

Представлені дослідження з синтезу наночастинок магнетиту. Утворені дисперсії досліджені спектрофотометричним методом. Проаналізовані спектри оптичного поглинання дисперсій наномагнетиту за допомогою теорії плазмонних коливань.

Синтез наночастинок здійснювали у водному розчині та з використанням в якості дисперсного середовища 3,5 % полівінілпірролідону. Співвідношення солей феруму (III)/(II) становило 1,5:1. Підібрані робочі концентрації реагуючих речовин, у результаті чого утворюються стійкі дисперсії наночастинок з магнітними властивостями. Показано, що при варіюванні кількості та способу введення в систему розчину амоніаку, утворюються більш стабільні дисперсії наночастинок. В результаті дослідження поверхневого плазмонного резонансу дисперсій наночастинок магнетиту встановлено, що всі синтезовані дисперсії характеризуються максимумом поглинання при довжині хвилі 350 нм, однак інтенсивність смуг поглинання напряму залежить від розмірів частинок. Наночастинки магнетиту синтезовані з використанням в якості дисперсного середовища 3,5 % полівінілпірролідону (ПВП) характеризуються наявністю трьох хвиль поглинання при 350 нм, 950 нм, 1050 нм. Запропонований можливий механізм стабілізації наночастинок магнетиту в полівінілпірролідоні. В ході роботи було встановлено, що полівінілпірролідон, з одного боку, сприяє зародкоутворенню, а з іншого боку, ефективно стабілізує наночастинки

Ключові слова: наночастинки, магнетит, радіус наночастинок, агрегативна стійкість, плазмонний резонанс, полівінілпірролідон (ПВП), смуги поглинання

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SYNTHESIS OF MAGNETITE NANOPARTICLES STABILIZED BY POLYVINYL-PYRROLIDONE AND ANALYSIS OF THEIR ABSORPTION BANDS

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1. Introduction

The past decades saw active creation of new materials with decreased dimensionality. Among their diversity, we can separate magnetic nanomaterials.

Iron, nickel, cobalt, and oxides of these metals are normally used in order to obtain magnetic nanoparticles. The disadvantage of metals is that their magnetization decreases considerably at oxidation of the surface that is in contact with atmospheric oxygen. Magnetite Fe_3O_4 is devoid of this disadvantage [1]. The main advantages of magnetite include low susceptibility to oxidation, high magnetic properties, low cost, and significantly lower toxicity, unlike oxides of other metals [2].

The methods of chemical synthesis are used most often to control the size, shape, composition, structure, and physical properties of nanoparticles. By changing the dimensions, shape, composition and structure of nanoparticles, it is possible to control the magnetic characteristics within certain limits. The chemical method of

co-sedimentation is the simplest and effective way of obtaining magnetic particles, the method was first described by Elmore [3], further his technique was modified by Massar [4].

Taking into account that the synthesis in aqueous medium is aimed primarily on preparation of magnetic dispersions of nanoparticles, one of the most effective and promising methods of stabilization was using different polyelectrolytes in the reaction mixture (that is *in situ*).

Control over processes of the synthesis of magnetite nanoparticles, selection of an appropriate stabilizer and analysis of its stabilizing action is a relevant task, because all this gives the opportunity to produce unique devices, based on magnetic nanoparticles, for various industries. Some of the most important requirements for such particles are non-toxicity, sedimentation, and chemical resistance [5]. In this regard, development of new ways for obtaining magnetite nanoparticles without the use of toxic reagents, such as oleates, trimethylamines or penthacarbonyls is a promising task.

2. Literature review and problem statement

Procedures of magnetite synthesis with the use of the method of co-sedimentation according to Elmor and Massar are currently employed increasingly often. For synthesis, solutions of ferrous salts are used in different ratios. For example, in paper [6], the process of co-sedimentation with solutions of salts of ferrum (II) chloride (FeCl_2) and ferrum (III) chloride (FeCl_3) with equal mole ratio of salts was carried out. 1 M solution of sodium hydroxide (NaOH) was used as a precipitant. As a result, particles with the radius of about 8 nm were formed. The main disadvantage of this method is duration of synthesis (4 hours), during which the magnetization of magnetite particles decreases considerably, moreover, they are devoid of their magnetic properties. In contrast to that research, scientists in article [7] used the same sedimentation agent, however, they replaced FeCl_2 with ferrum (II) sulfate (FeSO_4), and mole ratio of salts of $\text{Fe}^{2+}/\text{Fe}^{3+}$ was 1:2. As a result of such synthesis, particles of dimensions in the range of 11–12 nm with highly pronounced magnetic properties were formed. However, the synthesis was conducted at low temperatures (about 0 °C), which required the use of additional refrigerants and greatly affected viscosity of the reaction mass. In article [8], the synthesis of salts FeSO_4 and FeCl_3 at mole ratio of 1:2 with the use of concentrated solution of ammonium hydroxide (NH_4OH) as a precipitant was carried out. The synthesis was performed in inert nitrogen medium. As a result, magnetite nanoparticles in the range from 4 to 17 nm with magnetic properties were formed. The advantage of this method over the other is a significant acceleration of the reaction, the synthesis lasted 30 min. The disadvantage is that the system is devoid of sedimentation stability and the process of synthesis should be carried out under rigid conditions at constant temperature control (70 °C). In such a system, there will be gradual oxidation of magnetite to ferrum (III) oxide and particulates will become larger.

An important issue for subsequent use of colloidal systems is stability of the system, which is getting particularly important in application of colloids. Therefore, stabilizers are added to create a potential barrier of repulsion of colloidal particles and to ensure aggregation resistance. Inorganic and organic substances, as well as synthetic and natural polymers can be used as stabilizers.

Thus, in paper [9], the magnetite particles (Fe_3O_4) were synthesized by the method of co-sedimentation with the use of sodium citrate (sodium salt of citric acid) and oleic acid as stabilizers. Phase composition and microstructure analysis indicate that sodium citrate and oleic acid were successfully grafted on the surface of Fe_3O_4 , however, due to the surface effect, magnetization decreased considerably and the increased concentration of stabilizers led to a significant decrease in crystallinity of the resulting oxide. Formation of polysaccharide coating on the nanomagnetite surface also prevents aggregation of particles [10]. The advantages of using polysaccharides is that most of them are non-toxic substances, the downside is that their molecules can be desorbed from the surface of ferrous oxide by heating up to 120 °C or dilution, which considerably decreases the scope of application of the resulting colloids.

PVP was used as a stabilizer during synthesis of nanoparticles of silver. Scientists found that PVP acts as a surface stabilizer, a modifier of an increase in nanoparticles and a disperser [11]. It has protective properties due to its unique structure (Fig. 1) [12].

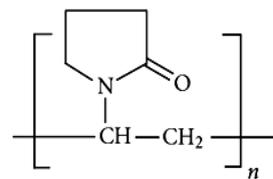


Fig. 1. Formula of polyvinylpyrrolidone

A molecule contains a highly polar amide group, which provides hydrophilic properties, as well as non-polar methyl groups both in the skeleton and in the ring, which provide hydrophobic properties. In addition, it is a non-toxic, biocompatible substance. However, in this work, the PVP were applied using the method of post-synthetic coating, which involved application of the polymer to the surface of nanoparticles that have already been synthesized. This method considerably complicates the process of synthesis since it requires strict control over all components of the reaction. In addition, the method of post-synthetic coating leads to passivation of the active surface of nanoparticles, which is not appropriate for magnetite nanoparticles.

Critical analysis proved that there is no universal technique for the synthesis of magnetite nanoparticles. The use of the method for co-sedimentation using ferrum $\text{Fe}^{2+}/\text{Fe}^{3+}$ in a certain ratio as salts requires optimization and selection of the required concentrations of reagents and the reacting substances. It is advisable to carry out the synthesis in the solution of a stabilizer, rather than add it after the co-sedimentation process to increase stability of the resulting dispersions. In this way, the time spent on synthesis will be saved, in addition, formation of stable particles of certain dimensions is possible during the synthesis, since a stabilizer will resist aggregation and enlargement of the particles at the nucleation stage. All these assumptions require thorough research and proving.

3. The aim and objectives of the study

The aim of this work was to develop a procedure for obtaining magnetite nanoparticles using polyvinylpyrrolidone (PVP 3.5 %) as a dispersed medium, and to study the spectra of optical absorption of the resulting nanomagnetite dispersions with the help of the spectrophotometric method of analysis.

To accomplish the aim, the following tasks have been set:

- to select working concentrations of the reacting substances and to perform synthesis of magnetite nanoparticles using PVP (3.5 %) as a dispersed medium;
- using the method of spectrophotometry, to obtain the bands of absorption of aqueous dispersions of nanomagnetite and analyze them using the theory of plasmon oscillations;
- using the method of spectrophotometry, to get the bands of absorption of nanomagnetite dispersions using 3.5 % PVP as the dispersed medium and to analyze them using the theory of plasmon oscillations;
- to propose a possible mechanism of stabilization of magnetite nanoparticles with polyvinylpyrrolidone.

4. Materials and methods of the study

4. 1. Materials used for obtaining the nanoparticles of magnetite

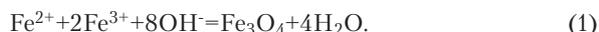
In work, the following chemical reagents were used for the synthesis of magnetite: ferrum (II) sulfate heptahydrate

(FeSO₄·7H₂O) – “chemically pure” GOST 4148-66, ferrum (III) chloride hexahydrate (FeCl₃·6H₂O) – “chemically pure” GOST 4147-74, 25 % water solution of ammoniac (NH₄OH) “chemically pure” GOST 3760-64. The synthesis was carried out separately in water and separately in aqueous solution of PVP of 3.5 % concentration, with average molecular weight of 3·10⁴.

4. 2. Procedure for the synthesis of magnetite nanoparticles

To carry out the reaction, the batch of FeSO₄·7H₂O and the batch of FeCl₃·6H₂O were dissolved in 100 ml of water and in 100 ml of PVP (3.5 %). Then the solutions were filtered to remove insoluble residues of salts. After that, the solutions were stirred with a magnetic stirrer. Concentrated ammoniac solution (25 %) was added to solution of ferrous salts at the rate of one drop per second.

The process can be represented as the following chemical equation:



4. 3. Determining main parameters of the nanoparticles synthesized in an aqueous solution

Sedimentation constant *K* can be calculated from formula:

$$K = \sqrt{\frac{9\eta}{2g(\rho - \rho_0)}}, \tag{2}$$

where ρ is the density, kg/m³; g is the gravitational acceleration, m/s²; η is the viscosity of the medium, Pa·s.

Sedimentation constant *K* is a constant magnitude for the given system, which is why the particle’s radius was calculated from formula:

$$r = K \sqrt{\frac{H}{\tau}}, \tag{3}$$

where *K* is the sedimentation constant, *H* is the height, mm, τ is the time, necessary for a particle to reach the bottom of a vessel, s.

The motion velocity of a particle relative to the medium, in which a particle is weighed, was determined from formula:

$$u = \frac{2\Delta\rho gm^2}{9\eta}, \tag{4}$$

where ρ is the density, kg/m³; g is the gravitation acceleration, m/s²; η is the viscosity of the medium, Pa·s, the weight of a particle, g.

The weight of a particle was determined from formula:

$$m = V \cdot \rho = \frac{4}{3} \pi \cdot r^3 \cdot \rho. \tag{5}$$

From formula (2), it is possible to estimate the time of sedimentation of dispersion *t_s* as the time, necessary for particles to pass the path that is equal to the height of the vessel *H*:

$$t_s = \frac{H}{u}. \tag{6}$$

4. 4. Procedure for determining the spectral characteristics of dispersions

Spectra of absorption of magnetite nanoparticles solutions in water and in 3.5 % PVP were registered by spectrophotometer SF-56 in quartz drainage ditch with the length of the absorbing layer of 10 mm in the range of 200–800 nm for aqueous solutions and the range of 190–1,110 for dispersions in 3.5 % of PVP.

5. Results of synthesis of magnetite nanoparticles with the use of 3.5 % PVP as dispersed medium and analysis of spectra of optical absorption of resulting dispersions taken with the use of the spectrophotometric method

5. 1. Selection of operating concentrations of reacting substances and performing synthesis of magnetite nanoparticles

Salts of ferrum (II) sulfate and ferrum (III) chloride and concentrated aqueous ammoniac solution were used for co-sedimentation in the study. Most of the sources recommend to perform interaction at the mole ratio of salts of iron Fe²⁺/Fe³⁺ equal to 1:2, at the same time, the concentration of salts and the added base differ significantly. In this regard, the first stage of the study was aimed at the selection of operating concentrations of salts and ammoniac and sedimentation took place in the aqueous solution. There were 5 preparations of magnetic particles, in the process of synthesis of which solution of 7.5–0.25 % by weight of ferrous salts (final concentration) was used, to which concentrated ammoniac solution was added (Table 1).

Table 1

Main characteristics of synthesized solutions

No. by order	NH ₄ OH, %	Concentration (Fe ²⁺ /Fe ³⁺), %	Sedimentation rate, m/s	Radius of particles, nm	Weight of particles, g
1	25.0	7.5	5·10 ⁻¹	70	1.5·10 ⁶
2	12.5	3.8	1·10 ⁻¹	55	7.8·10 ⁴
3	3.5	1.0	2.5·10 ⁻³	20	2.1·10 ³
4	2.0	0.5	2.0·10 ⁻³	8	2.7
5	1.5	0.3	1.0·10 ⁻⁴	4	0.1

In the course of the experiment it was found that the excess of ammoniac solution leads to unstable dispersions. The most stable, and thus the least aggregated particles were obtained by adding 1.5–2.0 % ammoniac at concentration of ferrous salts of 0.5–0.3 %, respectively. In this case, the ratio of Fe²⁺/Fe³⁺ was not 1:2, as most researchers have, but was on average 1.0:1.5. At such ratio of salts, there were formed black dispersions of magnetite nanoparticles of the radius of 4–8 nm with magnetic properties that were checked by carrying the dispersions into the magnetic field (magnetite nanoparticles were attracted to a magnet). High concentrations of ferrous salts do not form dispersions with magnetic properties, such dispersions are grayish brown, the formed particles are non-homogeneous, the average radius of them is 55–70 nm.

Next, to conduct synthesis of magnetite particles with the use of PVP (3.5 %) as dispersed medium, the concentration of ferrous salts Fe²⁺/Fe³⁺ 0.5–0.3 % was selected and the amount of the added ammoniac was within 1.5–2.0 %. At the

first stage of the synthesis, selected concentration of ferrous salts $\text{Fe}^{2+}/\text{Fe}^{3+}$ was dissolved in 100 ml of 3.5 % PVP. At the second stage, the solution with ferrous salts was stirred with a magnetic stirrer and the required volume of concentrated ammoniac solution was added at the rate of one drop per minute.

As a result of the synthesis, aggregation resistant dispersion of magnetite nanoparticles of black color was formed.

The dimensions of nanoparticles and chemical composition of the dispersed medium affect the main spectral characteristics of the formed solutions, which helped analyze the major changes that occur in the electronic structure of synthesized particles. Therefore, based on the ideas of plasmon resonance, the spectrophotometry method with further analysis of the bands of optical absorption of dispersions was used for the characteristic of the synthesized nanoparticles [13].

5. 2. Analysis of spectral characteristics of the formed dispersions

Nowadays, when analyzing metallic nanoparticles, the dimensions of which are smaller or similar to the depth of penetration of electromagnetic wave in metal, increased attention is paid to the study of surface plasmon resonance [14].

For magnetite nanoparticles, synthesized in aqueous solution based on measurement of absorption spectra, existence of a peak at wave length of 350 nm was shown (Fig. 2, 3). Light absorption occurs in close ultraviolet, this absorption is associated with appearance of the surface plasmon resonance on the nanoparticle's surface. Electronic density of the layer in magnetite nanoparticles is much higher than in typical plasmons, respectively, for transition of electrons from the d to s^2 sub-level, it is necessary to spend less energy. As a result of absorption at 350 nm, it is formed due to transition of electrons from one d orbital to another and by transfer of electrons from anion to cation in Fe_3O_4 . That is, there is a shift of the central metal ion that forms a strong covalent bond with the surrounding oxygen ions, using its empty d orbital.

A significant decrease in concentration of reacting substances in the synthesis of nanoparticles affects the position of the absorption band, which is characterized by maximum at 350 nm. As a result of high concentrations of reacting substances (concentration of salts of $\text{Fe}^{2+}/\text{Fe}^{3+}$ is 7.5–1.0 %; concentration of ammoniac is 25–3.5 %), synthesized nanoparticles are characterized by large dimensions of 55–70 nm and a high aggregation degree (Fig. 2, sample 3). Due to electrodynamic interaction between closely spaced nanoparticles, the spectral state of plasmon resonance changes [15]. Dense packing of nanoparticles results in formation of collective plasmon resonance [16]. The result of manifestation of strong lateral interactions in a densely-packed mono-layer is a considerable long-wave shift of the maximum of the absorption band from 300 nm to 380 nm (bathochromic shift by 80 nm). The formed shoulder indicates a totality of partially aggregated particles (Fig. 1, sample 1, sample 2).

Fig. 3 shows the spectra of absorption of fluids with low concentrations of reacting substances (concentration of salts of $\text{Fe}^{2+}/\text{Fe}^{3+}$ is 0.5–0.3 %; ammoniac concentration is 1.5–2.0 %). As Fig. 2 shows, the shift of absorption band did not occur, however the value of optical density is different. The highest $D=0.8$ is for sample 4, the lowest $D=0.25$ is for standard 5. Absorption maximum in all solutions is at

350 nm. The frequency of the band decreases, a hypochromic band shift by 30 nm with the hypochromic effect by 80 % for sample 4 and by 93 % for sample 5.

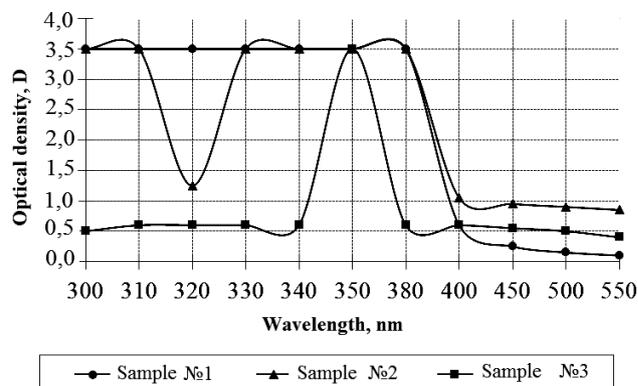


Fig. 2. Spectra of absorption of solutions of magnetite nanoparticles, synthesized in aqueous medium (length of absorbing layer is 10 mm). Sample 1: concentration of salts of $\text{Fe}^{2+}/\text{Fe}^{3+}$ is 7.5 %, ammoniac concentration is 25 %. Sample 2: concentration of salts of $\text{Fe}^{2+}/\text{Fe}^{3+}$ is 3.8 %, ammoniac concentration is 12.5 %. Sample 3: concentration of salts of $\text{Fe}^{2+}/\text{Fe}^{3+}$ is 1.0 %, ammoniac concentration is 3.5 %

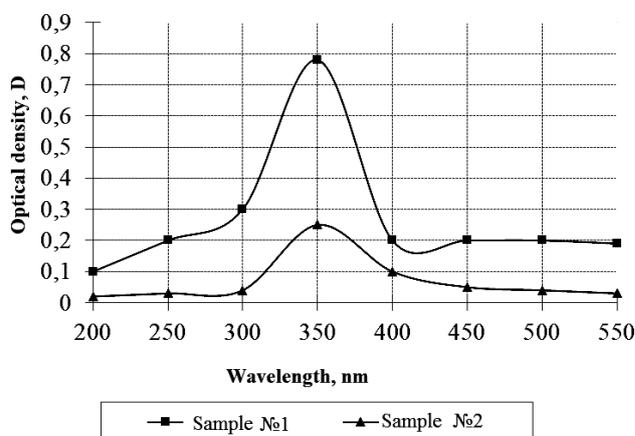


Fig. 3. Spectra of absorption of solutions of magnetite particles, synthesized in aqueous medium (the length of the absorption layer is 10 mm). Sample 4: concentration of salts of $\text{Fe}^{2+}/\text{Fe}^{3+}$ is 0.5 %, ammoniac concentration is 2.0 %. Sample 5: concentration of salts of $\text{Fe}^{2+}/\text{Fe}^{3+}$ is 0.3 %, ammoniac concentration is 1.5 %

As Fig. 2, 3 show, high concentrations of reacting substances (concentration of salts of $\text{Fe}^{2+}/\text{Fe}^{3+}$ is 7.5–1.0 %; ammoniac concentration is 25–3.5 %) characterize the changes in absorption spectra as hyperchromic effect, whereas low concentrations of reacting substances (concentration of salts of $\text{Fe}^{2+}/\text{Fe}^{3+}$ is 0.5–0.3 %; ammoniac concentration is 1.5–2.0 %) characterize spectral changes by hypochromic effect.

Absorption spectra of magnetite nanoparticles, synthesized using 3.5 % PVP as dispersed medium, are shown in Fig. 4. An intense absorption band appears on the spectrum at 950 nm. Absorption peak shifts toward longer wavelengths due to a decrease in dimensions of nanoparticles. The absorption band is characterized by existence of three peaks at 350 nm, 950 nm and 1,050 nm. Existence of several absorption peaks indicates that in the presence of PVP, the

co-sedimentation reaction occurs stage by stage. First, there is a process of rapid nucleation, which corresponds to the value of the peak at $\lambda=350$ nm, then concentration of the substance reaches the critical over-saturation, which is proved by disappearance of the peaks to $\lambda=950$ nm. At the given wavelength, there occurs a slow nucleus growth by diffusion of the PVP chains to the nanomagnetite surface.

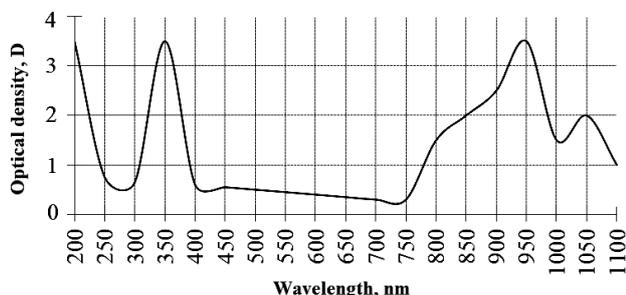


Fig. 4. Spectrum of absorption of dispersion of magnetite nanoparticles, synthesized with the use of 3.5 % polyvinylpyrrolidone $M(PVP) 3 \cdot 10^4$ as dispersed medium. The length of the absorption layer is 10 mm. Concentration of salts of Fe^{2+}/Fe^{3+} is 0.5 %; ammoniac concentration is 2.0 %

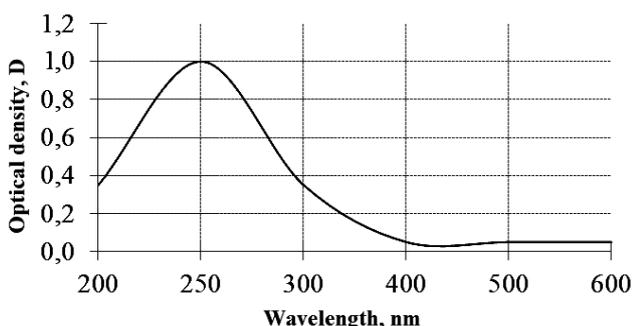


Fig. 5. Spectrum of absorption of 3.5 % solution of polyvinylpyrrolidone $M(PVP) 3 \cdot 10^4$, the length of absorbing layer is 10 mm

As Fig. 5 shows, the absorption band of 3.5 % PVP has a maximum at 250 nm, which corresponds to absorption of the solution slurry in close ultraviolet, the absorption band is weak $\epsilon < 10^2$ transition $n \rightarrow \pi^*$. Disappearance of the band at 250 nm shows that formation of a coordinating bond between PVP and magnetite at the expense of free electrons of oxygen and nitrogen occurred (Fig. 6):

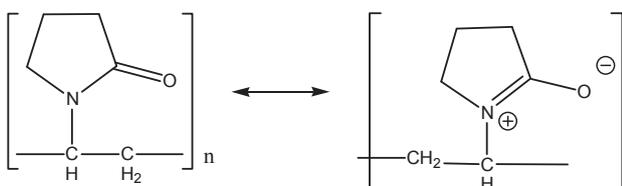


Fig. 6. Schematic of polyvinylpyrrolidone regrouping into molecules

The existence of a peak at 350 nm indicates formation of magnetite nanoparticles. Magnetite nanoparticles interact with PVP, the bathochromic shift with a maximum at 950 nm appears on the spectrum (Fig. 4).

Sensitivity of plasmon absorption resonances is due to the interaction of the magnetite electrons with π -electrons of PVP [17] (Fig. 7).

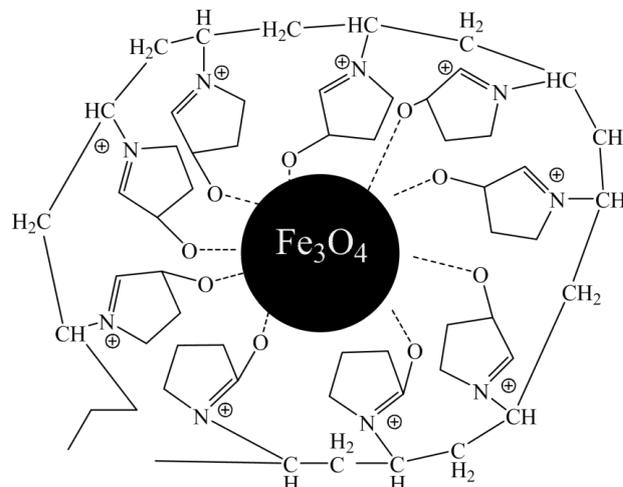


Fig. 7. Schematic representation of magnetite nanoparticles' stabilization by polyvinylpyrrolidone

During synthesis of magnetite nanoparticles with the use of 3.5 % PVP as dispersed medium, most atoms of metal contact with the surface of the polymer. As a result of the interaction, greater number of magnetite electrons is able to interact actively with π -electrons of PVP in the process of nanoparticles formation. Dimensions of synthesized nanoparticles significantly decrease, which is proved by existence of peaks in the absorption spectrum at $\lambda=950$ nm and at $\lambda=1050$ nm.

Polyvinyl groups have significant repulsive power [18], taking into account the large molecular mass of the polymer, the phenomenon of steric obstacle occurs (Fig. 8).

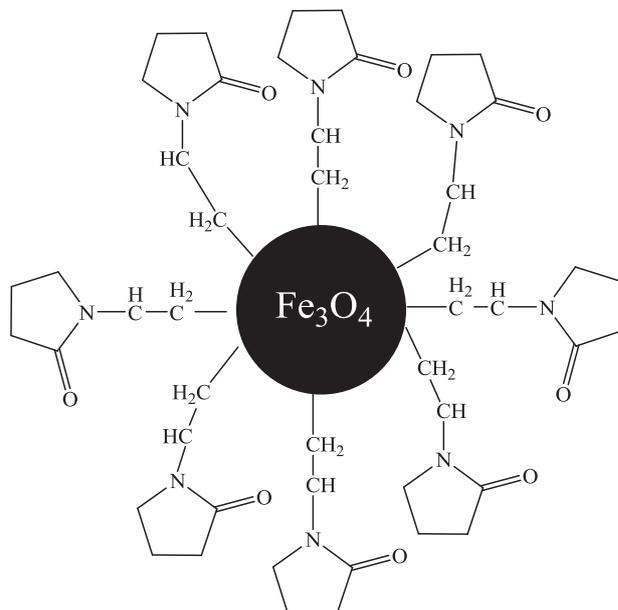


Fig. 8. Schematic representation of magnetite nanoparticles' stabilization by polyvinylpyrrolidone

Let us assume that the stabilization mechanism is associated with the possibility of PVP to spread in a limited way, thus forming short polymer chains, which are able to be ab-

sorbed on the surface of magnetite and prevent aggregation of nanoparticles.

6. Discussion of the results of synthesis of magnetite nanoparticles using 3.5 % PVP as a dispersed medium

The approach that combines synthesis and modification of magnetite nanoparticles was proposed, as a result, aggregation resistant dispersions of nanoparticles with sedimentation rate of $2.0 \cdot 10^{-3}$ – $1.0 \cdot 10^{-4}$ m/s are formed. Non-toxic 3.5 % PVP is used as a stabilizer. During this synthesis, particles with the radius of 4–8 nm are formed. It was shown that to resist aggregation of magnetite nanoparticles and for synthesis of nanoparticles with a small distribution by dimensions, it is advisable to carry out the synthesis with the use of 3.5 % PVP as dispersed medium. Currently, this research is relevant, because in the work, the spectra of optical absorption of resulting dispersions of nanomagnetite were studied with the help of the spectrophotometric method.

A significant simplification and acceleration of the process of synthesis of magnetite nanoparticles compared with the known research [6–9] was shown. Thus, in contrast to papers [6–9], it was possible to decrease the duration of synthesis from 4 hours to 2 minutes. The process of synthesis was carried out without the use of refrigerants, without constant passing nitrogen and without rigid temperature control of the system. It was determined that the concentration of 2:1 of ferrous salts, proposed in [7], is not advisable, and at a decrease in the ratio of ferrous salts to 1.5:1.0, magnetite particles are also formed, in this case, reagents are saved. The optimal way of introducing the reagent, which was not described in previous works, was proposed. Thus, for example, during simultaneous introduction of all components (direct pouring), magnetite oxidation to Fe_2O_3 is possible, particles get larger, the system loses aggregation resistance, and the process should be carried out at low temperatures [8]. In this study it was found that a parallel way of reagents' introduction is the most appropriate. In the proposed synthesis, the rate of ammoniac introduction is one drop per minute at constant stirring of the reaction mixture, in this case, the reaction goes at high rate.

It was found that an increase in concentration and volume of a reducing agent leads to formation of particles of large radius of 70 nm. Thus, at high concentrations of reacting substances ($\text{Fe}^{2+}/\text{Fe}^{3+}$ – 7.5–1.0 %; NH_4OH – 25–3.5 %), dispersions with particles of 55–70 nm, which are characterized by weak magnetic properties (not attracted to a magnet) and have grayish-brown-black color, which indirectly indicates that the particles contain impurities of goethite ($\text{FeO}(\text{OH})$). The most aggregation resistant dispersions are produced during a short time of hydrolysis (up to 2 minutes) after adding ammoniac and a change of concentration of salts of ferrum $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the ratio of 1.0–1.5. Under such conditions and at such ratio of the components, magnetite with the average radius of 4–8 nm was obtained.

Analysis of the absorption bands of the formed dispersions showed that at the change in dimensions of nanoparticles, there is no change of a spectral shift of the plasmon absorption band, but there is a change in its amplitude. At a subsequent change of dimensions of nanoparticles from 70 nm to 8 nm, a two-wave shift of the plasmon band by 30 nm and a decrease in its amplitude by 80 % occur.

The conducted studies of the surface plasmon resonance of the synthesized solutions made it possible to establish existence of the absorption peak at 350 nm in all aqueous dispersions of nanomagnetite. The nature and intensity of absorption bands depend on the concentration of reacting substances and the method of reagents' introduction (direct introduction or parallel introduction of reagents). Intensity of weak absorption bands is determined mainly by d–p shift, i. e. the transition of electrons d→d in some degree takes on the character of transitions p→d, which occur between ions in magnetite.

During the synthesis of magnetite nanoparticles in 3.5 % PVP, dispersion of free electrons on the surface of a particle occurs, so plasmon frequency of free oscillations of electrons is shifted from the ultraviolet to the visible region of the spectrum. Analysis of absorption bands of nanoparticles, synthesized in 3.5 % PVP, showed existence of 3 absorption waves at $\lambda=350$ nm, $\lambda=950$ nm and $\lambda=1,050$ nm. The existence of several absorption bands indicates that in the presence of PVP, a co-sedimentation reaction occurs stage by stage, first there is a process of rapid nucleation, and then, there is a slow nucleus growth through diffusion of the PVP chains to the surface of nanoparticles. Accordingly, these two stages should be separated for the controlled synthesis of magnetite nanoparticles, and nucleation should be avoided during the growth of nanoparticles. In such a case, particles with dimensions in the nanometer range will be synthesized, and formed dispersions will be characterized by aggregation resistance and stability, which will significantly expand the scope of application of the formed nanocolloids in medicine for addressed delivery of medicines, in the textile industry for finishing of textile materials, in the chemical industry for wastewater treatment, etc.

The spectrophotometric method, which was used in the study (SF-56), make it possible to register the indicators in the visible and ultraviolet region of the spectrum (190–1200 nm), which is the main limitation of this study. The minimum value of optical density, which can be measured using SF 56 with necessary precision, is typically equal to 0.01, and the thickness of the layer is on average 1 cm. The minimum value of the concentrations, which is determined on SF-56, is approximately 10^{-7} M (10^{-2} µg/ml or mg/l). Therefore, when working with SF-56, it is necessary to ensure selectivity mostly at the stage of sampling through selection of reagents, as well as by conditions of determining (pH variation and choice of a solvent).

In the further research, it would be advisable to combine this method with translucent electron microscopy in order to establish the relationship between the morphology of the formed nanoparticles and their plasmon absorption bands.

7. Conclusions

1. In the course of the study, it was found that particles with the smallest radius of 4–8 nm were formed at concentrations of salts of ferrum $\text{Fe}^{2+}/\text{Fe}^{3+}$ of 1.0:1.5 respectively, and the amount of added ammoniac was 2.0 %. The character of reagents' introduction was parallel, the rate of ammoniac introduction was one drop per minute at constant stirring of the reaction mixture.

2. An analysis of the absorption bands of the nanoparticles, synthesized in aqueous solution, showed that the resulting dispersions are characterized by a peak at 350 nm.

The dimensions, weight and radius of the nanoparticles affect the character of absorption bands. Thus, high concentrations ($\text{Fe}^{2+}/\text{Fe}^{3+}$ is 7.5–1.0 %; NH_4OH is 25–3.5 %) of the reacting substances lead to formation of large particles of 70 nm, which create agglomerates and shift the absorption band in a bathochromic way by 30 nm. Low concentrations of the reacting substances ($\text{Fe}^{2+}/\text{Fe}^{3+}$ is 0.5–0.3 %; NH_4OH is 1.5–2.0 %) lead to formation of more stable, lower in size particles of 4–8 nm, and the resulting solutions are characterized by a distinct absorption band at 350 nm.

3. Analysis of bands of absorption of solutions of magnetite nanoparticles, synthesized with the use of 3.5 % PVP as dispersed medium, showed existence of 3 absorption strips at $\lambda=350$ nm, $\lambda=950$ nm and $\lambda=1050$ nm. A band at 350 nm

indicates formation of magnetite nanoparticles. At 250 nm, the band that is typical of valence fluctuations of PVP disappears on the spectrum. The bathochromic shift by 600 nm occurs in the system. The absorption band is quite intense and typical of transitions of electrons from π orbital in the conjugated system.

4. The mechanism of stabilization of nanomagnetite PVP occurs due to the interaction of magnetite electrons with π -electrons of PVP in the process of nanoparticles formation. At the first stage of the process of synthesis, magnetite nanoparticles are formed, which is proved by the existence of a peak of the absorption band at 350 nm. At the second stage, partial adsorption of PVP chains to the surface of magnetite nanoparticles occurs, which is proved by disappearance of the absorption band at 250 nm.

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