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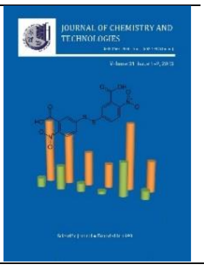

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INVESTIGATION OF INFRARED SPECTRA OF AGAR-BASED GEL SYSTEMS FOR THE PRODUCTION OF JELLY BARS

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Abstract

The purpose of this work was to determine the effect of glycerin TM BASF, sunflower honey and sesame powder TM "Korysne Boroshno" on the state of water in gel systems based on agar 1200 TM "Fujian Province" for the production of jelly bars. The research was carried out using infrared spectroscopy on a Perkin-Elmer Spectrum One FTIR Spectrometer. The study showed that gel formation in the "agar-water-glycerol" system leads to redistribution of OH groups, an increase in the number of associated hydroxyls, and water adsorption. This is confirmed by the appearance of a characteristic broad intense absorption band in the region of 37002600 cm^{-1} in the IR spectrum. The addition of honey to the gel system leads to a change in the intensity of the band of valence vibrations of the C–C bond in honey carbohydrates (at 1245 cm^{-1}) and its shift towards higher frequencies compared to the "agar-water-glycerol" gel, which is confirmed by the presence of a band absorption in the region of 1200–700 cm^{-1}. Spectroscopy data also showed that the addition of sesame powder during the preparation of an agar-based gel reduced the intensity of the OH valence vibrations of the water group (2151 cm^{-1}), and also led to a shift of the intense broad band towards higher frequencies compared to gels without sesame (2139 cm^{-1}).

Keywords: IR spectra; gel systems; agar; glycerol; honey; sesame powder.

ДОСЛІДЖЕННЯ ІНФРАЧЕРВОНИХ СПЕКТРІВ ГЕЛЕВИХ СИСТЕМ НА ОСНОВІ АГАРУ ДЛЯ ВИРОБНИЦТВА ЖЕЛЕЙНИХ БАТОНЧИКІВ

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Анотація

Метою роботи було визначення впливу гліцерину ТМ BASF, меду соняшникового та порошку кунжутного ТМ "Korysne Boroshno" на стан води у гелевих системах на основі агару 1200 ТМ "Fujian Province" для виробництва желейних батончиків. Дослідження проводили із застосуванням інфрачервоної спектроскопії на Фурьє-спектрометрі Perkin-Elmer Spectrum One FTIR Spectrometer. Було встановлено, що процес гелеутворення в системі «агар-вода-гліцерин» супроводжується перерозподілом асоційованих і неасоційованих груп ОН, збільшенням кількості асоційованих гідроксилів та адсорбційнозвязаної води, що підтверджується появою у ІЧ спекрі широкої інтенсивної смуги поглинання в області 3700–2600 см$^{-1}$ характерної для валентних коливань ОН-групи. Додавання меду до гелевої системи призводить до зміни інтенсивності смуги валентних коливань зв'язку С–С у вуглеводах меду (при 1245 см$^{-1}$) та зміщення її у бік вищих частот порівняно з гелем «агар-вода-гліцерин», що підтверджується наявністю смуги поглинання в області 1200–700 см$^{-1}$. Також дані спектроскопії показали, що додавання кунжутного порошку при виготовленні гелю на основі агару, знизило інтенсивність валентних коливань ОН групи води (2151 cm^{-1}), а також призвело до зсуву інтенсивної широкої смуги у бік вищих частот порівняно з гелями без кунжуту (2139 см$^{-1}$).

Ключові слова: ІЧ-спектри; гелеві системи; агар; гліцерин; мед; порошок кунжутний.

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Introduction

The confectionery industry is one of the leading branches of the food industry. Among the wide range of confectionery, a special place is occupied by jelly bars. They are popular, delicious, and often used as a snack. Taking into account modern trends, we have proposed an innovative technology for jelly bars using honey and sesame powder [1].

In the proposed technology of jelly bars, in order to improve the organoleptic properties and increase the nutritional and biological value of the finished product, a compatible combination of sesame powder and honey is proposed. Honey is a natural product that bees produce from the nectar of flowers. It has a pleasant sweet taste and aroma [2]. Adding honey to the composition of jelly bars will improve the texture of jelly bars, helping to bind other ingredients in the mass and reducing the fragility of the product, improve the taste properties of the bars, adding natural sweetness and aroma. In addition, adding honey to jelly bars will improve their biological value, as honey contains various beneficial substances, such as flavonoids, which have antioxidant properties, amino acids, minerals and vitamins [3].

Adding sesame to the composition of jelly bars will significantly improve the biological value of the finished product. Sesame seeds are a rich source of protein, vegetable fats and carbohydrates, and contain a number of vitamins and minerals, including iron, magnesium and calcium[4]. Also, the addition of sesame will improve the taste of the bars, as sesame has a characteristic taste and aroma that can add richness and uniqueness to the bar. Sesame also contains a lot of vegetable fats, which can provide important energy for the body. These fats can help reduce the risk of heart disease and other illnesses [5].

We chose agar as a structure former for fixing the structure of the jelly bar body, as it was established that gels based on agar have high rheological properties [6]. Also, unlike other structuring agents, such as gelatin, agar does not add calories and unpleasant taste to the finished product. Agar is a polysaccharide extracted from seaweed [7]. The chemical structure of agar consists of a mixture of agaropectin (non-gelling fraction) and agarose (gel-forming fraction) [8]. Agaropectin is removed from agar during industrial production to obtain greater gel strength [9; 10]. Agar is widely used in the food industry as a stabilizer and thickener. The addition of agar to the composition of jelly bars aims to improve the texture and stability of the product. In addition, agar has a high ability to retain moisture, so it helps the product retain its freshness. Also, agar provides better stability and fluidity of the jelly, so it allows you to get a product with a uniform consistency.

The use of agar in the technological process of production of bars with a gel-like structure requires scientific justification, since agar, when interacting with other products, is able to regulate the structural-mechanical and physico-chemical characteristics of the finished product.

Therefore, to determine the regularity of the effect of individual components of the bar on the state of water in agar-based gel systems, we chose the infrared spectroscopy method, since this method can provide a fast and accurate analysis of the chemical composition of the sample without the need to destroy it. Infrared spectroscopy can also detect even very small changes in the chemical composition of a sample, allowing for quality detection and aiding in the development of new products.

The IR spectroscopy method is one of the most important methods of analysis available to modern scientists. One of its greatest advantages is that it allows obtaining spectra of substance in all its aggregate states [11]. Near-infrared (NIR) spectroscopy is widely used for routine analysis of food, technological mixtures and quantitative determination of water, proteins, fats and carbohydrates [12]. However, the most significant advances in IR spectroscopy have occurred as a result of the introduction of spectrometry with Fourier transform and increased resolution. This type of device is based on the idea of interference of radiation between two plates to obtain an interferogram [11].

The advantages IR spectroscopy with Fourier transform include high resolution and accuracy in determining wave numbers, increased scan speed, wide spectral region coverage during a single scan, and the ability to register weak signals. It also allows measurement of complex reflection and transmission coefficients in amplitude spectroscopy.

The structural properties of agar systems with the addition of glycerol were investigated in [13; 14]. It was investigated that the presence of these two components in the system can change the absorption bands. In particular, change the absorption bands between 3600 and 3100 cm^{-1}, which are related to the stretching of the O–H group, which shows an increase in the band width due to an increase in the peak intensities at 3500, 3340, and 3180 cm^{-1}. These peaks are associated with the hydrophilic behavior of glycerol and the formation of hydrogen vibration bonds of a single bridge of interaction between the structures of agar, polyvinyl alcohol and glycerol. Scientists [15] studied the spectra of the agar system with the addition of glycerol as a plasticizer. FT-IR analysis confirmed that the interaction between agar and plasticizer is based on hydrogen bonds due to the presence of -OH and -NH_2 groups. The hydroxyl group of the plasticizer and agar can be found as an overlapping peak at approximately 3200–3600 cm^{-1}.

A group of scientists [16] performed a spectral analysis to assess possible chemical interactions and structural changes in the functional groups of agar and glycerol, and also investigated the presence of additional connections in the system. The spectra of agar and glycerol showed a peak at about 3400 cm^{-1}, which the authors claimed was due to the stretching of the O–H group, while the peak at 2900 cm^{-1} was attributed to methoxyl groups [17]. The spectra of agar systems with the addition of glycerol were investigated in works [18; 19]. The spectra showed a broad band at approximately 3440 cm^{-1}, which the authors attributed to complex vibrations associated with free hydroxyl groups (-OH) both inter- and intramolecular [20]. This signal increased with the presence of glycerol, indicating that the functional groups of the agar system exhibit hydrogen bonding interactions between the OH groups of glycerol.

However, during the analytical review, it was found that there are almost no studies related to the determination of infrared spectra of gel-like agar systems in combination with glycerin, honey and sesame flour.

The aim of our work was to determine the effect of glycerin, honey and sesame powder on the water condition in gel systems based on agar. Since agar is used as a gelling agent in the food industry, its structure, physicochemical properties, and relationship with other components require a wider study, which determines the prospects of the chosen direction.

Results and discussion

Materials. The initial components for the preparation of gels were samples of agar 1200 TM "Fujian Province" (China) (1), glycerol food TM BASF (Germany) (2), sunflower honey (3), sesame powder TM "Korysne Boroshno" (Ukraine) (4).

Preparation of samples of "agar-water-glycerol", "agar-water-glycerol-honey", "agar-water-glycerol-honey-sesame powder". Gels based on aqueous solutions of agar with glycerol (sample 5) or agar with glycerol and honey (sample 6), or agar with glycerol, honey and sesame powder (sample 7) were obtained.

To prepare samples 5–7, 1 g of agar was soaked in 22 g of water, 22 g of glycerol was added and left to swell for 60–120 minutes at a temperature of 20±2°C. Next, samples 5–7 were heated to 85–90°C until complete dissolution of the dry component (agar).

Sample 5 was cooled to form a gel. Samples 6 and 7 were cooled to a temperature of 40–45 °C, then added to sample 6–30 g of honey, sample 7–30 g of honey and 25 g of sesame seeds, mixed and left to form a gel. As a result, gel-like systems with a homogeneous, smooth surface were obtained.

Methods. The qualitative composition and regularities of influence of separate prescription components on the state of water in model gel systems "agar-water-glycerol", "agar-water-glycerol-honey", "agar-water-glycerol-honey-sesame powder" are studied. The study was performed using IR spectroscopy on a Fourier spectrometer Perkin-Elmer Spectrum One FTIR Spectrometer. Liquid samples (glycerol, honey, gel systems) were examined by the method of crushed drop and recorded in a thin layer between selenide zinc plates. Solid samples (agar, sesame powder) were pre-dried to constant weight of the sample and mixed with potassium bromide (3 mg sample / 300 mg KBr).

IR spectra of agar, glycerol, gel system "agar-water-glycerol". By chemical nature, agar is constructed with slight variations from the residues of molecules of D-galactose and 3,6-anhydro-L-galactose with a low content of sulfate ester. The addition of glycerol as a moisture-retaining agent to aqueous agar gels reduces their dehydration. According to literutature [21] the presence of tannic acid in agar inhibits the gelation process. It was shown that small amount of glycerol can prevent this inhibition [21].

To study the IR spectra of agar-based gels, the following main absorption bands can be noted: 3600–3200 cm^{-1}, 3000–2800 cm^{-1}, 2150 cm^{-1}, 1650–1500 cm^{-1}, 1600–800 cm^{-1} [21–23]. In paper [22] for agar specific absorption bands of secondary axial (850 cm^{-1}), secondary equatorial (830 cm^{-1}) and primary (820 cm^{-1}) sulfate were noted. The sulfate group in position 2 of the 3,6-anhydrogalactose residues has its own absorption band at 810 cm^{-1}. In paper [23], sulfates were determined by the following absorption coefficients: total sulfates – 1250/2920, galactose-4-sulfate – 845/2920, 930/2920 and 3,6-anhydrogalactose-2-sulfate – 805/2920. The absorption at 930 cm^{-1}, which corresponds to 3,6-anhydrogalactose, is also related to the content of galactose-4-sulfate in agar.

The main provisions of the maximum absorption bands in the IR spectrum of water (liquid) corresponding to such vibrations are known: asymmetric stretching et 3600 cm^{-1}, symmetric stretching et 3450 cm^{-1}, overtones et 3290 cm^{-1}, combination modes et 2150 cm^{-1}, bending et 1645 cm^{-1}, twisting et 780 cm^{-1} [23; 24]. It should be noted, that due to various interactions there is a change in the position of characteristic maximums of absorption in the IR spectra of food model systems based on aqueous gels compared to the IR spectra of water or gels.

As a result of the study, IR spectra of experimental model samples of gels based on agar with glycerol with the addition of honey and sesame were obtained. In fig. 1 shows the IR spectra of samples of agar, glycerol, gel system "agar-water-glycerol".

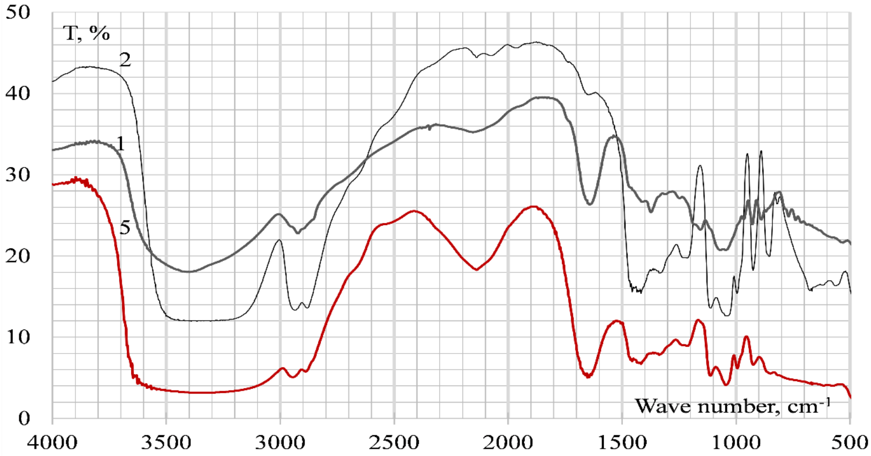

Fig. 1. IR spectra of samples: 1 – agar, 2 – glycerol, 5 – gel system "agar-water-glycerol"

Experimentally determined data on the assignment of the bands of the IR spectra of agar, glycerol and water-glycerol gels of agar are given in Table 1.

Table 1

Frequency positions (cm^{-1}) of the main bands of the IR spectra of the absorption of functional groups of agar and glycerol before and after the interaction

Wave number, cm^{-1}			Band assignments
agar	glycerol	"Agar-water-glycerol"	
3500-3300	3500-3200	3600-3100	–OH (stretching); H_2O adsorption bound (stretching); –NH (stretching)
2924 –	2935 2882 –	2945 2889	C–H (stretching antisymmetric and symmetric); –CH_2 groups in glycerol; –OCH_3 methoxyl groups in agar
2156*	2138	2139	–OH (stretching of associated groups); in carboxyl group*; in water (2150 cm^{-1}) [23, 24]
1644	–	1645	–NH–CO– (stretching in conjugated peptide bond); –COO– in agar's pectin substances (1650–1500 cm^{-1}) [22, 23]; H–O–H water (bending)
–	1647	1652	
–	1417	1417	C–O–H (bending) in alcohols
1374	–	1373	H–C–H (scissoring bending) in methyl group; –S=O (symmetric stretching) in sulfate ester
–	1337	1337	C–O–H (bending) in alcohols
1248	–	1234	S–O/C–O (symmetric stretching) common to all sulfate groups/esters
–	1215	–	–C–C (bending) in alcohols
1159	–	–	S–O/C–O (antisymmetric stretching) in R–SO_2–R
–	1112	1112	C–O (bending) in polyhydric alcohol
1072, 1047, 930	–	– 1045, 925	–CH_2– (bending) of pyranose ring of 3,6- anhydrogalactose (1070 i 930 cm^{-1}) [27]
1047 967	1044, 1039, 996, 925	1045, 994, 925	C–O–H (bending)

Continued table 1

891, 857	–	850	C–C/C–O/S–O (stretching) in D-galactose-4-sulfate (845 cm^{-1}) [27];
812			C–O–S (bending) in D-3,6-anhydrogalactose-2-sulfate (805 cm^{-1})[27]
–	854,	850	C–O–H (bending) in O–H associated
–	667	–	

In the IR spectrum of agar (3 mg pre-dried to constant weight of the sample / 300 mg KBr) there are the following bands of absorbtion: intense bands corresponding to stretching of O–H, N–H bonds and fluctuations of adsorption band of water (in the range of 3600–3200 cm^{-1} with a maximum of 3400 cm^{-1}); band for antisymmetric stretching of C–H bonds in methoxyl groups $-OCH_3$ (at 2924 cm^{-1}); C=O symmetric stretching and N–H bending in conjugated peptide bond in pectin substances (at 1644 cm^{-1}); S=O symmetric stretching in sulfate ester; methyl group vibration (at 1374 cm^{-1}); band of symmetric stretching of S–O, C–O bonds common to all agar sulfate groups (at 1248 cm^{-1}); average intensity bands characteristic to CH_2 bending of pyranose ring of 3,6-anhydrogalactose (at 1072, 930 cm^{-1}); C–C, C–O, C–O–S stretching, C–O–H bending represented by weak band characteristic to galactose-4-sulfate (at 857 cm^{-1}) and weak band characteristic to 3,6-anhydrogalactose-2-sulfate (at 812 cm^{-1}). Literature data describes the analogous values for characteristic bands of agar sample [22, 23, 24].

Glycerol (Fig. 1, sample 2) being a triatomic alcohol has three –OH groups in the molecule that contribute to the formation of intermolecular hydrogen bonding, which is manifested in the form of a very wide blurred band in the range of 3500–3200 cm^{-1}. The region of 1400–1000 cm^{-1} is the region of bending vibrations in the molecule of glycerol. The presence of a polar C–O bond causes an intense band in the range of 1200–1000 cm^{-1}. In the IR spectrum of glycerol (Fig. 1, sample 2 and Table 1) there are the following bands of absorbtion: intense bands corresponding to stretching of associated –OH, (a maximum of 3391 cm^{-1}); band for antisymmetric stretching and symmetric stretching of C–H bonds in $-CH_2$, –CH– groups (at 2935 cm^{-1} and 2882 cm^{-1}); associated –OH bending (at 1647 cm^{-1}); C–O–H, –OH bending (at 1417 cm^{-1}, 1337 cm^{-1}); –C–C, C–O bending in alcohols (at 1215 cm^{-1} and 1112 cm^{-1}); C–O–H bending (at 1044 cm^{-1}, 1039 cm^{-1} and 996 cm^{-1}, 925 cm^{-1}).

The process of gelation in the system water-glycerol-agar is characterized by a variety of physicochemical interactions between functional groups. After the formation of the gel "agar-water-glycerol" (sample 5) there is a wide blurred intense band in the region 3700–2600 cm^{-1}, significantly expanded compared to the data for the samples agar (1) and glycerol (2) due to redistribution of associated and non-associated OH groups together with increasing of the quantity of associated hydroxyls, also due to the adsorption of bound water and overlaping with the band 3600–3200 cm^{-1} (stretching –OH in glycerol, adsorption-bound water and –OH, –NH in agar) and bands 3000–2800 cm^{-1} (antisymmetric stretching of –CH– bonds in groups $-CH_2-$, $-OCH_3$). Bands of antisymmetric stretching of –CH–, $-CH_2-$, $-OCH_3$ bonds at 2924 cm^{-1} (agar), 2935 cm^{-1} (glycerol) and symmetric stretching of bonds at 2882 cm^{-1} (glycerol) in agar-water-glycerol gel are shifting towards higher frequencies – 2945 cm^{-1} and 2889 cm^{-1}. The peak positions of antisymmetric (2935 cm^{-1} → 2945 cm^{-1}) and symmetric (2882 cm^{-1} → 2889 cm^{-1}) CH_2 stretching shifted to bigger wavenlenghth region with decreasing glycerol concentration (Table 1) [25].

In the gel (Fig. 1, 2, sample 5) stretching vibrations of the associated hydroxyl groups are represented by an intense wide absorption band in the region 2500–1800 cm^{-1} with a maximum of 2139 cm^{-1} caused by the formation of a significant number of intermolecular hydrogen bonds in chains with different molar mass. Compared with a spectrum of liquid water (et 2150 cm^{-1}) [23, 24] the maximum of the gel absorption band shifts towards the smaller wave numbers, the intensity of the band increases, as well as the intensity of the band of its bending component (et 1645 cm^{-1}). At the same time, the band of symmetric stretching (3450 cm^{-1}) significantly expands in the spectrum due to the formation of new hydrogen bonds between carbon chains with different molar masses.

In the gel spectrum (Fig. 1, 2, sample 5) in the frequency range 1800–1500 cm^{-1} there is an overlap of the bands of bending vibrations of C–O–H in glycerol (1647 cm^{-1}) and stretching vibrations of the conjugated peptide bond –NH–CO–, the –COOH group in pectin substances of agar (1644 cm^{-1}) with the formation of a wide intense band with two practically superimposed maxima at 1652 cm^{-1} and 1645 cm^{-1}. The shift of the maxima of the absorption bands in the gel (1644 cm^{-1}, 1652 cm^{-1}) towards higher frequencies compared to the maxima in agar (1644 cm^{-1}) and glycerol (1647 cm^{-1}) is more clearly visible in Fig. 2. This maximum of absorption band in the gel (1652 cm^{-1}) is shifted towards higher frequencies compared to the absorption maximum, which corresponds to the bending vibrations of water (et 1645 cm^{-1}), primarily indicates on the formation of new hydrogen bonds between agar polysaccharides, glycerol molecules and water.

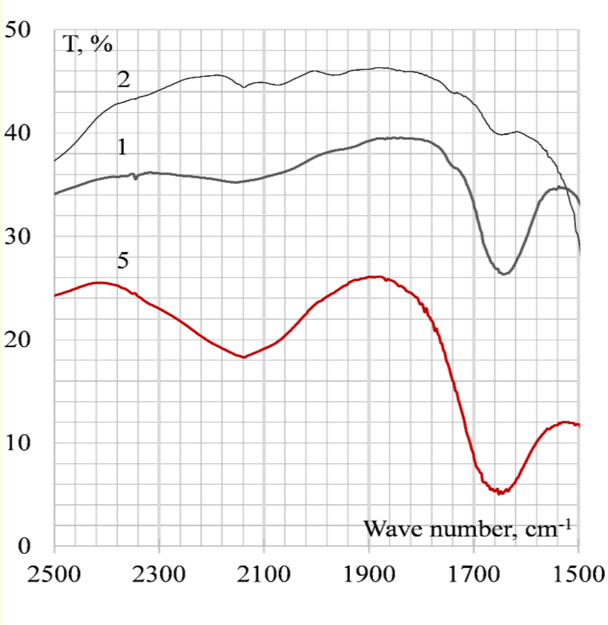

Fig. 2. IR spectra of samples: 1 – agar, 2 – glycerol, 5 – gel system "agar-water-glycerol" in the frequency range 2500–1500 cm^{-1}

The weak absorption band at 1417 cm^{-1}, which corresponds to the bending vibrations of C–O–H bonds in glycerol (Fig. 1, sample 2), decreases in intensity in the agar-water-glycerol gel.

Similarly, the intensity of the weak band of bending vibrations of C–O–H bonds in alcohol groups decreases (1337 cm^{-1}). For the gel, the character of a wide triad of bands in the frequency range from 1200 to 900 cm^{-1} (maximums at 1112, 1045, 994 cm^{-1}, which attributed to –C–C, C–O bending in alcohols, C–O–H bending in polyhydric alcohol) is preserved and their intensity decreases compared to glycerol (maximums at 1112, 1039, 1044, 996 cm^{-1}). Apart of hydrogen bonds formation the gelation process may be favorised by participation of certain amount of glycerol hydroxyl groups in the formation of ester bonds with carboxylic groups of tannic acid in agar. As it was indicated before, the binding of tannic acid by glycerol promotes the gelation process in the agar gel [25].

After the gel formation, there is a significant change in a character and intensity of the weak absorption band of sulfate esters in agar (maximum at 1374 cm^{-1}). In the gel system, the position of the maximum is preserved, but the band itself is practically not pronounced. The band with a maximum at 1159 cm^{-1}, which can be attributed to R–SO$_2$–R groups in agar, is weakly expressed as a shoulder in the gel spectrum in the range from 1168 cm^{-1} to 1148 cm^{-1}. The intensity of the weak agar band at 1248 cm^{-1}, which is common to all sulfate groups, significantly decreases in the gel. In addition, it shifts towards the lower frequencies in the gel (at 1234 cm^{-1}).

After the formation of the agar gel the character of the bands in the range from 1140 cm^{-1} to 950 cm^{-1} changes significantly. In the spectrum of the gel, the band of average intensity at 1072 cm^{-1}, which belongs to 3,6-anhydrogalactose, overlaps with the band corresponding to C–O stretching vibrations in glycosidic bonds of carbohydrates. Single band at 1045 cm^{-1} is formed due to this overlap. The band at 967 cm^{-1} (a band attributed to C–O–H bending vibrations in agar) overlaps with the band at 996 cm^{-1} (a band attributed to C–O–H bending vibrations in glycerol). Single band at 994 cm^{-1} is formed due to this overlap. Instead of the bands at 857 cm^{-1} (weak bands attributed to galactose-4-sulfate), 812 cm^{-1} (weak band attributed to 3,6-anhydrogalactose-2-sulfate) there is a single band at 850 cm^{-1} formed as a result of the overlapping of the abovementioned bands in this range.

IR spectra of honey and gel system "agar-water-glycerol-honey". Honey is a very useful natural product used in confectionery technology. It is also used to make various fillings. Natural honey is an invert sugar. It contains about 400 different compounds [26]. The main substances of honey are carbohydrates and water. Carbohydrates in honey are represented by monosaccharides of glucose and fructose, disaccharides - mainly sucrose and maltose, dextrins of starch and glycogen, and pectin substances [26; 27]. Protein compounds, mostly enzymes, predominate among the nitrogenous substances in honey. Non-protein substances are mainly represented by amino acids and a small amount of alkaloids. In addition, there are organic (gluconic, malic, citric, lactic, linoleic, linolenic and other) and inorganic (phosphate, chloride) acids in the form of salts and esters, minerals (about 40 micro and macro elements), coloring compounds (carotenoids, chlorophyll, xanthophyll, anthocyanins, tannins, melanoidins), aroma-forming compounds. Honey is characterized by a rather attractive vitamin profile. It contains thiamine, riboflavin, pantothenic acid, vitamins PP, C, H, E [26]. Carbohydrates and nitrogenous compounds, as well as water are important substances for the analysis of infrared spectra [27; 28].

The results of the study of the IR spectra of honey and gels based on agar with glycerol with the addition of honey "agar-water-glycerol-honey" in comparison with the spectrum of the gel "agar-water-glycerol" are shown in Fig. 3.

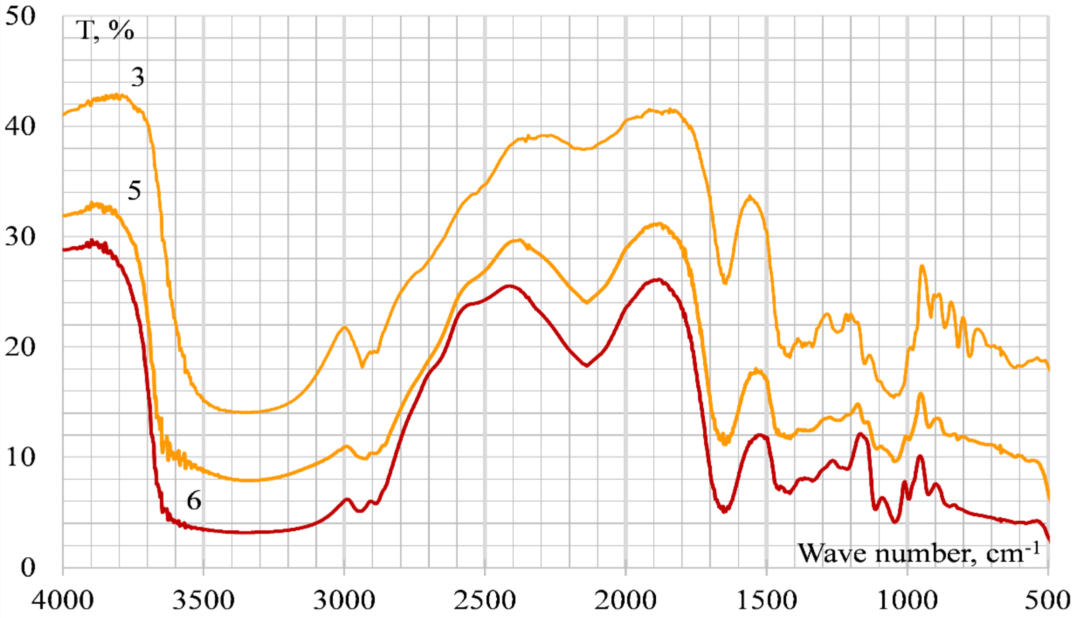

Fig. 3. IR spectra of samples: 3 – honey, 5 – gel system "agar-water-glycerol", 6 – gel system "agar-water-glycerol-honey"

The IR absorption spectrum typical for natural honey was determined (Fig. 3, sample 3) with the corresponding assignment of characteristic frequencies in 6 regions of the spectrum: 3600–3200, 3000–2800, 1700–1600, 1540–1175, 1175–940, 940–700 cm^{-1}. In particular, there are absorption bands:

in the region of 3600–3200 cm^{-1} with a maximum of 3365 cm^{-1} – –OH stretching in carbohydrates and carboxylic acids, –N–H stretching, – NH_2 stretching in free amino acids (intense);

2936 cm^{-1} i 2903 cm^{-1} – –C–H, $-CH_2-$ stretching in carbohydrates;

2152 cm^{-1} – –OH stretching of associated groups of carbohydrates wiht water;

1645 cm^{-1} – –OH stretching, H–O–H bending in water, –C=O stretching in carbohydrates, bending – Amide I of proteins (intensive);

1417 cm^{-1} – H–O–H bending in water combinations wiht –CH–OH bending in carbohydrates (weak);

1373 cm^{-1} – C–O–H bending (weak);

1249 cm^{-1} – C–C stretching in carbohydrates (average);

1048 cm^{-1} – C–O stretching in glycosidic bonds of carbohydrates (average);

916 cm^{-1}, 866 cm^{-1}, 819 cm^{-1} 778 cm^{-1} – –C–H bending of anomers and cycles in carbohydrates (average).

The honey spectrum also contains a weak band with a maximum at 1151 cm^{-1} attributed to the bending vibrations of C–O–H, which is associated with the presence of the pyranose cycle in carbohydrates. A weak peak observed at 1102 cm^{-1} could be associated with the C–O stretching vibrations in the C–O–C bond, which is present as a glycosidic bond in sucrose.

Since the spectral range from 1200 to 700 cm^{-1} (maximum et 1048 cm^{-1}) is set as characteristic for natural honey, it was decided to investigate this spectral region during further analysis of the model gel with the addition of honey. The absorption spectra of gels "agar-water-glycerol-honey" (Fig. 3, sample 6) and "agar-water-glycerol" (Fig. 3, sample 5) have a similar character and differ in the intensity of some bands. Thus, the intensity of the band of a stretching vibrations of C–C bond in carbohydrates (at 1245 cm^{-1}) decreases and at the same time shifts to higher frequencies compared to honey (at 1249 cm^{-1}) and “agar-water-glycerol” gel (at 1234 cm^{-1}). The character of the spectrum of the gel with honey (Fig. 3, sample 6) changes in the region of 900–600cm^{-1}. In this region, the bands (maximums at 916 cm^{-1}, 866 cm^{-1}, 819 cm^{-1}, 778 cm^{-1}) attributed to the bending C–C–H vibrations of anomers and cycles of honey carbohydrates (Fig. 3, sample 4) are expressed insignificantly. This may be related to conformational changes between cyclic hemiacetal forms and linear oxoforms of the reducing carbohydrates of honey – glucose, fructose, maltose.

In the "agar-water-glycerol-honey" gel (Fig. 3, sample 6), a weak absorption band was noted at the frequency of 1151 cm^{-1}. This band was not present in the “agar-water-glycerol” gel. As mentioned above, the band can be attributed to C–O–H bending vibrations, which are associated with the presence of the pyranose cycle in honey carbohydrates. This is probably due to the presence of reducing carbohydrates in honey and their ability to cyclooxotautomerism.

IR spectra of gel system "aga-water-glycerol-honey-sesame powder". IR spectra of gel samples (Fig. 4), to which sesame powder was introduced "agar-water-glycerol-honey-sesame powder", differ from gels "agar-water-glycerol" and "agar-water-glycerol-honey" in all parts of the spectrum (3600–3200 cm^{-1}, 3000–2800 cm^{-1}, 2500–1800 cm^{-1}, 1800–1500 cm^{-1}, 1500–1200 cm^{-1}, 1200–940 cm^{-1}, 940–700 cm^{-1}). Therefore, it is advisable to analyze the effect of adding sesame powder and assigning the frequency positions of the main absorption bands of the functional groups of sesame powder substances (Fig. 4).

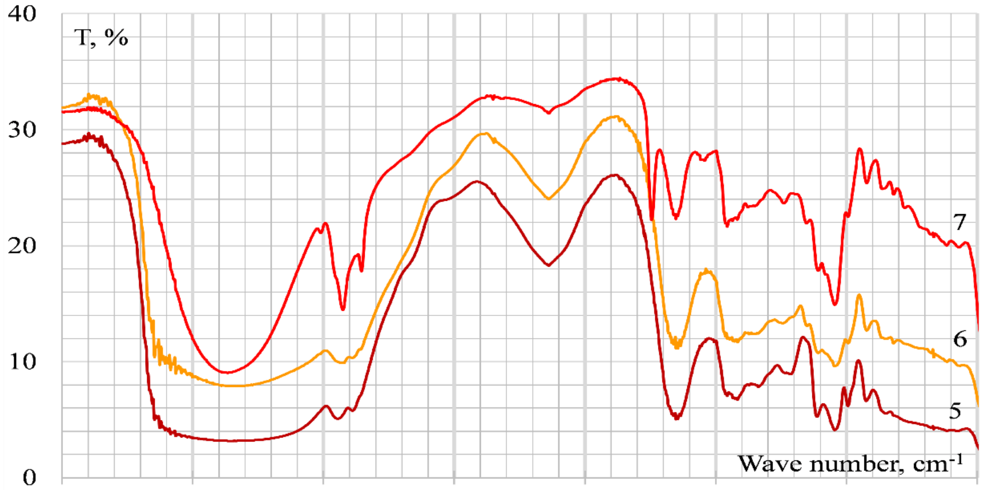

Fig. 4. IR spectra of samples: 5 – gel system "agar-water-glycerol", 6 – gel system "agar-water-glycerol-honey", 7 – gel system "agar-water-glycerol-honey-sesame powder"

Sesame powder has one of the highest oil contents among the main oilseeds [29]. It is also rich in proteins, carbohydrates, vitamins, polyunsaturated fatty acids in the composition, such as triacylglycerols fat, lignans (sesamin and sesamolin), tocopherol, phytosterols, phytates and other micronutrients [30]. Features of its chemical composition are reflected in the IR absorption spectra (Fig. 5, sample 4).

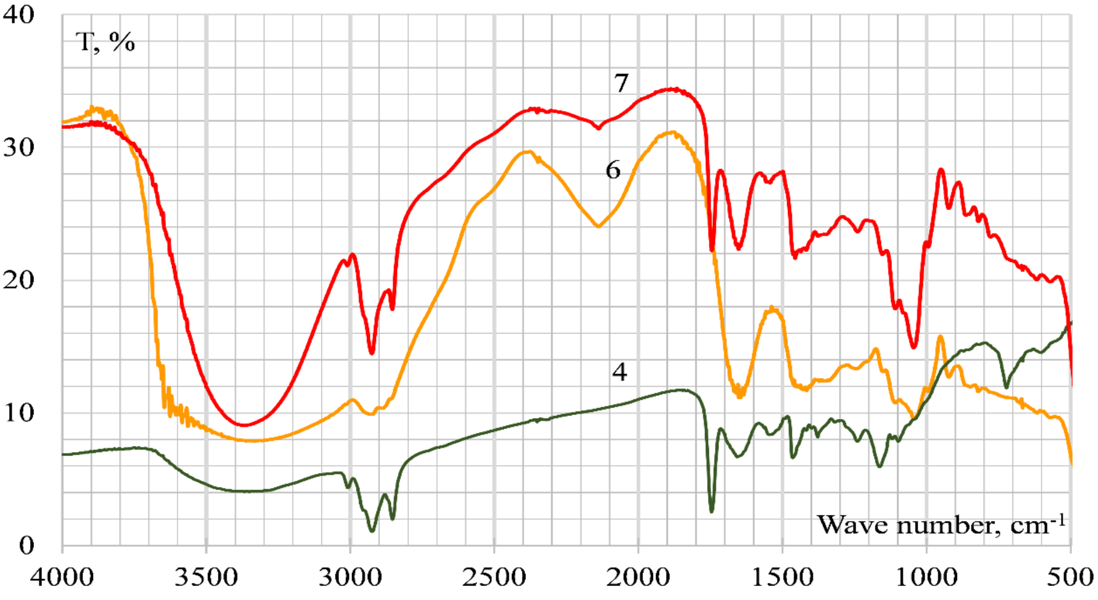

Fig. 5. IR spectra of samples: 4 – sesame powder, 6 – gel system "agar-water-glycerol-honey", 7 – gel system "agar-water-glycerol-honey-sesame powder"

The IR spectra of sesame powder were studied (Fig. 5, sample 4) and the analysis of the characteristic absorption bands attributed to the corresponding types of stretching and bending vibrations was made:

in the region of 3600–3200 cm^{-1} with a maximum of 3351 cm^{-1} – there are –OH stretching in carbohydrates and phenolic groups, –NH stretching – Amide A (intensive);

3009 cm^{-1} – C–H asymmetric stretching vibrations in groups –CH=CH– in the cis-form (mostly linoleic acid in the composition of triacylglycerols in sesame oil);

2927 cm^{-1} i 2855 cm^{-1} – C–H stretching in groups –CH$_2$–;

1736 cm^{-1} – C=O stretching in esters (triacylglycerols of sesame oil);

1653 cm^{-1} – –OH, –C=O stretching in esters (triacylglycerols of sesame oil);

1546 cm^{-1} – –OH, –C=O stretching in carbohydrates, combinations of C–N–H bending vibrations and CN stretching – Amide II (average);

1465 cm^{-1} – –CH$_2$– bending (intensive);

1398 cm^{-1} – –CH$_3$ symmetric bending vibrations (weak);

1240 cm^{-1}, 1163 cm^{-1} 1098 cm^{-1} – triad of ester bands (sesame oil triacylglycerols) with a combination of stretching vibrations of groups –CH$_2$–OCO– and –OCH$_2$–CH$_2$ (weak, average and weak);

722 cm^{-1} – C–O–C stretching (intensive).

It can be assumed that a weak band at a frequency of 1240 cm^{-1} can be attributed to the band Amide III and which corresponds to a combination of –NH bending vibrations and CN stretching.

The absorption spectrum of the gel with sesame powder (Fig. 4, 5, sample 7) is consistent with the profile of the spectrum of sesame powder and significantly changes the nature of the absorption bands compared with gels "agar-water-glycerol" (Fig. 4, sample 5) and "agar-water-glycerol-honey" (Fig. 4, 5, sample 6) in the region of 3600–2600 cm^{-1}, 2400–1800 cm^{-1}, 1800–1500 cm^{-1}.

Thus, the very addition to the gel of sesame powder, rich in protein, phenolic compounds, fats containing polyunsaturated acids, causes the formation of a clear broad intense band with a maximum of 3366 cm^{-1}, (–OH stretching vibrations in carbohydrates and phenolic hydroxyl, –NH stretching vibrations of Amide A, adsorption bound water); weak band at 3011 cm^{-1} (C–H asymmetric stretching vibrations in the groups –CH=CH– in the cis-form of mostly linoleic acid in the composition of triacylglycerols of sesame oil); increasing the intensity of the broad band at 2926 cm^{-1} and 2855 cm^{-1} (C–H stretching vibrations in the groups –CH$_2$–).

Also in the region at 1800–1500 cm^{-1} for the spectrum of the system "agar-water-glycerol-honey-sesame powder" in comparison with the samples "agar-water-glycerol" and "agar-water-glycerol-honey" there is a separation and the appearance of three pronounced bands – at 1745 cm^{-1} (C=O stretching vibrations of esters in sesame oil triacylglycerols), 1652 cm^{-1} (–OH,

–C=O stretching vibrations in carbohydrates, –NH bending vibrations of Amide I, bending vibrations of water), 1544 cm^{-1} (–OH, –C=O stretching vibrations in carbohydrates, combination of –NH bending vibrations and CN stretching vibrations of Amide II).

The high-frequency shift of the band at 1652 cm^{-1} compared to the absorption maximum, which corresponds to the bending vibrations of water (1645 cm^{-1}), primarily indicates on the formation of new hydrogen bonds between polysaccharides in agar and polypeptides in sesame powder. Also, this shift indicates on a transition from single water molecules to associates containing up to 6 molecules. This statement was formulated taking into account the results of the study of the state of moisture in gels of a protein-polysaccharide nature by the method of infrared spectroscopy [31]. The authors of the study prove that the strengthening of the structure of protein-polysaccharide gels based on agar occurs not only due to intermolecular interactions of polymers. Strengthening also occurs due to the significant limitation of water mobility through the formation of polymer associates containing from three to six water molecules [31].

For the gel "agar-water-glycerol-honey-sesame powder" (Fig. 4, 5, sample 7) is noteworthy the fact of reducing the intensity of the wide band of stretching vibrations of the associated –OH groups and water with a maximum of 2151 cm^{-1}, as well as its shift towards higher frequencies compared to water (2150 cm^{-1}) and gels without sesame (2139 cm^{-1}). The formation of gels "agar-water-glycerol" and "agar-water-glycerol-honey" in the water-glycerol binary solvent was accompanied by a significant increase in the number of intermolecular hydrogen bonds between the chains of agarose, agarose and water, agarose and oligosaccharides of honey etc., that resulted in widening the band with a maximum of 2139 cm^{-1} together with increasing of its intensity, which was observed in the IR spectra. The addition of sesame powder in the manufacture of gel can potentially reduce the intensity of bending stretching of water molecules, the number of hydrogen bonds formed in the system that means an increase in the amount of weakly bound water. However, this hypothesis can only be finally proved experimentally.

In other parts of the spectrum, there were also some differences in the absorption bands of the gel samples, the nature of which can be more clearly compared in the spectrum. 1600–800 cm^{-1}.

The triad of bands at 1240 cm^{-1}, 1163 cm^{-1}, 1098 cm^{-1} (Fig. 5, sample 4) is an attribute of sesame oil triacylglycerols and is formed as a combination of C–O, –C–O–C stretching vibrations and –CH$_2$– bending vibrations in ester groups –CH$_2$–OCO–. The intensity of these bands decreases in the spectrum of the gel "agar-water-glycerol-honey-sesame powder" (Fig. 5, sample 7) compared to sesame powder (Fig. 5, sample 4). These bands in the gel overlap with a wide intense band with a maximum at 1045 cm^{-1}, which is attributed to the combination of –C–O–H bending vibrations and C–O stretching vibrations in glycosidic bonds of carbohydrates. The band of –C–O–H bending vibrations and C–O stretching vibrations is distinctly visible in the spectra of samples 1, 2, 3, 5, 6, 7 (Fig. 1, Fig. 3, Fig. 5).

The absorption bands for samples 5, 6, 7 (Fig. 5) with maxima at 1234 cm^{-1}, 1245 cm^{-1}, 1240 cm^{-1}, respectively, can be attributed to C–C stretching vibrations of carbohydrates and all sulfate groups of agar.

A weak absorption band with a maximum at 1153 cm^{-1} is present in the spectrum of the gel "agar-water-glycerol-honey-sesame powder" (Fig. 5, sample 7).

The spectra of honey sample (Fig. 3, sample 3) and "agar-water-glycerol-honey" gel (Figs. 3, 4, 5, sample 6) form similar bands at 1151 cm^{-1}. These bands can be attributed to C–O–H bending vibrations in the pyranose cycle of reducing carbohydrates. This is probably due to the presence of reducing carbohydrates in honey samples – mainly glucose and fructose and their ability to cyclooxotautomerism.

For all gel samples 5, 6, 7 there are bands of C–O–H bending vibrations (at 1112 cm^{-1}, 1109 cm^{-1}, 1108 cm^{-1} and 994 cm^{-1}, 993 cm^{-1}, 994 cm^{-1}), C–O stretching vibrations in glycosidic bonds of carbohydrates (1045 cm^{-1}, 1046 cm^{-1}, 1045 cm^{-1}), C–C–H bending vibrations of anomers and cycles of carbohydrates in the region of 900–600cm^{-1}.

In the spectra of the gels samples 5, 6, 7 the band of average intensity at 1072 cm^{-1}, which belongs to 3,6-anhydrogalactose, overlaps with the band of C–O stretching vibrations of glycosidic bonds in carbohydrates. A single band is formed as a result of this overlap in the samples 5, 6, 7 at 1045 cm^{-1}, 1046 cm^{-1}, and 1045 cm^{-1}, respectively.

The band attributed to galactose-4-sulfate overlaps with the band attributed to 3,6-anhydrogalactose-2-sulfate forming a single band at 850 cm^{-1}.

For gel samples 6, 7 there are weak bands attributed to galactose-4-sulfate (at 848 cm^{-1}, 855 cm^{-1}), a weak band attributed to 3,6-anhydrogalactose-2-sulfate (at 820 cm^{-1}, 820 cm^{-1}).

Conclusions

The results of IR spectroscopy confirm the formation of a physical gel based on agar due to the formation of numerous hydrogen bonds. Glycerol in the agar gel contributes to the gel formation process due to the formation of additional intermolecular hydrogen bonds, as well as due to the possible binding of tannic acid present in the agar.

The data of analysis of IR spectra during the formation of gel in a binary solvent water-glycerol proved the emergence of additional links between the agar-based structurant and honey and sesames in the system, as well as a significant limitation of water mobility due to the formation of polymer associates containing.

It has been shown that the formation of "agar-water-glycerol" and "agar-water-glycerol-honey" gels in a binary water-glycerol solvent is accompanied by a significant increase in the number of intermolecular hydrogen bonds between the chains of agarose, agarose and water, agarose and honey oligosaccharides.

It has been found that the addition of sesame powder to the gel system can cause a certain decrease in the intensity of deformation oscillations of water molecules during gel production.

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