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STUDY OF NANOASSOCIATES OF FOOD NANOADDITIONS MAGNETOFOOD USING INFRARED SPECTROSCOPY

Abstract. The water and fat-retaining abilities of food nanoadditives “Magnetofood” were studied. The ability of “Magnetofood” food additive nanoparticles is noted to form electrostatic complexes with macromolecular compounds of food systems (proteins, carbohydrates, lipids) — quite stable structures such as “clusters”. This property promotes binding and retention of water and fat. Hydrophilic contacts of solvated “Magnetofood” nanoparticles with water dipoles, molecules of proteins and polysaccharides (carbohydrates) increase the stability of polyphasic systems.

Keywords: water retention, fat retention, iron oxide, nanoassociates.

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; special compositions of DSM enzymes; biologically active substances of vegetable, fruit and herbal supplements; various polysaccharides (citrus fibers; hydrocolloids of plant origin, cellulose esters); powders based on dairy and egg products; functional ingredients derived from industrial by-products (leather, hooves, feathers, offal, seeds, bran, whey, etc.); bioadditives based on wheat, soybeans, chickpeas, enzymes, microalgae, etc. 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); 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 is associated 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. 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 “Magnetofood” in food systems. “Magnetofood” food nanoadditives (Fe3O4) are marked with a wide range of functional and technological properties (structural, stabilizing, sorption, etc.) and promising technological applications.

Therefore, there is a need to study the water and fat retention capacities of the “Magnetofood” food nanoadditive. 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 “Magnetofood” (FAM).

Materials and methods. Model systems: Starch + Magnetofood, Egg white + Magnetofood, Fat + Magnetofood. Water and fat retention properties were examined with energy dispersive X-ray (EDX) and IR-Fourier spectroscopies (FTIR). The mass fraction of bound and free moisture was determined using the indicator method (IM) and differential thermal analysis (DTA).

Results and discussion. Chemical interaction of “Magnetofood” nanoparticles (MNP) with the main food ingredients. Previous studies show that the chemical activity of MNP is determined mainly by electrostatic interactions, i.e. dipole–dipole (van der Waals forces) and ion–dipole interactions. Donor–acceptor (coordination) interactions, such as hydrogen bonds, are also involved in the adsorption of proteins, fats, carbohydrates, and water on the surface of the MNP . In food systems, there are solvated nanoparticles (NP) of Fe3O4, which enter into hydrophilic contacts due to hydrogen bonds with water dipoles, molecules of proteins and polysaccharides (carbohydrates) containing hydrophilic groups — C–O, C–N, O–H, S–H. As a result, the stability of such systems as “Protein + Solvated MNP”, “Carbohydrate+Solvated MNP” increases but the formation of hydrophobic bonds between the fragments of macromolecules is slowed down, which prevents their aggregation.

Under the influence of NP of Fe3O4 macromolecular compounds (proteins, polysaccharides, higher fatty acids, and fats) undergo structural changes and form electrostatic complexes from NP of Fe3O4 – quite stable structures such as “clusters”, “clathrates”, “cavities”, and “supramolecular associates”. As a result, WRC and FRC of food systems increase.

Experimental confirmation of the interaction between the food nanoadditive “Magnetofood” (FAM) and proteins, fats, polysaccharides, water.

Fourier-transform infrared spectroscopy (FTIR). To establish the mechanism of chemical interaction of molecules of proteins, fats, polysaccharides with FAM, Fourier-transform infrared spectroscopy was carried out to study model systems of egg white, starch, linoleic acid and sunflower oil with FAM within the range of (400-4000) cm-1 (Table 1 and Table 2).

As can be seen from Table 1, the 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.

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 (νs) 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.

Table 1

Comparison of wavenumbers of individual peaks in IR-spectra of the "egg white+magnetofood" complex association and starting materials (egg white and "Magnetofood", food additive known as FAM)

Bond fluctuations	Wavenumber position of maxima, cm^{-1}			Offset, cm^{-1}
	egg white	FAM	egg white+magnetofood	
ν(O–H), ν(N–H) – Amide A	3406±5	–	3341±5	-65
ν_{as} (C–H)	2927±4	–	2927±4	0
ν_{s}(C–H)	–	–	2360±4; 2342±3	–
ν (C=O) – Amide I	1653±3	–	1642±3	-11
δ_{pl}(N–H)– Amide II	1539±3	–	1527±3	-12
δ_{pl}(C–H)	1451±3	–	1442±3	-9
δ_{pl}(C–C)	1239±2	–	1239±2	–
δ_{pl}(C–C)	–	–	1155±2	–
δ_{epl}(C–C)	1079±2	–	1027±2	-52
ν (Fe–O)	–	532±2	588±2	+56

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 δpl(N–H) to a lower frequency in the region: ν(C=O)=(1642±3) cm-1; δpl(N–H)=(1527±3) cm-1, respectively.

The absorption bands of planar and extraplanar deformation oscillations δpl(C–H) and δepl(C–C)=(1027±2)cm-1 to a lower frequency in the region □pl(C–H)=(1442±3) cm-1 and □epl(C–C)=(1027±2) cm-1 respectively. A new absorption band of planar deformation oscillations □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 (Table 1), 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 Fe3O4 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 (Table 2) 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.

As can be seen from Table 2, 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.

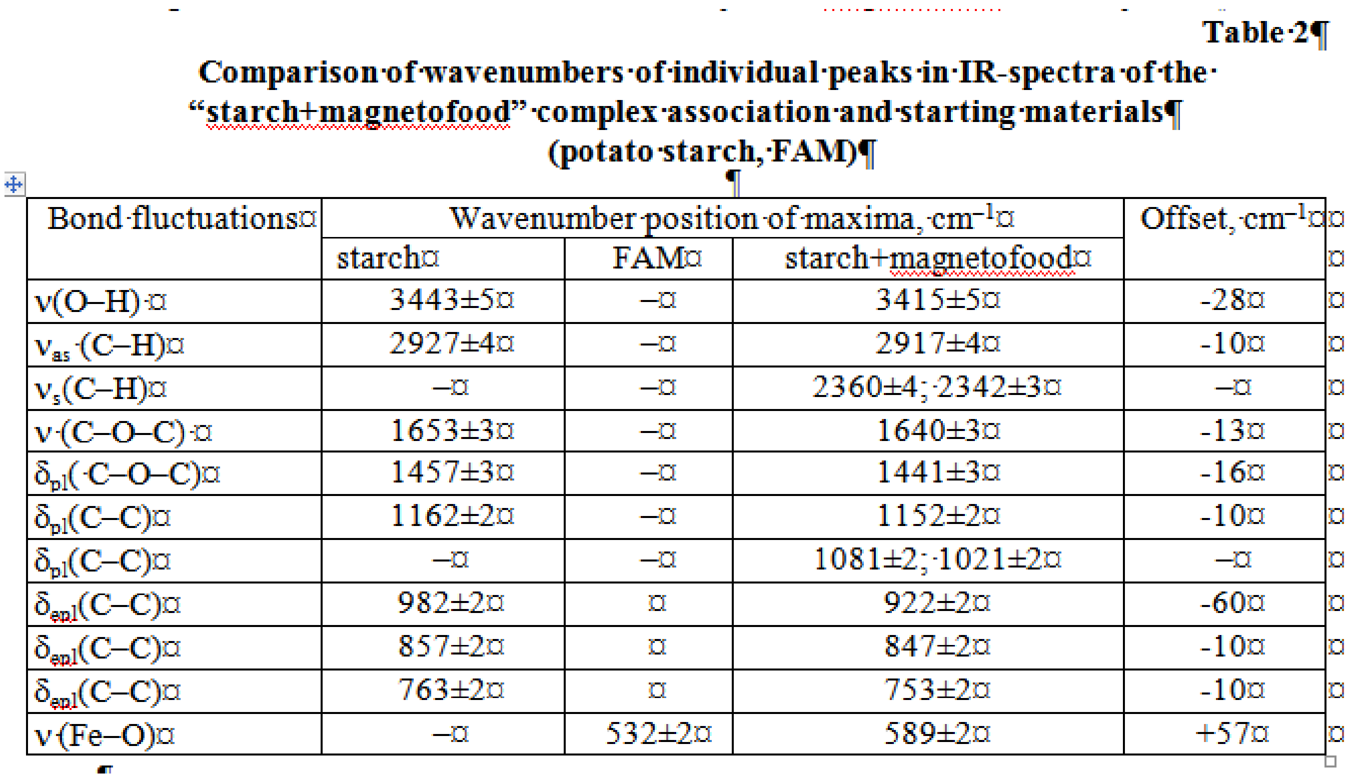

Table 2

Comparison of wavenumbers of individual peaks in IR-spectra of the “starch+magnetofood” complex association and starting materials (potato starch, FAM)

Bond fluctuations	Wavenumber position of maxima, cm^{-1}			Offset, cm^{-1}
	starch	FAM	starch+magnetofood	
ν(O–H)	3443±5	–	3415±5	-28
ν_{as} (C–H)	2927±4	–	2917±4	-10
ν_s(C–H)	–	–	2360±4; 2342±3	–
ν (C–O–C)	1653±3	–	1640±3	-13
δ_{pl}(C–O–C)	1457±3	–	1441±3	-16
δ_{pl}(C–C)	1162±2	–	1152±2	-10
δ_{pl}(C–C)	–	–	1081±2; 1021±2	–
δ_{epl}(C–C)	982±2		922±2	-60
δ_{epl}(C–C)	857±2		847±2	-10
δ_{epl}(C–C)	763±2		753±2	-10
ν (Fe–O)	–	532±2	589±2	+57

Shift of the peak of valence □ (C–O–C) by (13±3) cm-1 and planar deformation oscillations of □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 offset to 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 of FAM 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 Fe3O4 nanoparticles.

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. The experimental data presented in Figure 2 show that 1/5 of the water in solvated FAM is chemically bound moisture; ½ – bound moisture; 1/10 – free moisture and 1/2 –free, osmotic (swelling water) and physico-mechanical of the total amount of water.

Conclusions.

1. The ability of nanoparticles of food additive “Magnetofood” was noted 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-transform infrared spectroscopy proved chemosorption of macromolecular compounds (starch, egg white, higher fatty acid, triglyceride) on the surface of NP food additive “Magnetofood”: 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;

– 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.