a wide use: citrus fibers; hydrocolloids of plant origin, cellulose ethers [20–27]. *Citrus fiber* is a source of healthy fiber. The content of food fibers in them ranges from 88 to 93 % including soluble fibers (about 20 %). *Hydrocolloids*: banana and apple powders; buckthorn shroud; guar and xanthan gum; polyhedrosis being a polysaccharide consisting of glucose polymers of a low molecular weight. However, their influence on the technological indicators of semi-finished dough products and finished products is insignificant.

In order to increase water-absorption power of flour, it is suggested to use natural powdered preparations. They are obtained by drying milk and egg products: low-fat natural yoghurt, skimmed milk, egg yolk, etc. [16, 28–30].

Enrichment of biologically active substances of vegetable, fruit and herbal additives promotes increase in the moisture-retaining power of dough [20–23, 25, 26]. Disadvantages

of additives include low functionality regarding texture and physical and chemical properties of bakery products.

Recently, various functional ingredients derived from industrial by-products (skin, hoof, feathers, offal, seeds, bran, whey, etc.) are used in food technologies to increase moisture-retaining power. However, these dietary additives are characterized by narrow applicability and do not possess a complex action [31, 32].

In recent years, phenol-derivative compounds of vegetable origin are used in bakery to improve flour and dough moisture-retaining power [37, 38]. Disadvantages of these dietary additives include insufficient yield and shelf life of the finished products.

Wheat based food additives are used in bakery [35] to improve moisture-retaining power of dough. However, yield and structural and mechanical indicators of finished products are not improving.

In order to improve moisture-retaining power of flour and dough, bioadditives of various chemical compositions are also offered for bakery: soy, mince, enzymes, microalgae, etc. [36–39]. Lack of functionality regarding specific volume, porosity and form consistency of bread are disadvantages of these additives.

Analysis of information sources [2–6, 8, 9, 16, 18–39] shows the lack of data on bread technologies using nanopowder additives which improve technological indicators of flour and semi-finished bakery products. To create new functional and technological properties, in particular in rye-and-wheat bread, the Magnetofood polyfunctional food additive can be offered. In food systems, the Magnetofood exhibits reducing, antioxidant, sorption, complexing, emulsifying, moisture-retaining, fat-retaining, moisture-binding properties and can act as an additional source of easily assimilated iron [3, 6, 7].

3. The aim and objectives of the study

This study objective was to substantiate the mechanism of interaction of rye-and-wheat flour biopolymers with the Magnetofood nanoparticles to improve the moisture-retaining power of dough.

To achieve this objective, the following tasks were set:

- to substantiate the mechanism of interaction of the Magnetofood nanoparticles with functional groups of biopolymers (proteins, carbohydrates) of rye-and-wheat flour at various pH values of the medium;
- to establish the mechanism of influence of the Magnetofood nanoparticles on binding moisture in rye-and-wheat dough at various pH values of the medium;
- to substantiate the mechanism of interaction of the Magnetofood nanoparticles with gluten of rye-and-wheat dough and explain its moisture-retaining power. In doing so, use the results of previous experimental studies [6, 7, 10, 11] and those mentioned in [40].

4. Materials and methods used in the study of the Magnetofood food additive

4.1. Materials and equipment used in the experiment

Influence of nanoparticles of the Magnetofood polyfunctional food additive on the technological properties, in particular the moisture-retaining power of rye-and-wheat dough was studied.

Object of the study: the technology of rye-and-wheat bread.

Study subjects:

– *control sample 1*: dry rye-and-wheat gluten obtained from rye-and-wheat flour according to DSTU-P 4583:2006. The ratio of scored rye flour to the first-grade wheat flour was 60:40 according to the basic formula of Darnytsky rye-and-wheat bread [41];

– *sample 2*: dry rye-and-wheat gluten with the Magnetofood polyfunctional food additive in an amount of 0.15 % of the weight of powdered gluten [6];

– *control sample 3*: wet rye-and-wheat gluten obtained from rye-and-wheat flour according to DSTU-P 4583:2006. The ratio of scored rye flour to first-grade wheat flour was 60:40 according to the basic formula of Darnytsky rye-and-wheat bread [41];

– *sample 4*: wet rye-and-wheat gluten with the Magnetofood polyfunctional food additive in an amount of 0.15 % of the weight of powdered wet gluten [6];

– *control sample 5*: rye-and-wheat flour according to DSTU-P 4583:2006. The ratio of scored rye flour to the first-grade wheat flour was 60:40 according to the basic formula of Darnytsky rye-and-wheat bread [41];

– *sample 6*: rye-and-wheat flour with the Magnetofood polyfunctional food additive in an amount of 0.15 % of the weight of powdered flour [6].

Materials and equipment used in the experiment as well as the procedures for obtaining dry and wet gluten, determination of moisture, moisture-retaining power of gluten and flour, determination of free and bound moisture in gluten and flour are described in more detail in [40].

5. Results obtained in the study of the mechanism of interaction of the Magnetofood food additive with biopolymers of rye-and-wheat flour

The study of influence of the Magnetofood polyfunctional food additive on the moisture-retaining power of rye-and-wheat gluten and rye-and-wheat flour was carried out on model systems. As a basic formulation, a recipe of rye-and-wheat dough used in baking Darnytsky bread [41] was chosen in the study. The Magnetofood additive was introduced in a dry form when mixing rye-and-wheat gluten or rye-and-wheat flour in an amount of 0.15 % of powdered gluten or flour weight [6].

Properties of gluten, flour and bread depend on the state of water contained in them and the ratio of moisture in a free and bound state. To find out the mechanism of influence of the Magnetofood additive on the ingredient components of rye-and-wheat dough, the amount of bound and free moisture was studied.

The process of adsorption of water on the surface of the Magnetofood nanoparticles was mainly determined by electrostatic dipole-dipole (van der Waals) and ion-dipole method. Donor-acceptor (coordinative) interactions are also involved in the adsorption of moisture. They occur between the surface of nanoparticles and adsorbed water molecules.

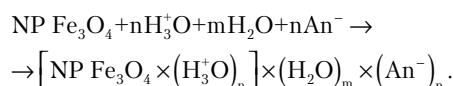
On the surface of the Magnetofood nanoparticles (Fe_3O_4), there are oppositely polarized regions (“+” for Fe) and (“-” for O) (Fig. 1). Fe^{2+} and Fe^{3+} cations of magnetic nanoparticles of the Magnetofood are structure-forming ions. The high intensity of the electric field created by the iron ions of magnetic nanoparticles increases polarization of

molecules of water and thiocompounds, which contributes to the additional ordering of dipoles, in particular H_2O outside the particle surface and adsorption.

It is evident from Fig. 1, *a* that in the neutral medium ($pH=6.8-7.0$), solvated Magnetofood nanoparticles are formed which then turn into solvated aqua complexes of the following chemical composition:



Solvated protonated Magnetofood nanoparticles appear in acidic medium ($pH<6.6$) (Fig. 1, *b*) which then form solvated aqua complexes having the following chemical composition:



In alkaline medium ($pH>7.0$) (Fig. 1, *c*), when interaction of the Magnetofood nanoparticles with water takes place, there are solvated hydroxylating nanoparticles which then form solvated aqua complexes of the following chemical composition:

It should be noted that the Magnetofood nanoparticles most intensively chemically interact in an acidic medium with formation of stronger bonds.

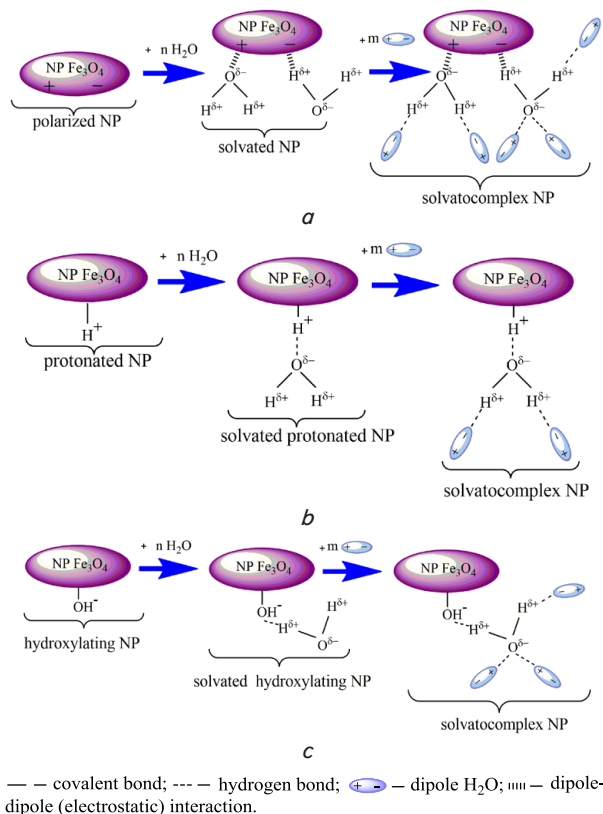


Fig. 1. Mechanisms of solvation of the Magnetofood nanoparticles at various pH abnormalities in aqueous media: neutral medium ($pH \sim 7.0$) (*a*); acidic medium ($pH < 7.0$) (*b*); alkaline medium ($pH > 7.0$) (*c*)

To understand the mechanism of interaction of rye-and-wheat flour biopolymers with the Magnetofood nanoparticles and the increase in the moisture-retaining power

of the rye-and-wheat flour dough, consider chemical and electrostatic interactions that occur between the Magnetofood nanoparticles and the ionogenic groups of biopolymers (proteins, lipids, carbohydrates).

According to Rehinder, water in food products is present in three main binding forms: physical-mechanical, physical-chemical, and chemical [38].

According to Bushuk, 31.1 % of the total amount of water absorbed by semfinished bakery product is absorbed by protein; 45.5 % by starch and 23.4 % by pentosanes [1].

Fig. 2 shows the mechanism of interaction of the Magnetofood food additive nanoparticles with ionogenic groups of biopolymers.

Fig. 2 shows how likely biopolymers interact with ions of the Magnetofood nanoparticles which are characterized by high binding energy (~500–1,000 kJ/mol).

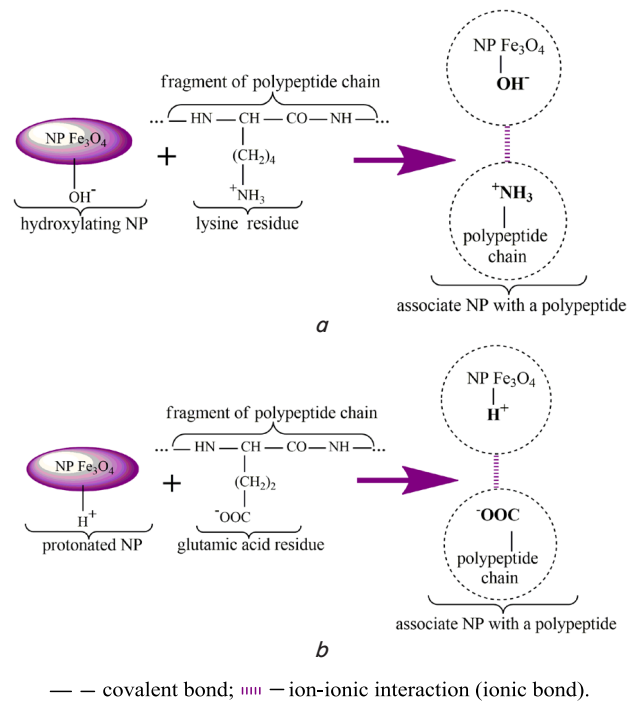


Fig. 2. Ionic interactions between ionized Magnetofood nanoparticles and charged ionogenic groups of polypeptides: hydroxylation of Magnetofood nanoparticles and lysine residues (a); protonated Magnetofood nanoparticles and residues of glutamic acid (b)

Fig. 3 demonstrates possible ion-dipole and dipole-dipole interactions of the Magnetofood nanoparticles with ionogenic groups of biopolymers.

It follows from Fig.3 that the ion-dipole interactions are possible between the protonated Magnetofood nanoparticles and the carbohydroxylated residues of proteins, lipids, carbohydrates. Dipole-dipole interactions are possible between polarized Magnetofood nanoparticles and a dipole of peptide bond.

Basically, the Magnetofood nanoparticles interact with biopolymers due to non-covalent coordination. Fig. 4 illustrates an intra-molecular complex, “clathrate” of a complex-cell type. This “clathrate” is formed at the expense of three intra-molecular coordination bonds between the Magnetofood nanoparticles and the nitrogen atoms of aromatic nuclei of histidine and tryptophan.

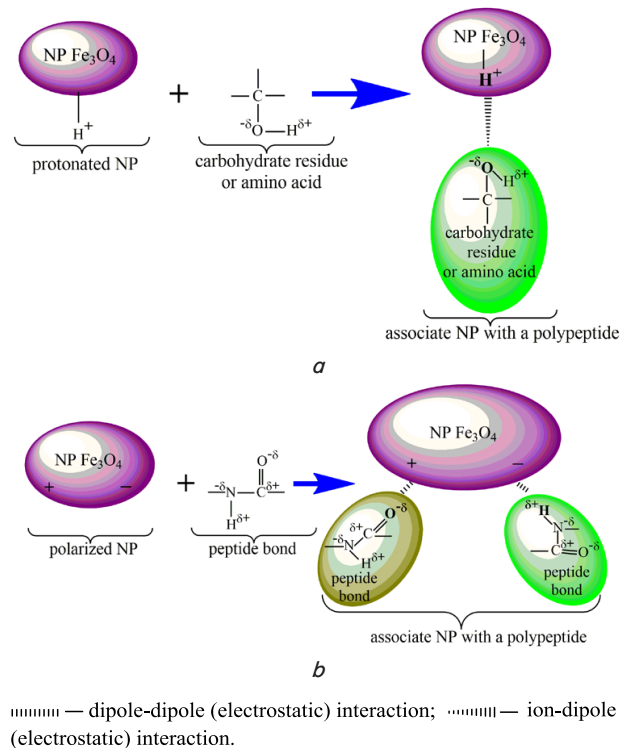


Fig. 3. Ion-dipole and dipole-dipole interactions between ionized and polarized Magnetofood nanoparticles and charged ionogenic groups of biopolymers: ion-dipole interaction (a); dipole-dipole interaction (b)

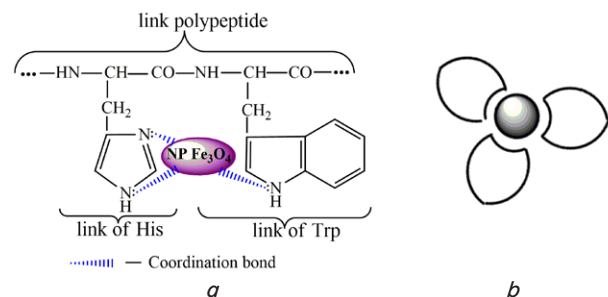


Fig. 4. Intra-molecular complex, “clathrate” of complex-cell type formed by the Magnetofood nanoparticles and a link of the polypeptide chain of gliadin: nanoparticles-protein “clathrate” (a); complex-cell (b)

This “clathrate” is formed at the expense of three intra-molecular coordination bonds between the Magnetofood nanoparticles and the nitrogen atoms of the aromatic nuclei of histidine and tryptophan.

An example of a complex associate of polyheterocyclic ligand of the Magnetofood nanoparticles which combines fragments of histidine and tryptophan of two polypeptide chains with cations of ferric iron (Fe^{2+} , Fe^{3+}) is shown in Fig. 5, 6.

It can be seen from Fig. 5, 6 that cations Fe^{2+} and Fe^{3+} of the Magnetofood nanoparticles enter intermolecular complex formation with nitrogen atoms of two polypeptide chains. The result of this interaction is the intermolecular complex, “cavitate”.

Hydrogen bond is considered a counterpart of coordination bonds. Fig. 7 shows possible hydrophilic contacts of solvated Magnetofood nanoparticles with ionogenic groups of biopolymers. The data of Fig. 7 prove that in the conditions of dough preparation, solvated Magnetofood nanoparticles appear which form hydrogen bonds with various ionogen-

ic groups of biopolymers (proteins, lipids, carbohydrates) through the donor-acceptor mechanism.

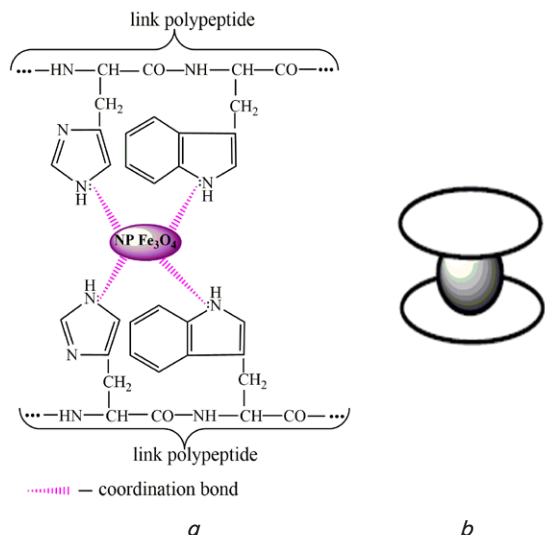


Fig. 5. Intermolecular complex, “cavitate” of a complex-sandwich type formed by the Magnetofood nanoparticles and links of two polypeptide chains of glutenin: nanoparticle-protein “cavitate” (a); complex-sandwich (b)

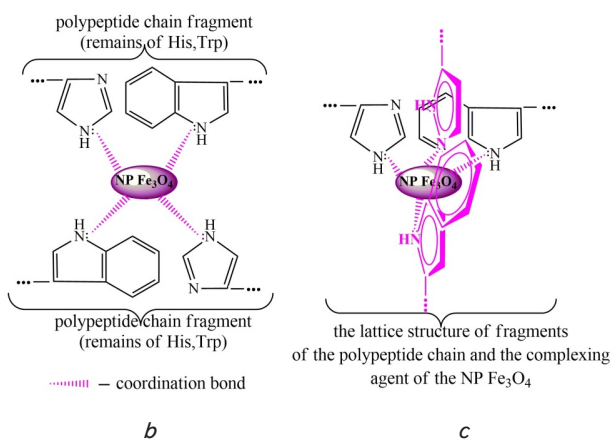
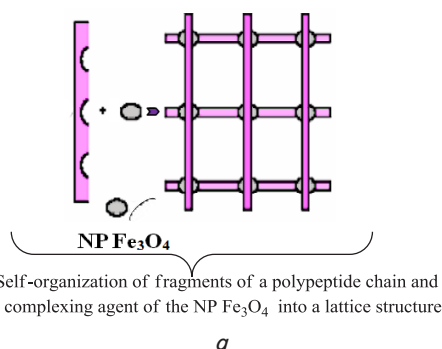


Fig. 6. Self-organization of the ligand and ferric iron ions of the Magnetofood nanoparticles into the lattice structure of the “cavitate” complex: self-organization of the ligand, fragments of two polypeptide chains and a complexing agent, ferric iron ions of the Magnetofood nanoparticles in a lattice structure (a); intermolecular complex, “cavitate” formed by the fragments of two polypeptide chains and the Magnetofood nanoparticles; spatial structure of “cavitate” formed by fragments of two polypeptide chains and Fe₃O₄ nanoparticles (c)

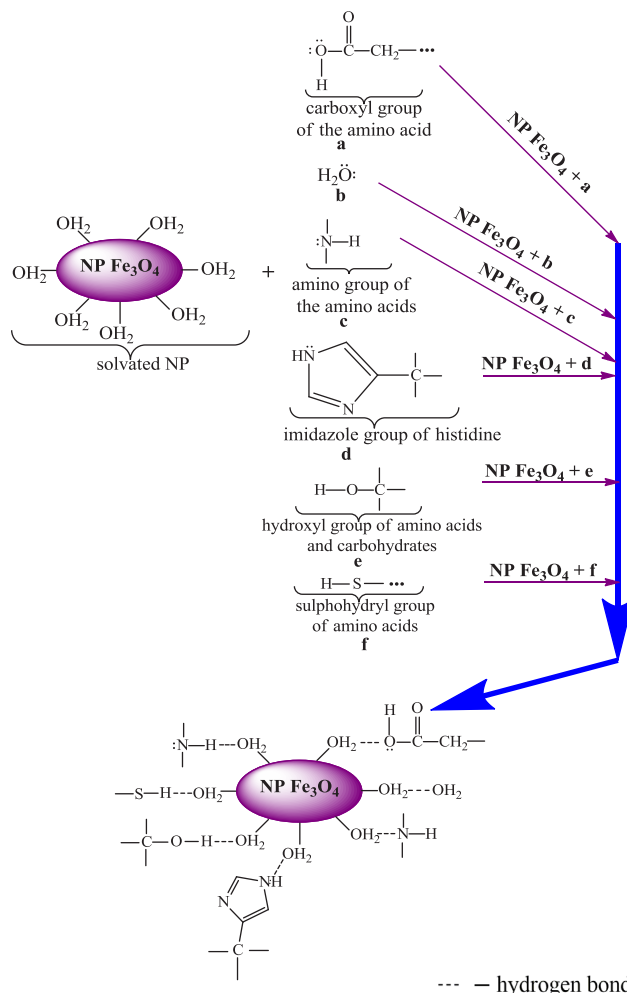


Fig. 7. Formation of hydrogen bonds between solvated Magnetofood nanoparticles and ionogenic groups of biopolymers: a carboxyl group (a); water (b); amino group of amino acids (c); the imidazole group of histidine (d); hydroxyl group of amino acid or carbohydrate (e); the hydrosulfide group of the amino acid (f)

A “cluster-loop-chain” model can be proposed to explain the increase in the moisture-retaining power of the rye-and-wheat flour with the Magnetofood nanoparticles which explains formation of bonds of a high-molecular subunit of glutenin (HMSG). Fig. 8, 9 show the results of the interaction of the Magnetofood nanoparticles with the fragments of polypeptide chains of the high molecular subunit of glutenin and gliadin (HMSGI).

Analysis of Fig. 8 shows that the following interactions occur within the link of the glutenin polypeptide chain: coordination interaction of the Magnetofood nanoparticles with nitrogen and oxygen atoms of the glutamine residues; electrostatic hydrophobic interactions of aliphatic side chains of leucine residues; π - π -stacking of interaction of aromatic fragments of the proline residues. As a result, formation of “clusters” and “loops” occurs.

It follows from Fig. 9 that there is a coordination interaction of the Magnetofood nanoparticles with nitrogen and oxygen atoms of glutamine and tryptophan residues within the links of two polypeptide chains of gliadin as well as electrostatic hydrophobic interactions of the aliphatic side chains of the leucine residues and π - π -stacking of the interaction of aromatic fragments of the tryptophan residues.

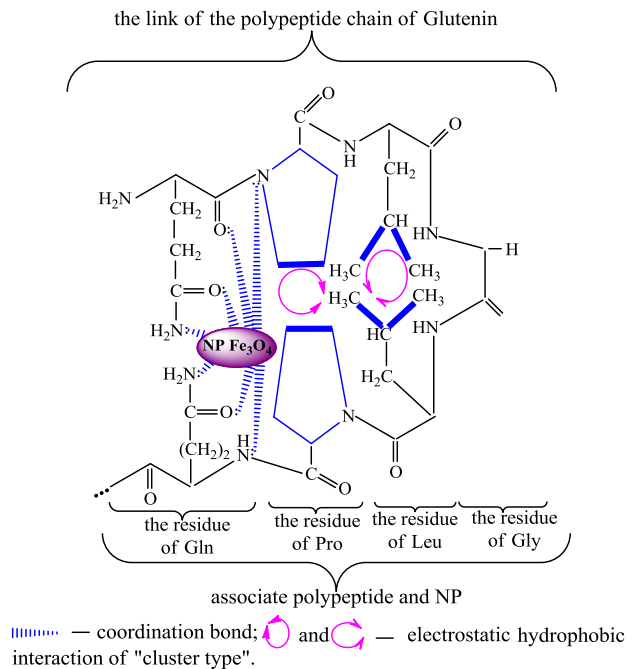


Fig. 8. Formation of a "loop" and "clusters" within the link of one polypeptide chain of glutenin

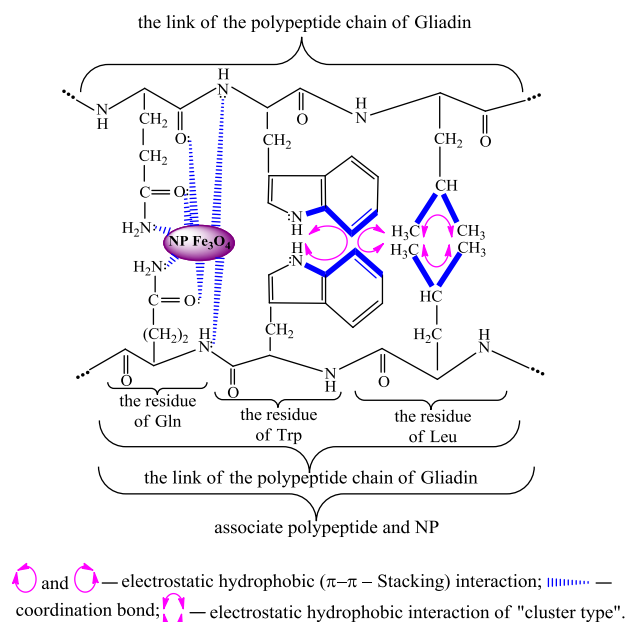


Fig. 9. Formation of a "loop" and "clusters" within the links of two polypeptide chains of gliadin

As a result, formations of "cluster" and "loop" types occur. Similar interactions are observed in formation of "loops" and "clusters" in the links of two polypeptide chains of glutenin.

According to this model, a significant amount of protein-protein interactions is formed as a β -helix at a low level of hydration with the participation of "loops" and "clusters" (Fig. 8, 9).

When the degree of hydration increases, the system is plasticized. In addition, the water-absorbing power and moisture-retaining power of the rye-wheat gluten, flour and dough increases under the influence of the Magnetofood nanoparticles (Fig. 10, 11).

Fig. 10, 11 show distribution of water dipoles in "clusters" and "loops" of the links of solvated polypeptide chains of glutenin and gliadin.

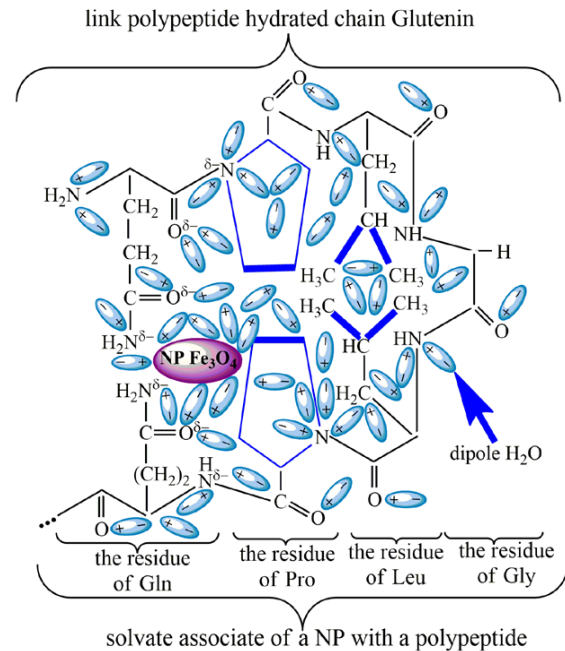


Fig. 10. Distribution of water dipoles in "clusters" and "loops" of a link of a solvated polypeptide chain of glutenin

Analysis of Fig. 10 shows that accumulation of water is observed around the Magnetofood nanoparticles and in "clusters" and a "loop" of the chain due to the presence of polarized Magnetofood nanoparticles, "clusters" and "loops" as well as a system of hydrogen bonds between water dipoles. This increases the moisture-retaining power of rye-and-wheat dough.

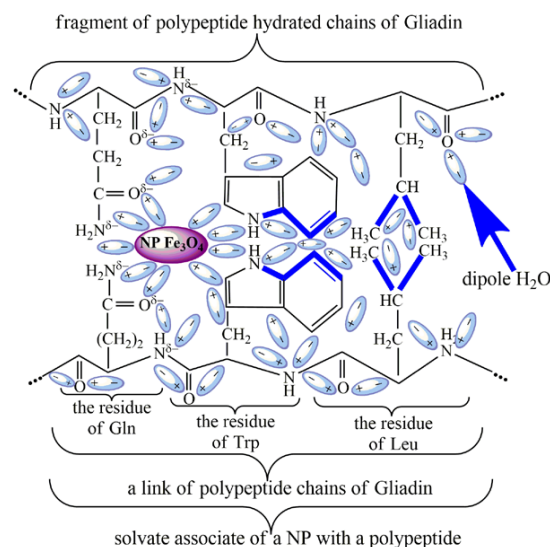


Fig. 11. Distribution of water dipoles in "clusters" and "loops" of the links of solvated polypeptide chains of gliadin

Fig. 11 data indicate that accumulation of water is observed around the Magnetofood nanoparticles and in the "clusters" and the "loop" between two chains. This helps to increase moisture-retaining power of rye-and-wheat dough.

6. Discussion of results obtained in studying the influence of the Magnetofood on the moisture-retaining power of rye-and-wheat dough

Analysis of Fig. 1 shows that at an isoelectric point and in a neutral medium (pH=6.8–7.0) when density of the surface charge of the Magnetofood nanoparticles is minimal, contact of the nanoparticle dipoles with water dipoles occurs at the expense of the intermolecular dipole-dipole interaction (Fig. 1, *a*). Energy of the dipole-dipole (van der Waals) interaction is small, about 5–50 kJ/mol. As a result, solvated particles of Magnetofood are formed. Their surface acquires hydrophilicity and ability to interact with ionogenic groups of biopolymers and water dipoles, mainly due to the formation of intermolecular hydrogen bonds. The hydrogen bond energy is 5–100 kJ/mole. Due to hydrogen bonds between water molecules, an aqua complex or a solvate complex appears.

In an acidic medium (pH<6.8) (Fig. 1, *b*), the Magnetofood nanoparticles are protonated and form the protonated particles of Magnetofood. These particles arise according to the type of coordination link (oxygen of Magnetofood acts as a donor; and the H⁺ proton of medium is an acceptor). The coordination bond energy is 50–200 kJ/mol. Next, the protonated particles of the Magnetofood can form bonds of ion-ion (with energy of ~100–400 kJ/mol) and ion-dipole (with energy of ~50–200 kJ/mol) types with ions and polarized molecules of biocompounds and water. Fig. 1, *b* shows the scheme of formation of a solvated protonated particle of the Magnetofood, which then reacts with H₂O dipoles by the ion-dipole type. Solvate complexes are formed in which the Magnetofood acts as a complexing agent and water dipoles are ligands. Further, an aqua complex appears due to hydrogen bonds between water molecules.

The mechanism of protonation of the Magnetofood nanoparticle in an acidic medium can be imagined as realized not only by H⁺ protons but also by hydroxonium ions. Since protons (H⁺ cations) interact with water molecules with formation of hydroxonium ions (H₃⁺O) which interact with dipoles of the Magnetofood nanoparticles (Fe₃O₄) by the ion-dipole mechanism with formation of hydroxylated Fe₃O₄ nanoparticles (Fig. 1, *b*), these hydroxylated nanoparticles form a system of hydrogen bonds with water molecules and hydrophilic groups of biosubstances by ion-dipole and ion-ion interaction types. Interaction of Fe₃O₄ nanoparticles with water molecules with the help of hydrogen bonds results in formation of the solvate complex.

In the alkaline medium (pH>7.0) (Fig. 1, *c*), the hydroxyl groups (OH⁻) interact with polarized Fe₃O₄ nanoparticles by ion-dipole and coordination mechanisms (oxygen of OH⁻ group is the donor and the vacant 3d-orbitals of Fe are the acceptors). The thus formed hydroxylated nanoparticles of Magnetofood acquire a negative charge. After that, they are able to interact by ion-ion and ion-dipole mechanisms with ions and dipoles of proteins and carbohydrates including H₂O with formation of hydrogen bonds according to the scheme in Fig. 1, *c*. Solvate complex is formed in the interaction of hydroxylated nanoparticles of the Magnetofood with water molecules.

As it follows from Fig. 2, when Magnetofood is added to dough based on rye-and-wheat flour, ionic interactions can occur between:

- negatively charged hydroxyl OH⁻ groups of hydroxylated Fe₃O₄ nanoparticles and positively charged NH₃⁺ groups of side radicals of lysine, arginine, histidine residues (Fig. 2, *a*);

- positively charged H⁺ cations of protonated Fe₃O₄ nanoparticles and negatively charged COO⁻ groups of the side radicals of the residues of asparagine and glutamic acids (Fig. 2, *b*).

When adding the Magnetofood to the food systems of Fig. 3, ion-dipole and dipole-dipole interactions may occur between the Magnetofood nanoparticles and the ionogenic groups of the rye-and-wheat dough: components:

- ion-dipole interaction between the protonated Magnetofood nanoparticles and the carboxylated residues of the amino acid, lipid, carbohydrate (Fig. 3, *a*);

- dipole-dipole interaction between polarized Magnetofood nanoparticles and the dipole of peptide bond (Fig. 3, *b*).

Interaction of the Magnetofood nanoparticles with aromatic fragments of histidine and tryptophan (Fig. 4–6) is possible due to the formation of electrostatic complexes: clathrates (“host molecules” coordinate the substrate in the intra-molecular cavities) (Fig. 4) and cavitates (“host molecules” coordinate the substrate in intermolecular cavities) (Figs. 5, 6). A coordinating (donor-acceptor) bond plays an important role in the occurrence of protein-nanoparticle complexes. In the case of histidine and tryptophan, the donor is a nitrogen atom of the aromatic system having a free electron pair in the outer shell. Iron cations (Fe²⁺, Fe³⁺) of the Magnetofood nanoparticles serve as an acceptor-complexing agent. They have vacant 3d-orbitals.

Iron cations (Fe²⁺, Fe³⁺) of the Magnetofood form several coordination bonds in clathrate (Fig. 4) with amino acid residues of one polymer molecule (chain) which determines a considerable strength of the complex.

Another example of the complex associate of the polyheterocyclic ligand grouping the fragments of histidine and tryptophan with iron cations (Fe²⁺, Fe³⁺) of the Magnetofood nanoparticles is shown in Figs. 5 and 6. Iron cations (Fe²⁺, Fe³⁺) are coordinated in the linear ligand and also firmly hold the perpendicularly positioned analogous ligand. Such complex construction proves to be strong due to the plurality of formed coordination bonds.

When hydrogen bonds are formed, hydrogen atoms are able to bind with atoms of oxygen, nitrogen, less with atoms of fluorine, chlorine, and sulphur (Fig. 7). In the case of proteins and carbohydrates, a hydrogen bond is formed between a hydrophilic uncharged group and any other hydrophilic group. In our case, solvated Magnetofood nanoparticles can enter hydrophilic contacts represented by hydrogen bonds. Hydrogen bonds of the Magnetofood nanoparticles form with water dipoles, molecules of proteins and carbohydrates containing *hydrophilic groups*, the groups having *polar bonds*: C–O, C–N, O–H, S–H (Fig. 7). Hydrophilic OH groups of carbohydrates when interacting with the dipoles of the Magnetofood nanoparticles provide hydrophilicity and stability to the protein-Magnetofood nanoparticle and carbohydrate-Magnetofood nanoparticle biosystems. Since formation of hydrophobic bonds between protein fragments can be blocked in this case, this prevents aggregation.

To explain the moisture-retaining power of rye-and-wheat dough, a “cluster-loop-chain” model can be offered. Its essence is as follows. The ability of the Magnetofood nanoparticles to enter electrostatic and coordination interactions with protein biomolecules determines a more branched structure and interweaving of protein macromolecules. In addition, the formation of “clusters” and “loops” takes place because of:

- hydrophobic interactions of aliphatic side chains and π - π -stacking interactions of aromatic fragments;

- electrostatic intra- and intermolecular complexes of the Magnetofood nanoparticles with fragments of polypeptide chains (Fig. 8, 9).

Fig. 8, 9 show the results of interaction of the Magnetofood nanoparticles with fragments of polypeptide chains of the high-molecular subunit of glutenin and gliadin (HMSGG). Fig. 8 illustrates how coordination interaction of the Magnetofood nanoparticles with nitrogen and oxygen atoms of glutamine residues and electrostatic hydrophobic interactions of the aliphatic side chains of the leucine residues and π - π -stacking interaction of the aromatic fragments of the proline residues occur within the glutenin polypeptide chain. As a result, formation of “clusters” and “loops” occurs. Thus, the high reactivity of the Magnetofood nanoparticles causes a more branched structure and interweaving of protein macromolecules, appearance of “clusters” and “loops”, electrostatic intra- and intermolecular complexes of the Magnetofood nanoparticles with fragments of polypeptide chains (Fig. 8, 9).

It is evident from Fig. 9 that coordination interaction of the Magnetofood nanoparticles with nitrogen and oxygen atoms of glutamine and tryptophan residues as well as electrostatic hydrophobic interactions of the aliphatic side chains of leucine residues and π - π -stacking interactions of aromatic fragments of the tryptophan residues take place within the links of two polypeptide chains of gliadin. As a result, formations of “cluster” and “loop” types occur. Similar interactions are observed in formation of “loops” and “clusters” in the links of two polypeptide chains of glutenin.

According to this model, a significant amount of protein-protein interactions are formed as a β -helix at a low level of hydration and participation of “loops” and “clusters” (Fig. 8, 9).

With increase in the degree of hydration, the system is plasticized due to accumulation of water around the Magnetofood nanoparticles and in formations of “cluster” and “loop” types (Fig. 10, 11). In these “clusters”, “clathrates”, “cavitates” and “loops”, intermicellar and intramicellar water may also be retained. This water is bound with hydrogen, dipole-ionic and dipole-dipole bonds with polarized Magnetofood nanoparticles and also with hydrophilic groups of amino acids since the Magnetofood nanoparticles and a part of the hydrophilic groups are contained both in “clusters” and the internal divisions of protein macrostructures. Finally, water dipoles can simply resort to hydrogen bonds without breaking strength. In addition, the lateral branching that appeared in the protein macrostructure promotes pulling apart the main chains without breaking the “stitching”. This action facilitates interaction of protein macromolecules with water dipoles and improves hydration of protein fragments.

According to this theory, elasticity of glutenin is determined by the equilibrium relationship between hydrated “loops” and hydrogen-bound zones of “chains” which depend on the degree of hydration. Stretchability of semi-finished dough products will ultimately consist in stretching of the “loops” and “divergence” of the “chains”. As a result of formation of hydrogen-bound chains, it is likely that there is a mechanism by which the elastic energy is stored in dough which gives an explanation of the increase in dough resistance to stretching during its kneading.

The disadvantage of this study is that the proposed “cluster-loop-chain” model of interaction of the Magnetofood

with biopolymers of rye-and-wheat flour was considered for only one type of dough system, i.e. the rye-and-wheat dough. Also, it is not known how this additive will affect technological parameters of semifinished dough products of another formulation (from other types and grades of flour).

The positive side of this study is that the model of interaction of the Magnetofood additive with biopolymers proposed in this work can be used to study functional and technological parameters, in particular, moisture-retaining power and for other protein-containing food systems (meat, milk, etc. products).

7. Conclusions

1. The mechanism of influence of the Magnetofood additive on retaining moisture in rye-and-wheat dough with various medium pH was established. In a neutral medium of polarized Magnetofood nanoparticles, solvated Magnetofood nanoparticles are formed. Their surface acquires hydrophilicity and ability to interact with ionogenic groups of biopolymers and water dipoles. Interaction of solvated Magnetofood nanoparticles with water molecules results in solvate complexes. In an acidic medium, the protonated Magnetofood nanoparticles contacting with water form solvated Magnetofood nanoparticles whose interaction bonds with water dipoles through hydrogen bonds results in formation of solvate complexes. In an alkaline medium, hydroxylated Magnetofood nanoparticles interact with water dipoles by ion-dipole mechanism forming solvated Magnetofood nanoparticles which interact with water dipoles through hydrogen bonds. This results in formation of solvate complexes.

2. The mechanism of interaction of the Magnetofood nanoparticles with ionogenic groups of biopolymers of dough systems was established.

The Magnetofood nanoparticles enter *ionic interaction* which arises between:

- negatively charged hydroxyl OH^- groups of hydroxylated Fe_3O_4 nanoparticles and positively charged NH_3^+ groups of side radicals of amino acid residues;
- positively charged H^+ cations of protonated Fe_3O_4 nanoparticles and negatively charged COO^- groups of side radicals of amino acid residues.

The Magnetofood nanoparticles enter *ion-dipole* and *dipole-dipole interactions*, which result from:

- *ion-dipole interaction* between the protonated Magnetofood nanoparticles and the carboxylated residues of amino acid, lipid, carbohydrate;
- *dipole-dipole interaction* between polarized Magnetofood nanoparticles and a dipole of the peptide bond.

Due to *coordination interactions*, the Magnetofood nanoparticles form electrostatic intra- and intermolecular complexes (“clathrates” and “cavitates”, respectively).

Solvated Magnetofood nanoparticles form hydrogen bonds with water dipoles. *Hydrogen bonds* arise in the interaction of solvated Magnetofood nanoparticles with molecules of biopolymers (proteins, carbohydrates) containing *hydrophilic groups*, the groups having *polar bonds*: C–O, C–N, O–H, S–H.

3. A “cluster-loop-chain” model of interaction of biopolymers of rye-and-wheat dough with the Magnetofood additive was proposed. The ability of the Magnetofood nanoparticles to enter electrostatic and coordination interactions with

protein biomolecules determines a more branched structure and interweaving of protein macromolecules. Formations of “cluster”, “clathrate”, “cavitate” and “loop” types arise. In these “clusters”, “clathrates”, “cavitates” and “loops”, intermicellar and intramicellar water bound by hydrogen, dipole-ion and dipole-dipole bonds with polarized Magnetofood nanoparticles and hydrophilic groups of amino

acids may be retained. According to this theory, elasticity of gluten proteins, in particular glutenin is determined by the equilibrium relations between hydrated “loops” and hydrogen-bound zones of “chains” that depend on the degree of hydration. Stretchability of the semi-finished dough products will ultimately consist in stretching of the “loops” and “divergences” of the “chains”.

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