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OBTAINING AND STABILIZATION OF NANOSULFUR

Abstract. On the basis of sodium thiosulfate in the presence of sodium sulfite and solid organic acids – citric and oxalic - sulfur nanoparticles were synthesized. By the method of spectrophotometry, it was shown that efficient for the synthesis of sulfur is the using of the molar ratio of $[Na_2S_2O_3]/[Na_2SO_3]$ 1:0.5 and of the catalyst is oxalic acid. Nonionic polymer polyethylene glycol (PEG) was used for stabilizing sulfur particles. By methods of light scattering, electron and light microscopy it is shown that the stabilizing effect of the polymer is achieved at a concentration of 10^{-3}base-mol/L, and a further increasing of the concentration of PEG leads to aggregation processes. The size of the obtained particles is determined on the Zetasizer Nano device. It was found that in the presence of PEG concentrations of 10^{-3} - 10^{-2}base-mol/L, the size of sulfur particles decreases from 321.8 nm to 259.1 nm and 270.4 nm, respectively.

Key words: sulfur, nanoparticles, stabilization, polyethylene glycol.

Interaction

With the development of industry, demand for elemental sulfur as raw material for many chemical products is continuously increasing. There are various applications of sulfur nanoparticles in nowadays, the most important fields of applications are: in electrochemistry, sulfur nanoparticle was used to enhance the electrochemical activity of lithium batterythrough a solution-based technique; as catalysis, for example, elemental sulfur nanoparticles can dramatically enhance the rate of Cr(VI) reduction; in medical sphere, using of anticancer, antibacterial properties of sulfur nanoparticles significantly increasing too.

It is known that sodium thiosulfate in an acidic medium decomposes with the release of sulfur in a finely dispersed state. The stability of the sulfur produced depends on the initial amounts of sodium thiosulfate and acid. According to this method, we previously synthesized colloidal sulfur particles [5]. It is shown that the size of the obtained colloidal sulfur particles increases from 250 nm to 4500 nm in 90 hours after the beginning of the experiment with some subsequent reduction. The increase in the particle size is justified by the aggregation of sulfur particles, and the decrease by the stabilizing action of the acid.

Aggregation of sulfur particles is a completely expected phenomenon due to its high hydrophobicity. Meanwhile, the preservation of the dispersion sulfur particles is very important in its practical use, since the magnitude of its adsorption on the stems and leaves of plants, tissues of living organisms will be determined by the specific surface of the powder particles. In this regard, the aim of the study is the synthesis and stabilization of nanosulfur.

Experimental part

Synthesis of sulfur particles was carried out according to the procedure described in [5]. We use solutions of sodium thiosulfate and sodium sulfite with a concentration of 0.001 mol / L. The use of such low concentrations of starting reagents is due to the fact that the abundant formation of a sulfur precipitate makes it difficult to measure the optical density of a sulfur suspension. Solid organic acids (SOA) were used as a catalyst for the synthesis process: citric and oxalic.

For the synthesis on solid substrates glass and polyethylene plateswere used, which were washed in distilled water and ethyl alcohol before using. Then the starting solutions of sodium thiosulfate and

sodium sulfite (0.5 ml each) were mixed on the surface of the substrates, after 60 minutes the substrate with the resulting sulfurwas washed with distilled water and air-dried.

To stabilize the synthesized sulfur in the solution volume, a solution of polyethylene glycol (PEG) was introduced into the reaction mixture. The polymer solution was mixed with a solution of thiosulfate, then a sulfite solution and solid acid crystals were added to the resulting mixture.

Results and discussion

The process of sulfur formation is accompanied by turbidity of the reaction mixture, so the most convenient method for studying this process is spectrophotometry. Table 1 presents data on sulfur synthesis using various molar ratios $[Na_2S_2O_3]/[Na_2SO_3]$ and two solid organic acids: citric and oxalic. As can be seen from the table, the use of different ratios of the initial reagents causes significant differences in the optical density of these systems: at $[Na_2S_2O_3]/[Na_2SO_3]$ equal to 1: 1, the optical density of the mixture is in the range 0.08-0.12. When switching to a system with the ratio $[Na_2S_2O_3]/[Na_2SO_3]$ equal to 1: 0.5, the optical density increases significantly, so the initial reagents were used in the ratio 1: 0.5. In addition, the data in Table 1 show that when usingoxalic acid as the catalyst for the reaction, the optical density of the system is higher than in the presence of citric acid.

Table1 - Ratio of reagents for obtaining nanoparticles of sulfur

№ of exp	Ratio $[Na_2S_2O_3]/[Na_2SO_3]$	Mass of citric acid, g	Mass of oxalic acid, g	D
1	1:1	0,2	-	0,08
2	1:1	-	0,2	0,12
3	1:0,5	0,2	-	0,36
4	1:0,5	-	0,2	0,40

The advantage of using solid organic acids for sulfur synthesis indicates the possibility of intensifying the synthesis process by using solid substrates of various types. The results of experiments on the use of plates of glass and polyethylene as substrates are shown in Fig. 1.

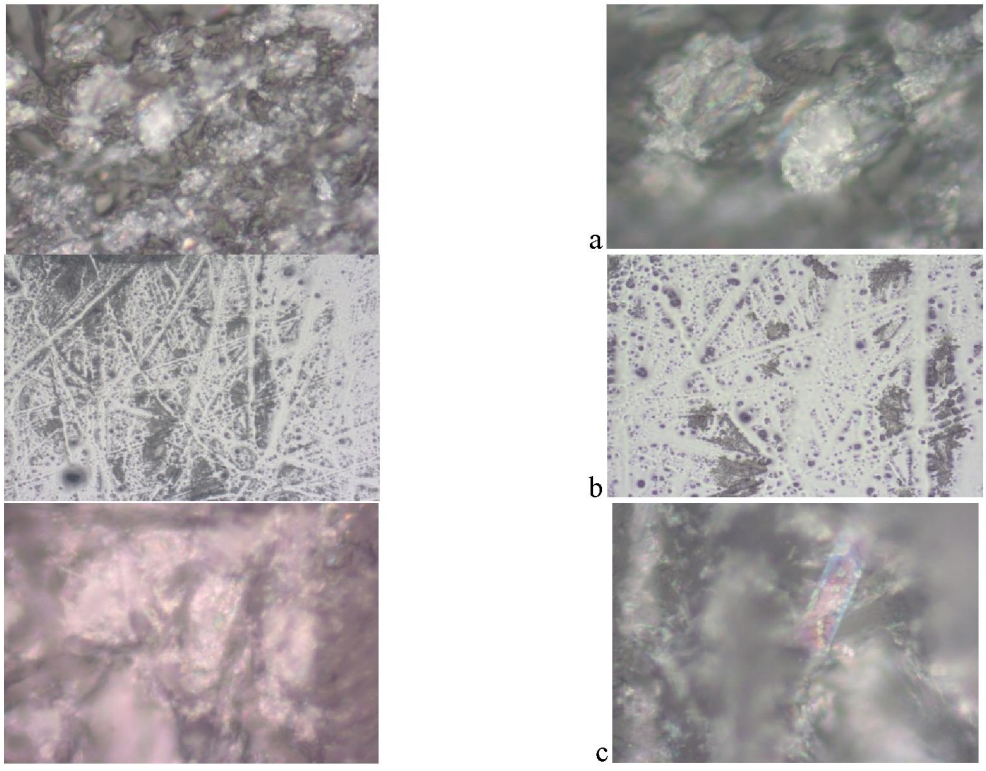


Figure 1 - Preparation of sulfur particles on the surface of glass (a) and polyethylene (b, c) in the presence of oxalic (a, c) and citric (b) acids. Magnification: x1000

As can be seen from Fig. 1a, on the surface of the glass the sulfur particles are in the form of large aggregates. On the surface of the polymer material (Fig. 1b, c), the sulfur particles are distributed more evenly. This difference in the distribution of sulfur particles on polymeric and inorganic materials can be explained by the high affinity of hydrophobic sulfur to the polyethylene substrate. At the same time, attention is drawn to the formation of an openwork mesh on the polymer when citric acid is used as a catalyst. This probably can also be due to the different hydrophobicity of the SOA molecules: citric acid is a tribasic acid, and oxalic is a dibasic acid.

Therefore, a more hydrophobic oxalic acid contributes to a more even distribution of sulfur particles on the non-polar surface. Nevertheless, the absence of separate sulfur particles on the light microscopy data indicates that the process of their aggravation has proceeded, which is a consequence of the high hydrophobicity of the sulfur particles.

Various high- and low-molecular surfactants can be used to stabilize and modify sulfur particles [6-8]. The use of a high molecular weight compound - polyethylene glycol (PEG) as a stabilizer can be very effective, since the -OH groups of the polymer can provide a high degree of lyophilization to the treated sulfur particles. The use of the PEG solution in the concentration range 10^{-5}-10^{-2} base-mol /L (Figure 2) showed that the polymer exerts a significant stabilizing effect on the system. If in the absence of PEG in the reaction mixture a monotonic increase in the optical density is observed with time, then in the presence of PEG, the optical density growth stops after 4-5 minutes after mixing the initial reagents, sodium thiosulfate,and sodium sulfite. In this case, the optical density of the mixture (D) in the presence of a PEG concentration of 10^{-3} base-mol /L is much higher than when using a lower-concentration PEG solution - 10^{-5}base-mol / L, and increasing the concentration from 10^{-3} to 10^{-2}, the base-mole / L does not show any difference in the D values, which may be due to the achievement in the case of PEG use of a concentration of 10^{-3}base-mole / L of the amount of polymer necessary to protect the sulfur particles from aggregation.

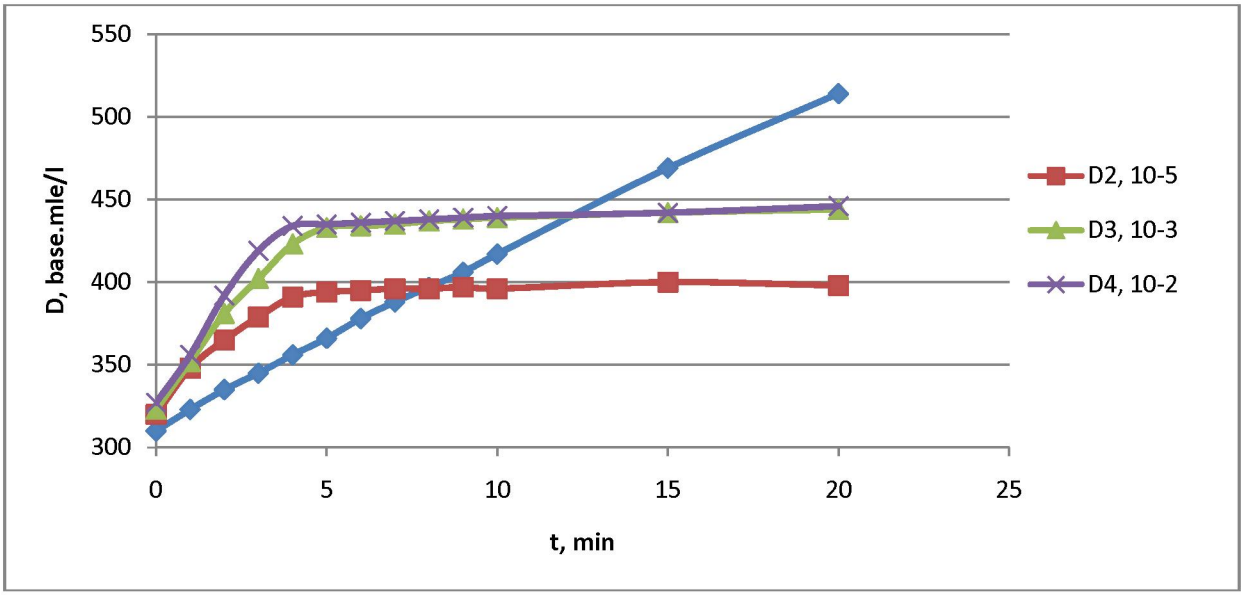
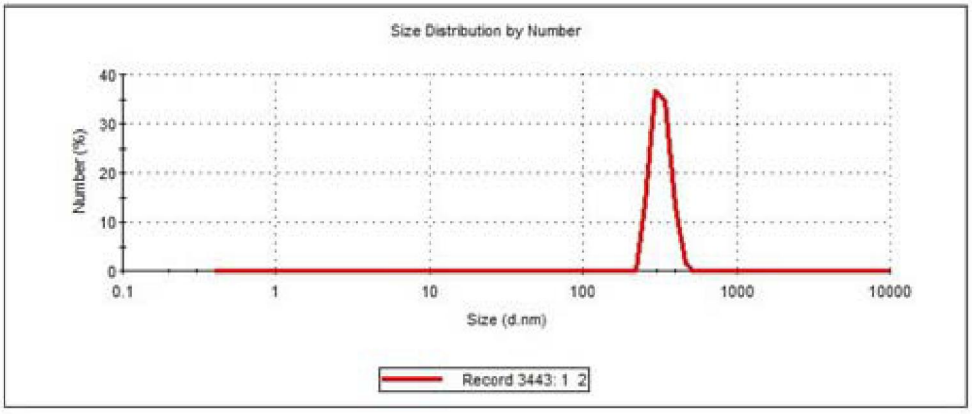


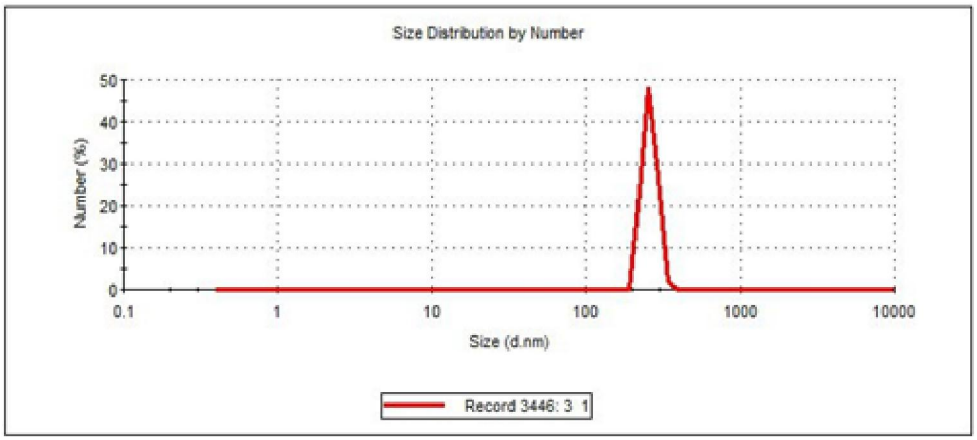
Figure 2 - The change in the optical density of the sulfur suspension in time in the absence (1) and the presence of PEG concentrations of 10^{-5}base-mol/L(2); 10^{-3} base-mol/L (3) and 10^{-2} base-mol/L (4)

The method of dynamic light scattering determines the size of the obtained sulfur particles. The particle size distribution of the sulfur obtained in the absence and presence of PEG (Figure 3) shows that the most probable particle size of sulfur without the addition of a stabilizer is 321.8 nm. Introduction to the PEG system of concentration 10^{-3} base-mol/Lleads to a reduction in particle size to 259.1 nm. In the case of PEG, a concentration of 10^{-2} base.mole / L, the average particle size is 270.4 nm. Another difference in the distribution curves in the absence and presence of PEG is the height and width of the peaks. If the scattering intensity for sulfur particles in the absence of a stabilizer was 36%, then in the presence of a polymer it rises to 48% and 41% in solutions with a PEG concentration of 10^{-3} and 10^{-2} base-mol/L,

respectively. In addition, the width of the peaks here is much less than in the case of an unstabilized sulfur suspension, that is, in these mixtures, the particles are predominantly close in size to each other. From these data, it follows that at a PEG concentration of 10-3 base-mol/L, a significant stabilizing effect is achieved in the system. A further increase in the concentration of the polymer can cause the system to become unstable due to flocculation processes as a result of hydrophobic interactions between the "loops" and "tails" of adsorbed polymer macromolecules.



a



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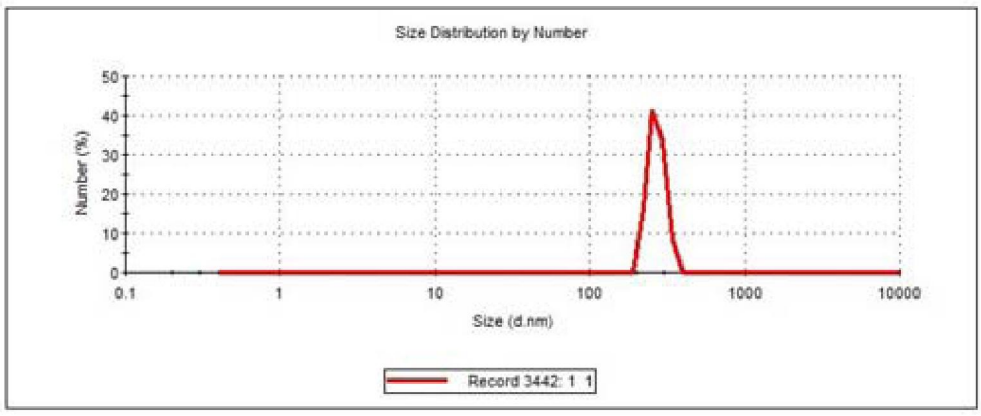

c

Figure 3 - The size distribution curves of sulfur particles in the absence (a) and in the presence of PEG concentrations of 10^{-3} base-mol/L(b) and 10^{-2} base-mol/L (c)

In figure 4 shows electron microscopic images of sulfur particles obtained in the presence of various concentrations of PEG. The smallest particles in the photographs are also observed at a PEG concentration of 10^{-3} base-mol/L.

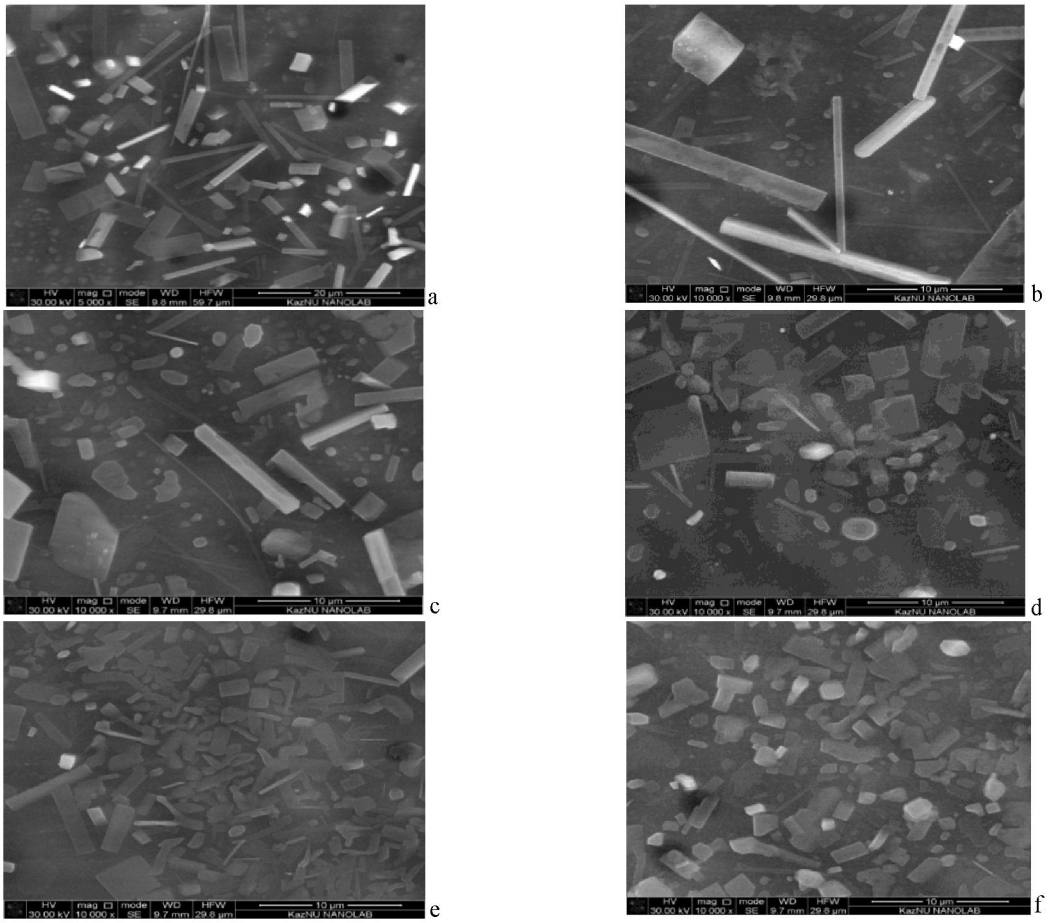

Figure 4 - Electron microscopic images of sulfur particles obtained in the absence of (a, b) and in the presence of PEG concentrations of 10^{-5} base-mol/L (c); 10-4 mol / l (d); 10^{-3} base-mol/L (e) and 10^{-2} base-mol/L (f)

The electron microscopy data also confirm the assumption of the protective effect of PEG (Figure 4). As can be seen from Fig. 4, the introduction of a solution of PEG into the reaction mixture decrease particle size of sulfur. The stabilizing effect of a nonionic polymer-PEGmay be due to adsorption of macromolecules by non-polar regions on the surface of sulfur particles. In this case, the polar functional groups of the polymer will be turned into a solution, imparting hydrophilicity to the sulfur particles. However, one should take into account the need to select a sufficient polymer concentration for the stabilization of dispersed particles. The lack of polymer cannot provide complete protection of particles from sticking, and excess leads to aggregation. At the same time, it should be noted that, in order to intensify the stabilization processes, it is probably necessary to study the kinetics of the process.

Conclusion

On the basis of sodium thiosulfate and sodium sulfite in the presence of solid organic acids - citric and oxalic - sulfur nanoparticles have been synthesized. Comparison of the effect of catalysts shows that the use of oxalic acid is more effective for the synthesis of sulfur. To stabilize the sulfur nanoparticles was used a nonionic polymer, polyethylene glycol. It is shown that the stabilizing effect of the polymer is achieved at a concentration of 10^{-3}base-mol/L. The size of the particles obtained is determined by light scattering. It was found that in the presence of PEG with concentrations 10^{-3} to10^{-2} base-mole /Ll, the particle size of sulfur decreases from 321.8 nm to 259.1 nm and 270.4 nm, respectively.

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НАНОКҮКІРТТІ АЛУ ЖӘНЕ ТҰРАҚТАНДЫРУ

Аннотация. Натрий тиосульфаты негізінде натрий сульфиты және қатты органикалық қышқылдар – лимон және қымыздық қышқылдары - қатысуымен күкірттің нанобөлшектері синтезделген. Спектрофото-метрия әдісімен күкіртті синтездеу үшін [Na2S2O3]/[Na2SO3] 1:0,5 мольдік арақатынасын және катализатор ретінде қымыздық қышқылын пайдаланудың тиімділігі көрсетілді. Күкіртті тұрақтандыру үшін иондық емес полимер - полиэтиленгликоль (ПЭГ) таңдалынды. Сәулені шашырату, электрондық микроскопия және сәуле микроскопиясы әдістерімен полимердің тұрақтандыру әрекеті оның 10-3 негіз-моль/л концентрациясында іске асатындығы, ал концентрацияны одан әрі ұлғайту агрегациялық үдерістерге апаратындығы көрсетілді. Zetasizer Nano құрылығысында алынған бөлшектердің өлшемі анықталды. Концентрациясы 10-3 - 10-2 негіз-моль/л ПЭГ қатысында күкірт бөлшектерінің өлшемі 321,8 нм-ден 259,1 нм және 270,4 нм-ге дейін төмен-дейтіндігі көрсетілді.

Түйін сөздер: күкірт, нанобөлшектер, тұрақтандыру, полиэтиленгликоль.

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ПОЛУЧЕНИЕ И СТАБИЛИЗАЦИЯ НАНОСЕРЫ

Аннотация. На основе тиосульфата натрия в присутствии сульфита натрия и твердых органических кислот – лимонной и щавелевой - синтезированы наночастицы серы. Методом спектрофотометрии показано, что эффективным для синтеза серы является использование мольного соотношения $[Na_2S_2O_3]/[Na_2SO_3]$ 1:0,5 и катализатора - щавелевой кислоты.

Для стабилизации серы использовали неионный полимер полиэтиленгликоль (ПЭГ). Методами свето-рассеяния, электронной и световой микроскопии показано, что стабилизирующее действие полимера дости-гается при концентрации 10^{-3} осново-моль/л, а дальнейшее увеличение концентрации ПЭГ ведет к агрега-ционым процессам. На приборе Zetasizer Nano определен размер полученных частиц. Установлено, что в присутствии ПЭГ концентрации 10^{-3} - 10^{-2} осново-моль/л размер частиц серы уменьшается от 321,8 нм до 259,1 нм и 270,4 нм соответственно.

Ключевые слова: сера, наночастицы, стабилизация, полиэтиленгликоль.

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