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STUDY OF STABILIZATION OF SELENIUM NANOPARTICLES BY POLYSACCHARIDES

Andrey Vladimirovich Blinov[1*], Konstantin Vasilevich Kostenko[2], Alexey Alexeevich Gvozdenko[1], David Guramievich Maglakelidze[1], Alexey Borisovich Golik[1], Andrey Ashotovich Nagdalian[1,3], Elena Nikolaevna Statsenko[3], Natalya Nikolaevna Nikulnikova[3], Danil Mihaylovich Remizov[1], Marina Nikolaevna Verevkina [4], Sergey Nikolaevich Povetkin[1]

[1]Physics and Technology Faculty, North Caucasus Federal University, Pushkina str. 1, 355029 Stavropol, Russia
[2]Institute of Engineering, North Caucasus Federal University, Kulakova str. 2, 355029 Stavropol, Russia
[3]Institute of Life Systems, North Caucasus Federal University, Pushkina str. 1, 355029 Stavropol, Russia
[4]Veterinary Medicine Faculty, Stavropol State Agrarian University, Zootechnichesky prosp., 12, 355017, Stavropol, Russia

[*]e-mail: blinov.a@mail.ru

Abstract

Selenium, being an essential trace element, plays an important role in the human and animal organisms. Selenium compounds are widely used in various fields of science and technology: from feed additives in agriculture and drugs with increased therapeutic activity against malignant neoplasms in medicine to optically active quantum dots in electronics. This paper presents the results of a study of the process of stabilization of selenium nanoparticles with different polysaccharides: hydroxyethyl cellulose, chitosan, maltodextrin, methylcellulose, amylopectin and hyaluronic acid.

Quantum-chemical modeling of the interaction of selenium nanoparticles with various polysaccharide stabilizers was performed in the QChem program using the IQmol molecular editor. Models with electron density distribution are obtained, and molecular orbitals and total energy values of the system are calculated for monomeric polysaccharide units, as well as for "Stabilizer-Se" molecular complexes. At the next stage, laboratory and experimental samples of selenium nanoparticles stabilized with various polysaccharides were obtained. As a precursor nanoselenium used the selenious acid and as a reducing agent - sodium borohydride. The obtained samples were studied by photon-correlation spectroscopy, acoustic and electroacoustic spectroscopy.

It was found that the most stable and energetically advantageous molecular system is the hyaluronic acid-Se system, which has E = - 13752.47 kcal/mol and ΔE = 0.299 a. u. By the results from photon-correlation spectroscopy, acoustic and electroacoustic spectroscopy, it was found that the samples stabilized with amylopectin, hyaluronic acid, and maltodextrin have a monomodal distribution with an average hydrodynamic radius of 191.7, 529.1, and 109.1 nm, respectively. The remaining samples have a bimodal size distribution. It is shown that the smallest hydrodynamic radius has a sample of selenium nanoparticles stabilized with hydroxyethyl cellulose, which contains 2 fractions: 1 - 11.40 nm (10.6%), 2 - 94.05 nm (89.4%). According to acoustic and electroacoustic spectroscopy data, the highest Zeta potential is found in a sample stabilized with maltedextrin (+36.25 mV), and the lowest-with hyaluronic acid (-143.09 mV). The obtained data on the Zeta potential correlate with the charges of functional groups in polysaccharide molecules.

As a result of the conducted research, it is shown that Se nanoparticles stabilized with polysaccharides can be used as a biological active supplement in the food industry.

***Key words**: Nanoselenium, Polysaccharides, Computer quantum-chemical modeling, Zeta - potential, Average hydrodynamic radius.*

1. Introduction

The main aspects of rational and preventive nutrition are related to the balance of the macro - and micronutrient composition of the diet. To maintain a balanced diet, functional biologically active food supplements containing a complex of essential macro - and micronutrients are often introduced into the daily diet. These complexes must be balanced, stabilized, and bioavailable to ensure that the correct biochemical effect is achieved. One of the essential trace elements used in such complexes is selenium [1 - 4].

Selenium is a metalloid trace element that is an important component for a full and healthy life of people and animals. It performs numerous functions in live organisms. Its biological activity is due to the participation of selenium in the regulation of the formation of antioxidants. There is a close correlation between the level of selenium in the body and the activity of the selenium-containing enzyme glutathione peroxidase, which prevents the accumulation of metabolic peroxides in cells. In addition, it is involved in maintaining the immune system [5 - 7], has a positive effect on sperm motility [8], activates thyroid hormones [9], and plays a significant role in cancer prevention [10 - 13]. Selenium also contributes to the growth of the body [14].

Technologies of food additives development, which are based on selenium is one of the promising areas of research of selenium. The selenium nanoform attracts even more attention due to its high bioavailability and lower toxicity than its inorganic and organic forms. Nanosolene has the following properties: antioxidant, antiviral and antibacterial, anti-cancer, immunostimulating, hypoglycemic, and others [15 - 18].

The biological properties of selenium nanoparticles depend on their size: smaller particles have greater activity [19]. The particle size affects the consumption of nanoparticles by cells; for example, in vitro absorption of 0.1 µm particles will be 2.5 and 6 times greater compared to 1 and 10 µm particles, respectively [20].

Nanoparticle stabilization is very important process in nanotechnology. Modern technologies are based on electrostatic and polymer stabilization methods. The most promising are polymer stabilizers, among which polysaccharide stabilizers are widely used. Due to their physical and chemical properties, polysaccharides are widely used in various fields of medicine and food industry [21 - 25].

The purpose of the work was to study the process of stabilization of selenium nanoparticles with various polysaccharides: hydroxyethylcellulose, chitosan, maltodextrin, metalcellulose, amylopectin, and hyaluronic acid.

2. Materials and Methods

The synthesis of selenium nanoparticles was conducted using the chemical reduction method 0.037 g of selenous acid and 0.055 g of stabilizer were dissolved in 20 mL of water and stirred until complete dissolution for 30 minutes at room temperature. Next, a reducing agent solution was prepared by dissolving 0.5 g of sodium borohydride in 10 mL of water. After the complete dissolution of the substances, both solutions were mixed with vigorous stirring. The resulting sol of selenium nanoparticles was stirred for 15 minutes. The resulting mixture was poured into an opaque brown glass container.

Disperse composition of nanoparticles Se different stabilizers was studied by photon-correlation spectroscopy with Spectrometer of dynamic and static light scattering Photocor Complex (Photocor, Russia). The obtained samples of selenium nanoparticles were studied using a DT-1202 spectrometer (manufactured by Dispersion Technology Inc., USA).

Computer quantum-chemical modeling of the process of stabilization of Se nanoparticles with various stabilizers was performed in the QChem program using the IQmol molecular editor. The calculation was performed on the equipment of the Data Processing Center (Schneider Electric) of the North Caucasus Federal University. Calculation characteristics were: Energy, method-HF, basis-6-31G, convergence-5, force field-Ghemic.

3. Results and Discussion

3.1 Computer quantum-chemical modeling of monomeric units of polysaccharides and polysaccharide-selenium molecular systems

At the first stage of research, quantum-chemical modeling of monomeric units of polysaccharides was performed. For indication atoms in models was used color index are shown in Figure 1. The obtained models of monomeric units of polysaccharides, electron density distributions, electron density distribution gradients, and molecular orbitals for each polysaccharide are shown in Figures 2 - 7.

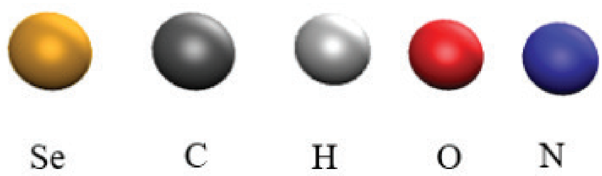


Figure 1. Color indication of atoms in models

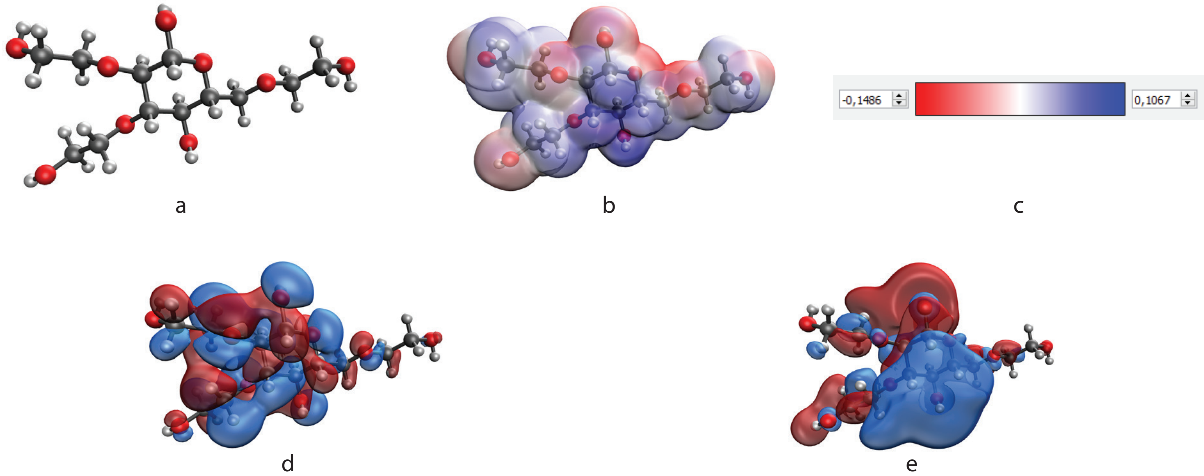


Figure 2. (a) Model of the hydroxyethylcellulose monomer unit, (b) electron density distribution, (c) electron density distribution gradient, (d) highest occupied molecular orbital HOMO, and (e) lowest unoccupied molecular orbital LUMO

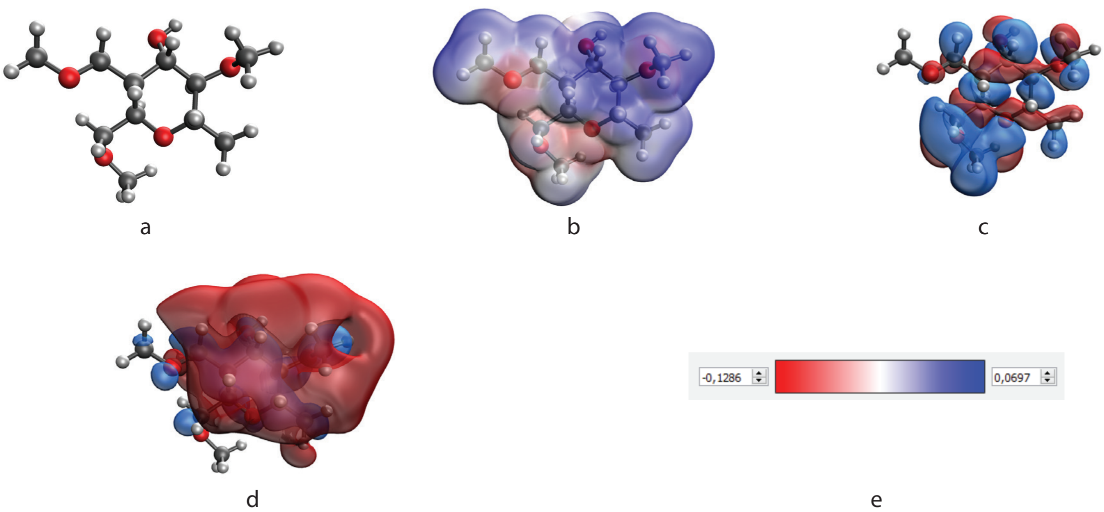


Figure 3. (a) Model of the methylcellulose monomeric unit, (b) electron density distribution, (c) highest occupied molecular orbital HOMO, (d) lowest unoccupied molecular orbital, (e) gradient of the electron density distribution

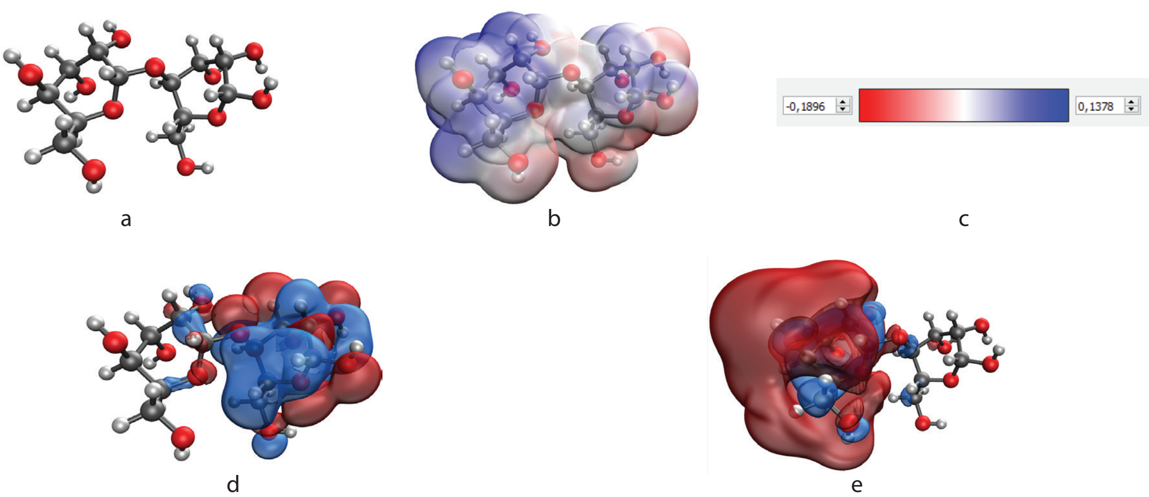


Figure 4. (a) Model of the maltodextrin monomeric unit, (b) electron density distribution, (c) electron density distribution gradient, (d) highest occupied molecular orbital HOMO, and (e) gradient of the electron density distribution LUMO

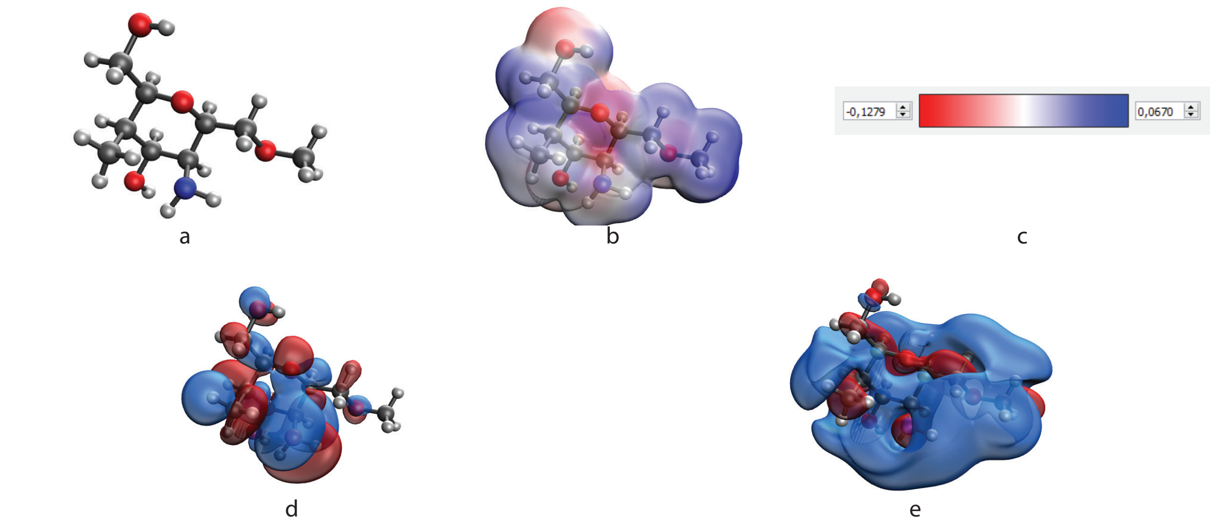


Figure 5. (a) Model of the chitosan monomeric unit, (b) electron density distribution, (c) electron density distribution gradient, (d) highest occupied molecular orbital HOMO, and (e) highest occupied molecular orbital LUMO

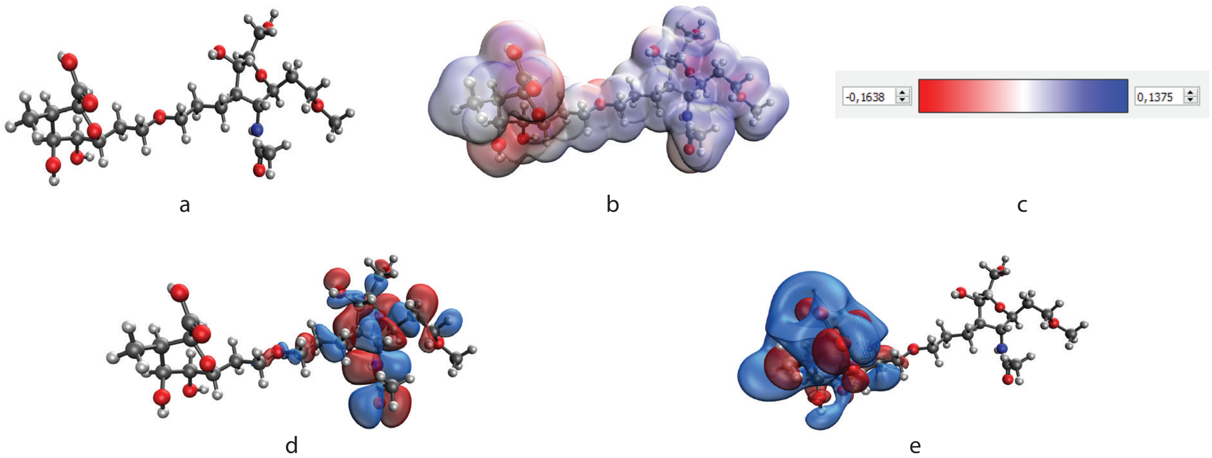


Figure 6. (a) Model of the hyaluronic acid monomeric unit, (b) electron density distribution, (c) electron density distribution gradient, (d) highest occupied molecular orbital HOMO, and (e) highest occupied molecular orbital LUMO

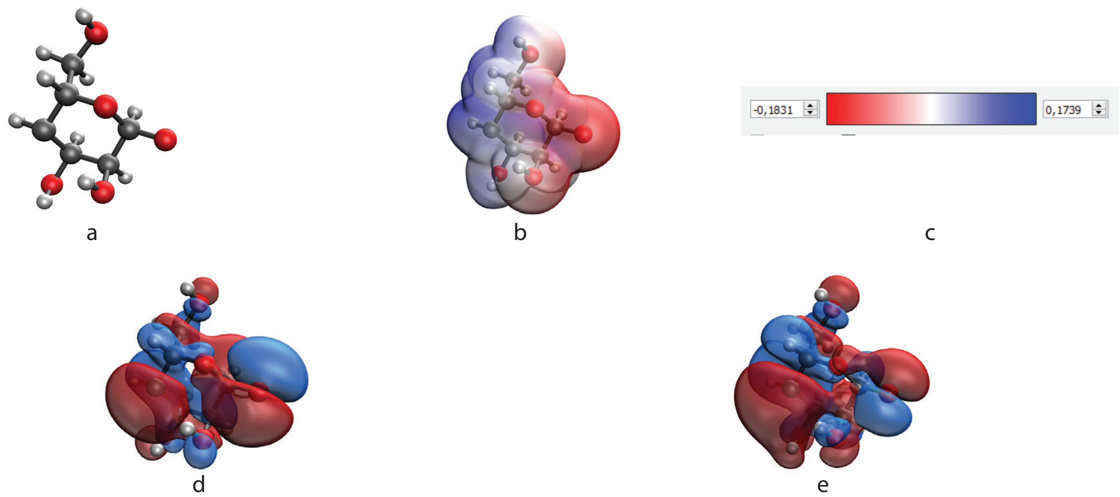


Figure 7. (a) Model of the amylopectin monomeric unit, (b) electron density distribution, (c) electron density distribution gradient, (d) highest occupied molecular orbital HOMO, and (e) highest occupied molecular orbital LUMO

It is important to note that in each monomeric unit of polysaccharides there are hydroxogroups with concentrated negative charge, as evidenced by the electron density distributions.

Also analysis of represented models showed the total energy of molecular units: E (hydroxyethylcellulose) = -1141.52 kcal/mol, E (methylcellulose) = -803.22 kcal/mol, E (maltodextrin) = -1290.01 kcal/mol, E (chitosan) = -705.40 kcal/mol, E(hyaluronic acid) = -1771.87 kcal/mol, E (amylopectin) = -606.73 kcal/mol.

The analysis of the data obtained has shown that the lowest energy is the hyaluronic acid monomeric unit [26-27].

The next stage of quantum-chemical modeling included modeling of the "stabilizer (polysaccharide) - selenium" molecular complexes. The data obtained are shown in Figures 8 - 13 and Table 1. The surface of selenium nanoparticles was represented as a chain structure consisting of 5 Se atoms. The terminal Se atoms were hydrogenated.

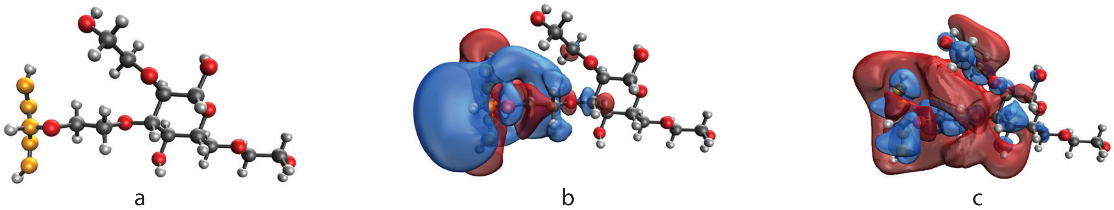


Figure 8. (a) Model of the "hydroxyethylcellulose - selenium" molecular complex, (b) highest occupied molecular orbital HOMO, and (c) lowest occupied molecular orbital LUMO

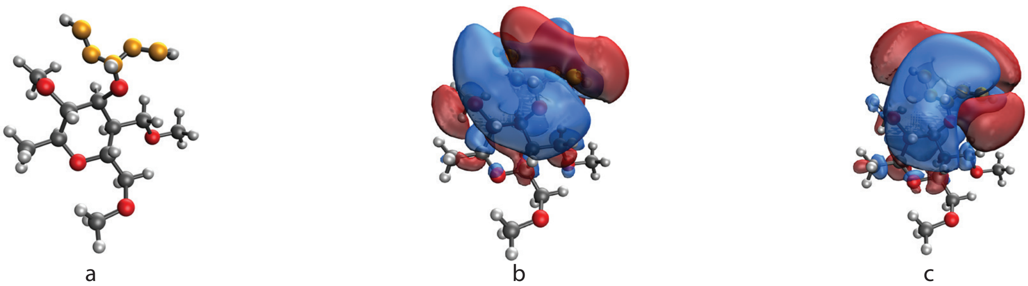


Figure 9. (a) Model of the "methylcellulose - selenium" molecular complex, (b) highest occupied molecular orbital HOMO, and (c) lowest occupied molecular orbital LUMO

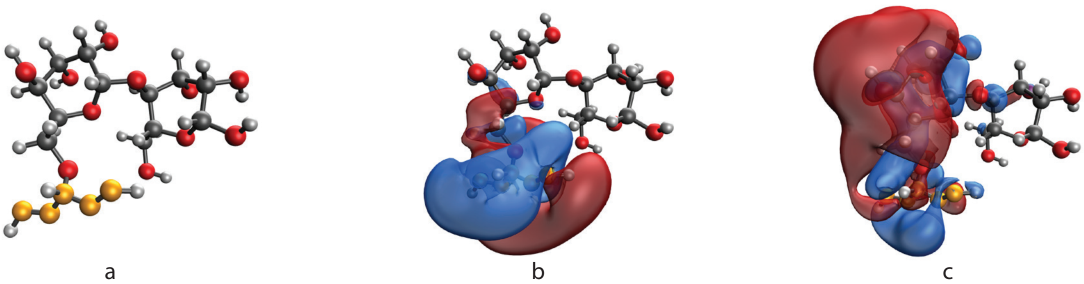


Figure 10. (a) Model of the "maltodextrin - selenium" molecular complex, (b) highest occupied molecular orbital HOMO, and (c) lowest occupied molecular orbital LUMO

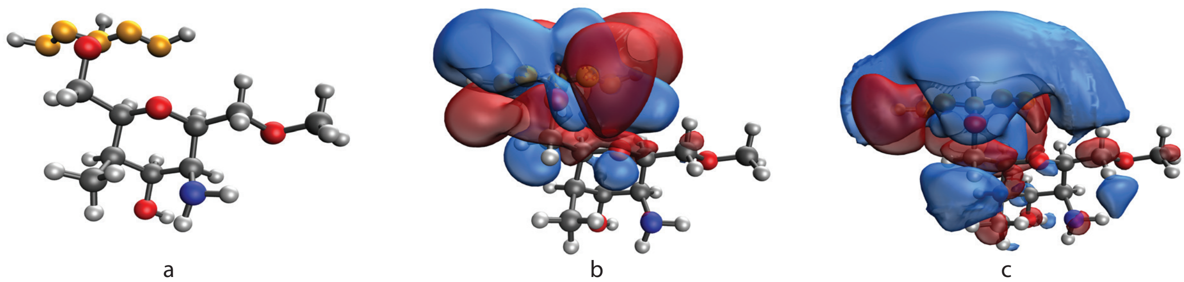
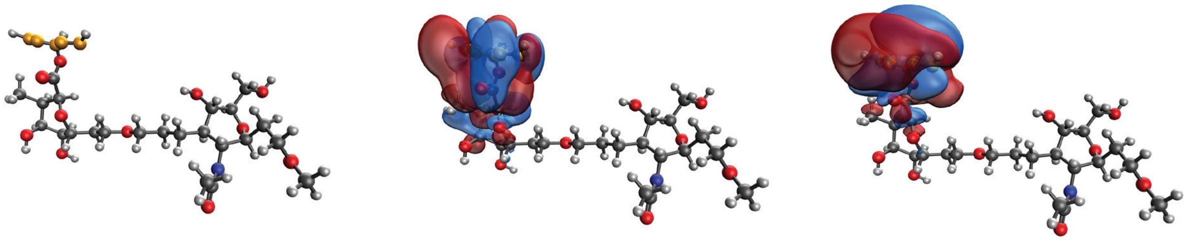


Figure 11. (a) Model of the "chitosan - selenium" molecular complex, (b) highest occupied molecular orbital HOMO, and (c) lowest occupied molecular orbital LUMO



a b c

Figure 12. (a) Model of the "hyaluronic acid - selenium" molecular complex, (b) highest occupied molecular orbital HOMO, and (c) lowest occupied molecular orbital LUMO

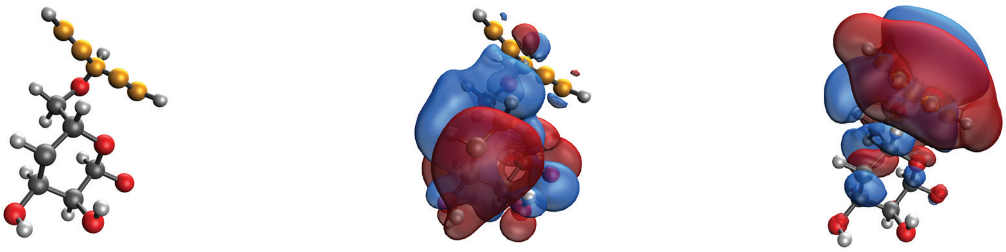


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Figure 13. (a) Model of the "amylopectin - selenium" molecular complex, (b) highest occupied molecular orbital HOMO, and (c) lowest occupied molecular orbital LUMO

Table 1. Results of quantum-chemical modeling of molecular systems "stabilizer (polysaccharide) - selenium"

Molecular systems	Energy, kkal/mol	Angle	Bond length, A	HOMO, a.u.	LUMO, a.u.	ΔE, a.u.
Hydroxyethylcellulose-Se	-13122.07	111.65	1,11466	-0,059	0,147	0,206
Methylcellulose-Se	-12783.70	108.54	1.11577	-0.047	0.14	0.197
Maltodextrin-Se	-13270.51	108.19	1.11811	-0.05	0.138	0.188
Chitosan-Se	-12685.52	110.54	1.10978	-0.121	0.157	0.278
Hyaluronic acid -Se	-13752.47	112.48	1.11447	-0.120	0.179	0.299
Amylopectin-Se	-12587.57	110.31	1.11558	-0.208	0.01	0.218

As a result of the analysis of the obtained data, it was found that the most energetically favorable and stable molecular system is the "hyaluronic acid - selenium" system, which has E = -13752.47 kcal/mol and ΔE = 0.299 a. u.

3.2 Investigation of dispersion characteristics of selenium nanoparticles stabilized with polysaccharides

At the next stage of research, laboratory samples of selenium nanoparticles stabilized with polysaccharides were obtained. Data on the stability and hydrodynamic radius of the particles were obtained for each sample. Photon correlation, acoustic and electroacoustic spectroscopy were used for the study. The data obtained are shown in Figure 14 and Table 2.

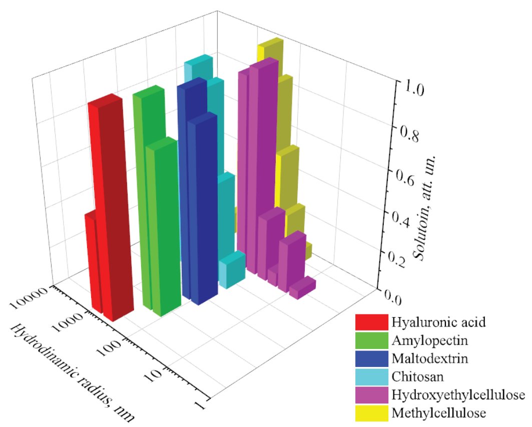

Figure 14. Histogram of the distribution of hydrodynamic radii of selenium nanoparticles stabilized with amylopectin, methylcellulose, hyaluronic acid, hydroxyethylcellulose, maltedextrin, and chitosan

Table 2. Results of determination of the Zeta potential and average hydrodynamic radius of selenium nanoparticles stabilized with polysaccharides

№	Polysaccharide	Zeta potential ζ, mV	Peak Num	Area, a. u.	Mean, nm	Position, nm	STD, nm
1	**Amylopectin**	+1.58	1	1.000	191.7	250.3	75.91
2	**Methylcellulose**	+7.5	1	0.014	2.726	1.979	0.961
			2	0.986	331.2	250.3	319.3
3	**Hyaluronic acid**	-143.09	1	1.000	529.1	429.2	211.8
4	**Hydroxyethylcellulose**	+5.49	1	0.106	11.40	12.15	2.739
			2	0.894	94.05	74.64	41.85
5	**Maltedextrin**	+36.25	1	1.000	109.1	138.2	36.74
6	**Chitosan**	+28.31	1	0.029	15,75	13,18	7,086
			2	0.971	468	497,1	339.4

As a result of analysis of experimental data obtained by photon-correlation spectroscopy, it was found that in samples stabilized with amylopectin, hyaluronic acid, and maltodextrin, a monomodal distribution is observed with an average hydrodynamic radius of 191.7, 529.1, and 109.1 nm, respectively. In other samples, the size distribution is bimodal. It was found that the smallest hydrodynamic radius in the sample of selenium nanoparticles stabilized with hydroxyethyl cellulose, which contains 2 fractions: 1 - 11.40 nm (10.6%), 2 - 94.05 nm (89.4%).

Using the method of acoustic and electroacoustic spectroscopy, the values were obtained ζ-potential of selenium nanoparticles stabilized by polysaccharides. It is established that the largest ζ-potential of a sample stabilized with maltodextrin (+36.25 mV), and the lowest-with hyaluronic acid (-143.09 mV).

The obtained data on the ζ-potential correlate with the charges of functional groups in polysaccharide molecules. For example, the presence of a large negative charge in a sample of selenium nanoparticles stabilized with hyaluronic acid is associated with the presence of carboxyl and hydroxy groups in the structure of hyaluronic acid.

Acknowledgment

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4. Conclusions

- The results of quantum chemical modeling correlates with the results of photon-correlation spectroscopy, acoustic and electroacoustic spectroscopy. Based on this, quantum-chemical modeling can serve as a method for studying various nanostructures and nanomaterials.

- It was found that the smallest hydrodynamic radius has a sample of selenium nanoparticles stabilized with hydroxyethyl cellulose, which contains 2 fractions: 1 - 11.40 nm (10.6%), 2 - 94.05 nm (89.4%).

- It is shown that selenium nanoparticles stabilized with polysaccharides can be used as an additive in the food industry.

5. References

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