MISTI 65.09.05

FUNCTIONAL AND TECHNOLOGICAL PROPERTIES OF NANOADDITIVES BASED ON DOUBLE OXIDE OF DIVALENT AND TRIVALENT IRON

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ABSTRACT

The waterand fat-retaining abilities of food nanoadditives based on the double oxide of divalent and trivalent iron (Fe_3O_4) known as *magnetofood* were studied. The ability of Fe_3O_4 food additive nanoparticles is noted to form electrostatic complexes with macromolecular compounds of food systems (proteins, carbohydrates, lipids) — quite stable structures such as *clusters*, *clathrates*, cavitates, *supramolecular associates*. This property promotes binding and retention of water and fat. Hydrophilic contacts of solvated Fe_3O_4 nanoparticles with water dipoles, molecules of proteins and polysaccharides (carbohydrates) increase the stability of polyphasic systems. An offset of the IR spectra of the maximum absorption of the Fe–O bond to the high-frequency region by (57±2) cm^{-1} in comparison with the experimental sample of pure food additive Fe_3O_4 indicates the chemical interaction of *magnetofood* iron cations with molecules of macromolecular compounds (starch, egg white, fat). The ratio of bound and free moisture in solvated *magnetofood*: 50.5…51.6% of water comprise bound moisture and 48.4…49.5% constitute free, osmotic (swelling water) and physico-mechanical water of the total amount.

Keywords: food raw materials, food ingredients, mineral compounds, water-retaining capacity, fat-retaining capacity.

INTRODUCTION

The most important functional and technological properties of food raw materials and food ingredients, which determine the course of technological processes and the quality of finished products, are water-retaining capacity (WRC) and fat-retaining capacity (FRC).

Mineral compounds [1]; special compositions of DSM enzymes [2]; biologically active substances of vegetable, fruit and herbal supplements [3–6]; various polysaccharides (citrus fibers; hydrocolloids of plant origin, cellulose esters) [7–10]; powders based on dairy and egg products [11–14]; functional ingredients derived from industrial by-products (leather, hooves, feathers, offal, seeds, bran, whey, etc.) [15, 16]; bioadditives based on wheat [17], soybeans, chickpeas, enzymes, microalgae, etc. [18–21] are used to increase the WRC of raw materials and food systems. The disadvantages of these additives are their narrow orientation and lack of complex action.

Food additives of various origins are used to improve the FRC of lipid-containing systems. They are nanopowders (silver, oxides of iron, magnetite, titanium and silicon dioxide, zinc oxide) [22–23]; modifications of magnetite nanoparticles with oleic acid; modifications of nanoparticles of iron oxides and gyroxides with higher fatty acids and fats. An adequate FRC of nanometer food additives isassociated with high dispersion – this allows not only to bind free fats, but also to keep them on the surface of nanoparticles during cooking, as well as with the good availability of numerous hydrophobic areas [22–23].

An analysis of the scientific papers revealed insufficiency of data on substantiating water and fat retention capacities of food nanoadditives, in particular, nanoparticles of food nanoadditives based on double oxide of divalent and trivalent iron *magnetofood* in food systems. Food nanoadditives Fe_3O_4 are marked with a wide range of functional and technological properties (structural, stabilizing, sorption, etc.) and promising technological applications [23].

Therefore, there is a need to study the water and fat retention capacities of the *magnetofood* food nanoadditive (FAM). The aim of the research is to study the water and fat retention of food additives based on double oxide of divalent and trivalent iron known as FAM. To achieve this goal, the following tasks are set:

– analyse the mechanism of interaction between macromolecular compounds (starch, egg white, higher fatty acid, fat) and FAM nanoparticles using FTIR spectroscopy;

– establish the chemical composition of the experimental samples of FAM – pure FAM, samples covered with starch / egg white / higher fatty acid (linoleic) / sunflower oil applying the method of energy-dispersive X-ray spectroscopy;

– determine the ratio of bound and free moisture in solvated FAM using the indicator method and differential thermal analysis.

MATERIALS AND METHODS

Research object: water retention and fat retention capacities of powdered ingredients in food raw materials, namely nanoparticles of food additives based on iron oxides known as *magnetofood* – Fe_3O_4 (FAM).

Research subject: magnetofood (FAM): highly dispersed nanopowder of brown or black colour with a particle size of 70… 80 nm. According to its chemical composition, *magnetofood* obtained by the method of chemical coprecipitation from aqueous solutions of salts of divalent and trivalent iron in an alkaline medium. Model systems: *Starch+magnetofood*, *Egg White+magnetofood*, *Linoleic Acid+magnetofood*, *Sunflower oil+magnetofood*: a suspension of FAM in 3% starch solution was obtained by introducing a portion of FAM into 3% polysaccharide solution at (55…60)ºC while constant stirring n=(2.0…2.2) s^{-1} for (5…7)·60 s with subsequent cooling of the mixture to a temperature of (18…20)ºC and constant stirring n=(2.0…2.2) s^{-1}. A suspension of FAM in a 3% solution of egg white was obtained by introducing a calculated amount of FAM into a 3% solution of egg white at a temperature of (18…20)ºCwhile constant stirring n=(2.0…2.2) s^{-1} for (3…5)·60 s followed by seasoning for (5…7)·60 s. Fatty suspensions of FAM were obtained by peptizing the calculated amount of FAM in oil (linoleic acid) at a temperature of (45…50) ºC (rational ratio of components –FAM: fat=1:1, i. e. 2.5 g of suspension contains 1.25 g FAM) under condition of thorough stirring (n=2.0…2.2 s^{-1}) for (3…4)·60 s, followed by cooling the mixture to a temperature of (18… 20) ºC and constant stirring n=(2.0…2.2) s^{-1}.

Fourier-transform infrared spectroscopy (FTIR). The vibrational spectra of the test samples were obtained using Fourier Transform Infrared Spectrometer (FTIR) Bruker Tensor

37 (Germany), controlled by the OPUS software package with standard calibration capabilities within the frequency range of (4000-400) cm-1 in the absorption format (Fourier spectra of samples were taken in KBr tablets).

Energy dispersive X-ray spectroscopy (EDX). To determine the chemical composition of the test samples used a scanning electron microscope JSM-820 (JEOL) with the prefix EDX. X-ray spectra were obtained by bombarding the test samples with electrons using an acceleration voltage of 20 kV (according to the lines of the characteristic spectra of Iron, Carbon and Oxygen). Establishment of the elemental composition of the experimental samples was performed by analysis of the obtained spectra of characteristic X-rays.

The algorithm for determining the mass fraction of bound and free moisture by the indicator method according to the *methods of Knyaginichev and Ermakova* and with the *differential thermal analysis (DTA)*.

The idea of therefractometric method is to determine the difference in dry matter (DM) between the indicator-solution of sugar and FAM solvated in sugar solution.

Differential thermal analysis (DTA). Thermographic determinations were carried out using derivatograph Q-1500 D by "MOM"(Hungry) for a sample weight of 0.5 g in the following modes of taking derivatograms: sensitivity of DTA galvanometer – 250, DTG galvanometer – 500, TG galvanometer – 500, heating temperature change rate – 4°C/60s. The dependences of the change rate for mass α on the temperature T were built based on the change curve TGwhich corresponds to the process of dehydration and the temperature curveT. To do this,every 5°C the researchers fixed a change in mass of the sample as well as the total mass fraction of moisture, which was determined by the TG curve, at the end of the crystallization process.

RESULTS AND DISCUSSION

Intense bands with maxima at (2360±4) cm^{-1} and (2342±3) cm^{-1}, which are absent in the spectrum of egg white, are also observed. These peaks can be attributed to symmetric valence (ν_s) oscillations of the C–H bond. This is confirmed by the electrostatic hydrophobic interactions of aliphatic side chains of amino acid residues in *clathrates* and *cavities* that occur under the action of MNP.

During the adsorption of egg white on the surface of the MNP, there is an offset of the absorption bands of the valence oscillations of amide I ν(C=O) and planar deformation oscillations of amide II δ_{pl}(N–H) to a lower frequency in the region: ν(C=O)=(1642±3) cm^{-1}; δ_{pl}(N–H)=(1527±3) cm^{-1}, respectively.

The absorption bands of planar and extraplanar deformation oscillations δ_{pl}(C–H) and δ_{epl}(C–C)=(1027±2)cm^{-1} to a lower frequency in the region δ_{pl}(C–H)=(1442±3)cm^{-1} and δ_{epl}(C–C)=(1027±2)cm^{-1} respectively. A new absorption band of planar deformation oscillations δ_{pl}(C–C) (1155±2) cm^{-1} is also observed. This confirms the electrostatic hydrophobic interactions of aliphatic and cyclic amino acid residues in the complex association.

In the spectrum of pure FAM , there is a line of absorption of the Fe–O bond with a maximum at a value of ~ 532 cm^{-1}, which agrees well with the data presented in the scientific studies, that is ~530 cm^{-1}. The offset of the maximum of the corresponding absorption band of Fe–O valence oscillations in the *Egg White+magnetofood* Complex to the region of ~ 588 cm^{-1} is associated with the influence of surface egg protein molecules, their interference in the near-surface layer of Fe_3O_4 nanoparticles and chemical interaction with iron cations. Thus, the results of the studies confirm the formation of a complex between egg white and FAM.

Comparison of IR spectra shows that the wave numbers of peaks differ in the spectra of the starting materials (starch, FAM) and the *Starch+magnetofood* complex, indicating the chemical interaction in the *Carbohydrate-magnetofood* model system. An offset of the IR spectra of the maximum absorption of the Fe–O bond to the high-frequency region by (57±2) cm^{-1} in comparison with the experimental sample of pure food additive *magnetofood* – Fe_3O_4 (FAM) indicates the chemical interaction of FAM iron cations with molecules of macromolecular compounds (starch, egg white, fat).

There is a shift of the intense band of free OH groups (3443±5) cm^{-1} to the low-frequency region (3415±5)cm^{-1} in the spectrum of the *Starch+magnetofood* complex – this indicates the participation of hydroxyl in the topic of hydrogen bonds and electrostatic coordination interactions with Fe atoms of FAM.

Shift of the peak of valence ν(C–O–C) by (13±3) cm^{-1} and planar deformation oscillations of δ_{pl} (C–O–C) на (16±3) $cm^{-1}$to the low-frequency region compared to the experimental sample of starch indicates the presence of Coulomb and coordination interactions between Fe atoms of FAM and oxygen (ether, pyranose and hydroxyl) residues of D-glucopyranose.

The appearance of new absorption bands in the region (700–1200) cm^{-1}, which characterize the oscillations of the carbon skeleton, and an offsetto the region of lower frequencies of some characteristic absorption bands (C–C) of bonds indicate the presence of hydrophobic and dispersive London forces between residues of glucopyranose.

An offset of the maximum absorption of the Fe–O bond to the high-frequency region by (57±2) cm-1 compared with the experimental sample of pure FAM indicates the chemical interaction of iron cations ofFAM with starch molecules. All this confirms the presence of chemical interaction in the *Starch+magnetofood* complex association.

The study of chemisorption of linoleic acid and 1-linoleyl-2-oleoyl-3-linolenoylglycerol on the surface of FAM nanoparticles has been reported in previous studies. This indicates the chemical interaction of higher fatty acid and fat with Fe_3O_4 nanoparticles.

So intense broadband with a maximum absorption (3341±4) cm^{-1}, which is shifted in the complex associate to the low-frequency region of cm^{-1} compared with the frequency of free OH groups and amide A (N–H) (3406±4) cm $^{-1}$, indicates the participation of hydroxyl oxygen and amide nitrogen in the formation of coordination bonds with Fe atoms of FAM.

The chemical composition of model systems of macromolecular compounds with FAM was determined in energy dispersive X-ray studies. For pure FAM, particles of Fe comprised 75.5%; O –24.5%; for the additive particles coated with egg white – Fe 44.7%; O 26.9%; C 21.4%; N 5.9%; S 1.1%; for the additive particles coated with starch – Fe 41.7%; O 35.7%; C 22.6%; for the additive particles coated with linoleic acid – Fe 45.6%; O 34.7%; C 19.7%; for the additive particles coated with sunflower oil – Fe 39.7%; O 36.7%; C 23.67%.

The mass fraction of bound and free moisture was determined using the indicator method (IM) according to the methods of Knyaginichev and Ermakova and the method of differential thermal analysis (DTA) in experimental samples of FAM after swelling at a temperature of (20±1)°C for(25±5)·60 s. (Fig. 1).

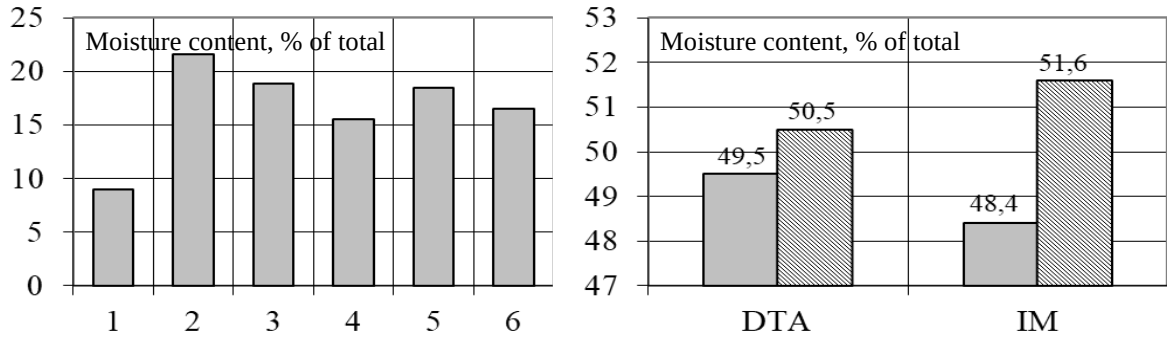

Fig. 1. The distribution of water by types of bonds in FAM after swelling determined by the methods: a – DTA (1 – free moisture; 2 – physically and mechanically bound; 3 – osmotically bound (swelling water); 4 – adsorption bound (polymolecular); 5 – adsorption bound (monomolecular); 6 – chemically bound); b – IM and the method of DTA (▯– amount of free, osmotic and physico-mechanical moisture; ▨– amount of bound moisture).

The experimental data presented in fig. 2 show that 1/5 of the water in solvated FAM is chemically bound moisture; 1/2 – bound moisture; 1/10 – free moisture and 1/2 –free, osmotic (swelling water) and physico-mechanical of the total amount of water.

The studies indicate the high hydration capacity of food nanoadditives based on double oxide of divalent and trivalent iron *magnetofood* (FAM), which can improve the functional and technological properties of heterogeneous dispersed systems in food production technologies.

RESULTS AND DISCUSSION

1. The ability of nanoparticles of food additive Fe_3O_4wasnoted to form supramolecular associations with macromolecular compounds of food systems, which promote the binding and retention of water and fat.

2. The interaction of macromolecular compounds (starch, egg white, higher fatty acid, fat) and water with nanoparticles of FAM was studied:

– Fourier-transforminfraredspectroscopyproved chemosorption of macromolecular compounds (starch, egg white, higher fatty acid, triglyceride) on the surface of NP food additive Fe_3O_4: a shift of the maximum of Fe–O bond absorption to the high-frequency region by (57±2) cm^{-1} in comparison with the experimental sample of pure FAM indicates the chemical interaction of FAM iron cations with molecules of macromolecular compounds (starch, egg white, fat, higher fatty acids); the spectrum of macromolecular *compound+magnetofood* complexes demonstrates an offset of the intense band of free OH groups (3443±5) cm^{-1} in the low-frequency region by (28±2) cm^{-1}, which indicates the participation of hydroxyl in the topic of hydrogen bonds and electrostatic coordination interactions with Fe atoms of FAM. The appearance of new absorption bands in the region of (700–1200) cm^{-1}, which characterize the oscillations of the carbon skeleton, and an offset in the region of lower frequencies of some characteristic bands that absorb (C–C) bonds indicate the presence of hydrophobic and dispersion interactions between residues of glucopyranose, aliphatic and cyclic amino acid residues and aliphatic triglyceride residues;

– Energydispersion X-rayspectroscopy determined the chemical composition of model systems of macromolecular compounds with food additiveFe_3O_4 (FAM): *sample a* (FAM) – Fe 75.5%; O 24.5%; *sample b* (MNP, coated with egg white) – Fe 44.7%; O 26.9%; C 21.4%; N 5.9%; S 1.1%; *sample c* (MNP, coated with starch) – Fe 41.7%; O 35.7%; C 22.6%; *sample d* (MNP, coated with linoleic acid) – Fe 45.6%; O 34.7%; C 19.7%; *sample e* (MNP, coated with sunflower oil) – Fe 39.7%; O 36.7%; C 23.67%.That is, the compounds (samples *b–e*) are chemisorbed on the particles of Fe_3O_4 food additive. And the band absorbing the C atom, which appeared in samples *b–e*, confirms the process of adsorption and chemical interaction between the particles of Fe_3O_4 food additive and macromolecular compounds;

–The ratio of bound and free moisture in solvated FAM was established using the indicator method and differential thermal analysis: 1/5 of water falls on chemically bound moisture; 1/2 – bound moisture; 1/10 – free moisture and 1/2 part – free, osmotic (swelling water) and physico-mechanical water of the total amount.

CONCLUSION

1 An offset of the IR spectra of the maximum absorption of the Fe–O bond to the high-frequency region by (57±2) cm-1 in comparison with the experimental sample of pure food additive Fe_3O_4 indicates the chemical interaction of magnetofood iron cations with molecules of macromolecular compounds (starch, egg white, fat).

2. The chemical composition of model systems of macromolecular compounds with FAM was determined in energy dispersive X-ray studies. For pure FAM, particles of Fe comprised 75.5%; O –24.5%; for the additive particles coated with egg white – Fe 44.7%; O 26.9%; C 21.4%; N 5.9%; S 1.1%; for the additive particles coated with starch – Fe 41.7%; O 35.7%; C 22.6%; for the additive particles coated with linoleic acid – Fe 45.6%; O 34.7%; C 19.7%; for the additive particles coated with sunflower oil – Fe 39.7%; O 36.7%; C 23.67%.

3. The ratio of bound and free moisture in solvated magnetofood: 50.5…51.6% of water comprise bound moisture and 48.4…49.5% constitute free, osmotic (swelling water) and physico-mechanical water of the total amount.

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