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# Self-Organization and Morphological Characteristics of the Selenium Containing Nanostructures on the Base of Strong Polyacids

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## 1. Introduction

This article represents the results of the study made by methods of molecular optics of nanostructures formed in process of reduction of ionic selenium in selenite-ascorbate redox system in water solutions of high molecular polymeric stabilizers of anion type: synthetic polyacid – poly-2-acrylamide-2-methylpropansulfacid with MM  $M_w = 3 \times 10^6$  and biopolyanion - deoxyribonucleic acid with  $M_w = 20 \times 10^6$ . It was shown that polyanion – nanoparticle complex obtained under conditions of total saturation of adsorption capacity of selenium nanoparticles (mass ratio  $v$  of the components selenium : polymer is equal to 0.1) is close to its thermodynamic stability boundary: the second virial coefficient made up  $A_2^* = -0.07 \times 10^{-4} \text{ cm}^3 \text{ mol} / \text{g}^2$  for system of deoxyribonucleic acid – nano -  $\text{Se}^0 - \text{H}_2\text{O}$  and  $A_2^* = 0.2 \times 10^{-4} \text{ cm}^3 \text{ mol} / \text{g}^2$  for system of poly-2-acrylamide-2- methylpropansulfacid – nano -  $\text{Se}^0 - \text{H}_2\text{O}$ . In the field of formation of stable dispersions the values of free energy  $\Delta G^*$  of interaction of macromolecule – nanoparticle of selenium have been calculated for anion type nanostructures. It was found that in both cases high-molecular structures with  $M_w^* = 200 \times 10^6$  (deoxyribonucleic acid as stabilizer) and with  $M_w^* = 75 \times 10^6$  (poly-2-acrylamide-2-methylpropansulfacid as stabilizer) were formed with close dimensions ( $R_g^*$  – statistic dimensions of the nanoformation,  $R_h^*$  – hydrodynamic dimensions of the nanoformation) and average densities  $\Phi^*$ . The values of conformational parameters  $\rho^*$  and  $p^*$  testify a form of nanostructures approximating to spherical form:  $\rho^* = R_g^* / R_h^* = 1$  (for both systems),  $p^* = 1.1$  for a system of deoxyribonucleic acid - nano -  $\text{Se}^0 - \text{H}_2\text{O}$  and  $p^* = 1.5$  for a system of poly-2-acrylamide-2- methylpropansulfacid – nano -  $\text{Se}^0 - \text{H}_2\text{O}$ . On the base of the experimental data related to the values of  $M_w^*$  for spherical nanostructures assuming their mono-nuclear morphology we estimated a radius of selenium nucleus that made up  $R_{\text{nucl}} = 12 \text{ nm}$  (deoxyribonucleic acid as stabilizer) and  $9 \text{ nm}$  (poly-2-acrylamide-2-methylpropansulfacid as stabilizer). The following conclusion has been made: under adsorption of macromolecules of strong acids on nanoparticles of selenium the spherical nanoparticles with similar types of morphology with similar dimensions, densities and width of polymer shell are formed.

At present many original articles and monographs are devoted the issues of synthesis of nanoparticles and nanosystems and studying of their properties. (see e.g. [1]). Nano-dimensional particles (NDP) in absence of stabilizer represent typical liophobic colloids characterized by very low stability. The most various substances, from which high-molecular compounds are the most important, are applied for increase of the stability of NDP.

In connection with development of biological nanotechnology the above mentioned particles represent interest as active ingredients of medicines [2, 3] as well as transport systems and adsorption matrixes for bioactive substances [4].

It should be pointed out that nanoparticles of nonmetals stabilized by polymer have not been practically studied. In this respect nanoparticles of amorphous selenium (nano- a-Se<sup>0</sup>) that are used as high-sensitive bio-sensors for immunoassay technology [5] and chromatography mobile affine reagents [6]. Nano-particles of amorphous selenium are characterized by the exclusive spectrum of bioactivity: even at very low concentrations in water (0.005 – 0.1%) they can adsorb antigens antibodies at their surface [7].

Previously (e.g. in [18 – 13]) it was demonstrated that under reduction of selenium ions in solutions of polymers two processes are going on: formation of selenium nanoparticles with narrow unimodal distribution by dimensions and adsorption of macromolecules on them. In the result self-organization of polymeric molecules on surface of nanoparticles and formation of nanostructures with high molecular masses of significant density and various morphologies occur.

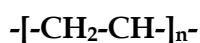
This work is focused on studying of process of self-organization and structural-morphological characteristics of selenium containing nano-structures on the basis of strong polyacids: synthetic polyacid - poly-2-acrylamide-2- methylpropansulfacid (PAMS) and biopolyanion - deoxyribonucleic acid (DNA).

## 2. The objects and methods of research

Selenium represents an exclusive interest as a chemical element with unique semiconductor, photoelectric and X-ray sensitivity properties as well as bioactive substance with anti-oxidant, anti-inflammatory, anticarcinogenic, antimutagenic and detoxicant activities.

In this study nanoparticles of a-Se<sup>0</sup> by reduction of selenitic acid by means of ascorbic acid were selected as subject of inquiry. Compared to nanoparticles of metals a-Se<sup>0</sup> represents an inorganic polymer including fragments of cycles of Se<sub>6</sub> and Se<sub>8</sub> linked by covalent bonds Se-Se [14] in its backbone.

We used the following compounds as polymeric stabilizers: poly-2-acrylamide-2-methylpropansulfacid and biopolyanion - deoxyribonucleic acid (DNA).



PAMS



Molecular Masses (MM) of polymeric matrix made up:  $M_w = 3 \times 10^6$  for PAMS (characteristic viscosity 1M NaNO<sub>3</sub> at 20°C made up  $[\eta] = 5.2$  dl/g) and  $M_w = 20 \times 10^6$  for DNA (see table).

Reduction reaction of ionic selenium was carried out at concentration of polymer in water solution equal to 0.1% and mass ratio of selenium : polymer  $v = 0.1$  i.e. under conditions of total saturation of adsorption capacity of nanoparticles as it was found for selenium – polymeric nanostructures [8].

Study of kinetics of selenium reduction (IV) was carried out at initial concentration of selenitic acid equal to 1.0 mmole/l in the regime with constant temperature (20°C) by means of spectrophotometer «Specord M-40» by means of registering changes of optical density of the solutions at wavelength equal to 320 nm. pH values of the solutions of the reaction mass made up 3.5. The values of the constant of the rate of reaction of formation of nanocomposites  $k^*$  calculated by well known method of Guggenheim [15] are given in the table. Calculation of  $k^*$  was carried out by the following formula:

$$k^* = \ln(D_k / (D_k - D_i)) / t_i, \quad (1)$$

where  $D_k$  – optical density characterizing the end of process,  $D_i$  – optical density at given moment of time  $t_i$ . Conditions of conducting of reaction of formation of nano - a- $\text{Se}^0$  polymer solution were kept constant: value of  $k^*$  was influenced only by structure of polymeric matrix stabilizing nano - a- $\text{Se}^0$  being formed.

MM  $M_w^*$  and root-mean-square radiuses of inertia  $R_g^*$  of nanostructures were determined by means of elastic (static) scattering of light in solutions in water [16] and their affinity to solutions was determined also by the values of the second virial coefficient  $A_2^*$ . Quantity of  $N^*$  of adsorbed macromolecules on the surface of nano-a- $\text{Se}^0$  was calculated by means of ratio MM for polyacids and nanostructures formed by these polyacids. The values of  $M_w^*$ ,  $N^*$ ,  $R_g^*$ , and  $A_2^*$  are shown in the table. We used photogoniometer «Fica» for determination of the reduced intensity of scattering of solutions  $R_\theta$ . Wavelength of vertical incident polarized light made up  $\lambda = 546.1\text{nm}$ . Measurements were carried out at scattering angles range  $\theta = 30^\circ - 150^\circ$ . Cleaning of cautions was carried out through millipore (Millex-HV) with diameter 0.45  $\mu\text{m}$ . The values of increment of the refractive index  $dn/dc$  were obtained from refractometric measurements by means of instrument IRF-23. Processing of experimental data of light scattering for solutions of nanostructures was carried out by means of Zimm method (see figures 1 and 2) using double extrapolation (to  $c = 0$  and  $\theta = 0$ ) of dependence of  $Kc/R_\theta$  on  $\sin^2(\theta/2) + k'c$  ( $K$  – calibration constant,  $k'$  – numeric constant).

Basing on data for  $M_w^*$  and root-mean-square radiuses of inertia by formula (2) we evaluated the values of average density of nanostructures

$$\Phi^* = 3 M_w^* / 4\pi N_a R_{\text{sph}}^3 \quad (2)$$

where  $R_{\text{sph}} = 1.29 R_g^*$  [17]. The values of  $\Phi^*$  are given in the table.

Average hydrodynamic dimensions of nanostructures  $R_h^*$  (see table) were determined by the method of quasi-elastic (dynamic) scattering [18]. The radiuses of the equivalent hydrodynamic spheres  $R_h^*$  were calculated from the values of diffusion coefficients ( $D^*$ ) by Einstein-Stokes equation  $R_h^* = kT/6\pi\eta_0 D^*$  ( $\eta_0$  – viscosity of solvent). The value of conformation-structural parameter  $\rho^*$  (see table) was found by means of ratio of experimental values of  $R_g^*$  and  $R_h^*$  [19 – 22].

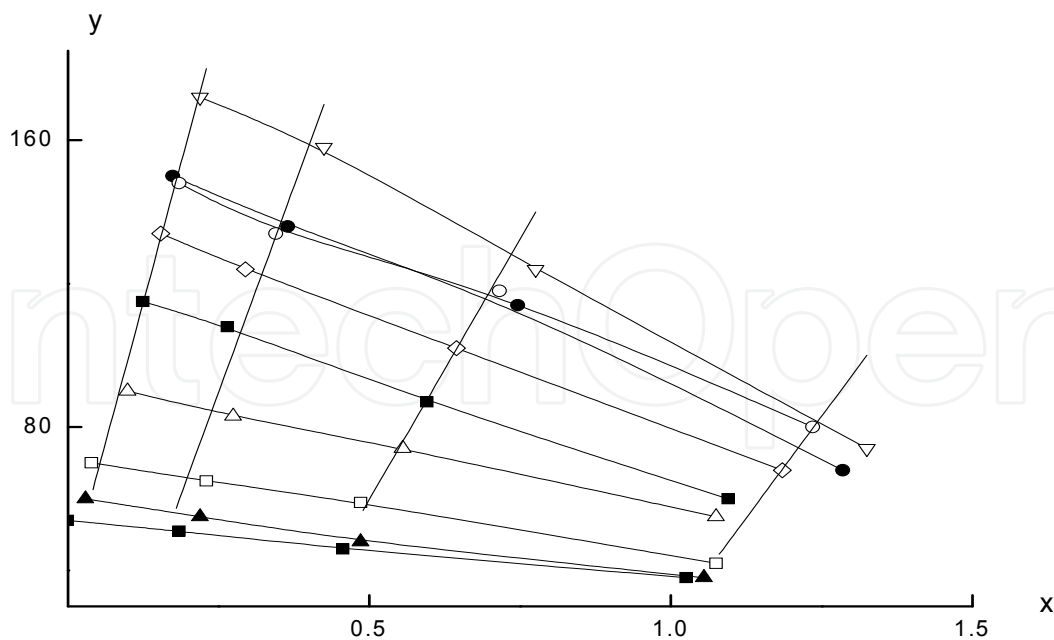


Fig. 1. Zimm Diagram for a system of DNA-Se<sup>0</sup>- water:  
 $x - \sin^2(\theta/2) + k'c$ ,  
 $y - Kc/R_\theta \times 10^8$

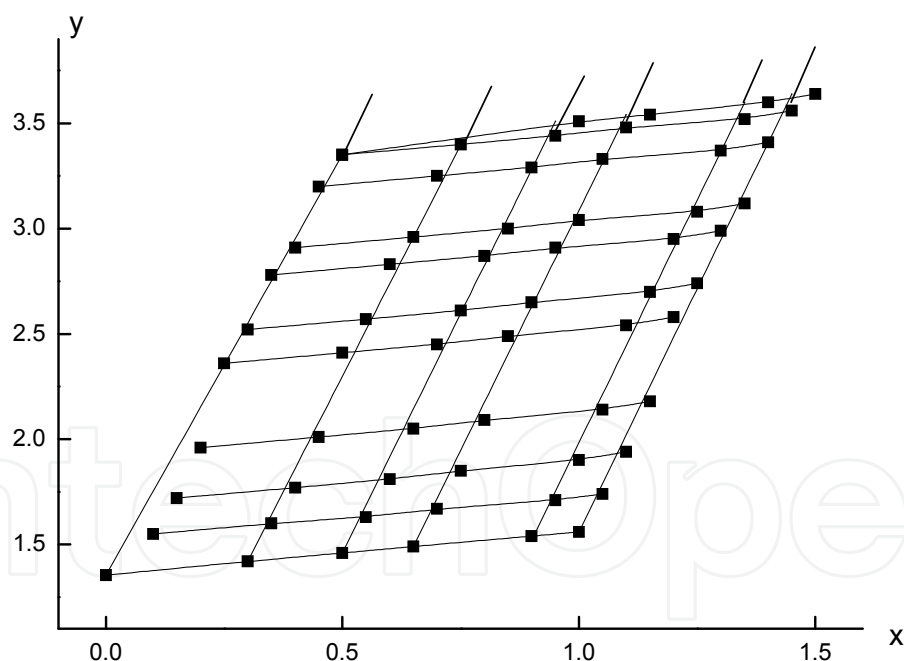


Fig. 2. Zimm diagram for a system of PAMS-Se<sup>0</sup>- water:  
 $x - \sin^2(\theta/2) + k'c$ ,  
 $y - Kc/R_\theta \times 10^8$

Optical part of the installation for measurement of quasi-elastic (dynamic) scattering was equipped with goniometer ALV-SP (Germany) with the following source of light: helium - neon (He - ne) laser Spectra-Physics with wavelength  $\lambda = 632.8$  nm. Correlation function of intensity of the scattered light was obtained by means of correlator Photo Cor-FC with 288.

Analysis of correlation function was carried out by means of quasi-elastic (dynamic) scattering data processing program Dynals (Helios firm, Russia).

Molecular dispersion of the solutions of the forming nanostructures was estimated by means of birefringence (double refraction) method [23] using a character of gradient dependence of the value of double refraction  $\Delta n$ . The value of  $\Delta n$  was determined subject to rate of rotation of the rotor "g" and concentration of the solution "c" provided constant ratio selenium : polymer. Titanium dynamo-optimeter with internal rotor with 4 cm height and 0.03 cm gap between rotor and stator was used for those measurements. All measurements of double refraction  $\Delta n$  were carried out using thermostating at 21°C to avoid changes of viscosity of solutions and optical distortions caused by temperature gradient. Phenethyl alcohol that has significant double refraction value ( $\Delta n/g = 17 \times 10^{-12}$ ) and system of polystyrene - bromoform were used for calibration of the installation. Inaccuracy of determination of characteristic value of double refraction  $[n] = \lim_{g \rightarrow 0, c \rightarrow 0} (\Delta n/gc\eta_0)$  did not exceed 10%. The measurements were carried out at  $g < g_k$ , where  $g_k$  is a gradient of velocity at which flow turbulence occurs.

In general case when  $dn/dc \neq 0$  experimental value  $[n]$  is formed from three effects:  $[n] = [n]_e + [n]_{fs} + [n]_f$  where  $[n]_e$  - intrinsic anisotropy,  $[n]_{fs}$  - microform effect,  $[n]_f$  - macroform effect [23]. In that a value of total segment anisotropy  $[n]_{fs} + [n]_e$  is determined by equilibrium stiffness of the polymer chain and structure of elementary unit of the polymer, and value  $[n]_f$  is connected with asymmetry of form of the particle by the following relation:

$$[n]_f = ((n_s^2 + 2)/3)^2 \times (M_w^* (dn/dc)^2 f(p)) / (30\pi RT n_s) = \text{const } M_w^* (dn/dc)^2 f(p), \quad (3)$$

where  $n_s$  - solvent refractory index, T - absolute temperature, R - universal gas constant,  $f(p)$  - tabulated function of ratio of axes of stiff ellipsoid approximating the particle [23].

Time variations of effective viscosity of PAMS solution during reduction of selenitic acid we registered by means of rheoviscosimeter «Brookfield» at rate of rotation of the rotor equal to 12 rpm.

Value of relative viscosity  $\eta_r$  was determined by means of Ostwald capillary viscosimeter with water outflow time equal to  $120 \pm 0.2$  sec at 21°C.

In this study we used for the first time a method of polarized light scattering for studying structural features of nanocomposite on the base of PAMS. The studies were carried out by means of ФПС-3М instrument with photoelectric system of registration of light intensity scattered in the range of angles  $\theta = 40^\circ - 140^\circ$  (wavelength of incident light = 578 nm). Calibration of the instrument was done by benzol: Rayleigh ratio for benzol at given wavelength of incident light made up  $13.1 \times 10^{-6} \text{ cm}^{-1}$ . Angle dependencies of vertical ( $V_V$ ) and horizontal ( $H_V$ ) polarized components of the scattered light were measured by method described in [16]. Calculation of the parameters of scattering media was carried out within the frames of Debye-Bekey [24]. Isotropic parameters of structure such as average square of scattering micro-volume polarizability fluctuation  $\langle \eta \rangle^2$  and radius of polarizability fluctuation correlations  $\alpha_V$  were determined from angle dependence  $V_V$ ; the following

isotropic parameters such as square of optical anisotropy average density  $\langle \delta \rangle^2$  and radius of correlation of optical axes of scattering elements of volume  $\alpha_H$ . The parameters of isotropic structure are connected with dimensions  $\alpha_V$  of macro-molecules or associates and with micro-heterogeneity  $\langle \eta \rangle^2$  as a function of density fluctuation [25, 26]. Nature of dependence of the parameters of anisotropic structure on concentration allowed determining of system order and statistic dimensions of oriented regions.

### 3. The results and discussion

When reducing selenitic acid by ascorbate in presence of polymeric stabilizers the rate constants were equal to  $k^* = 0.5 \times 10^{-3} \text{ sec}^{-1}$  for DNA and  $0.4 \times 10^{-3} \text{ sec}^{-1}$  for PAMS correspondingly that significantly differs from the value of  $k^*$  in absence of stabilizers when  $k^* = 1.6 \times 10^{-3} \text{ sec}^{-1}$ . In addition, the values of the rate constants illustrate comparable influence of selected polymeric matrixes on process of self-organization of nanostructures.

In that during the first 10 minutes of reaction efficient viscosity of nanocomposite solutions on the base of PAMS has been changed from 165 centipoise to 55 centipoise, and after that during 2 days it reduced to 18 centipoise that verified reduction of total number of the particles in the volume of solution due to adsorption of macromolecules on the surface of Se nanoparticles being formed. Studying of characteristic viscosity of water solutions of original PAMS and formed nanostructure of PAMS -nano-  $\text{Se}^0$  has demonstrated that estimated value  $[\eta]$  was reduced significantly from 70 to 12 dl/g (Figure 3). However, in that according to the data static light scattering the value of molecular mass  $M_w^*$  of nanostructure made up  $75 \times 10^6$  (table) i.e. it has been increased by 25 times ( $N^* = 25$ ) compared to free macromolecules of PAMS.

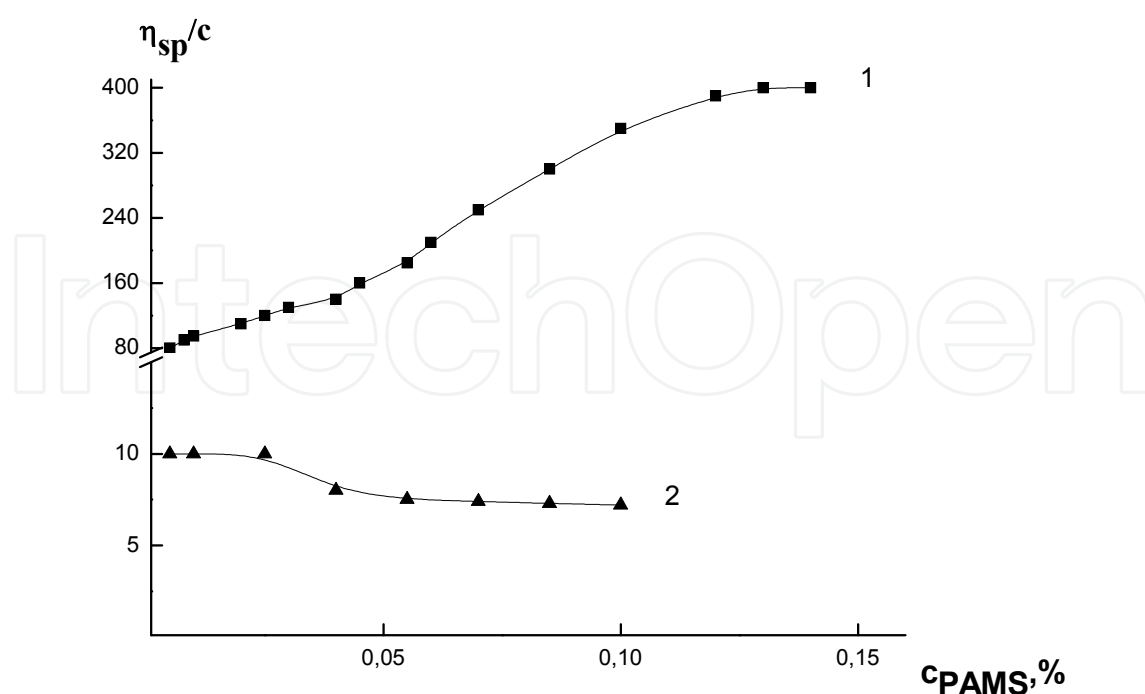


Fig. 3. Concentration dependence of reduced viscosity  $\eta_{\text{sp}}/c$  for systems PAMS-water (1) and PAMS- $\text{Se}^0$ - water (2).

Estimation of hydrodynamic radius  $R_h$  of Se nanoparticles by the method of dynamic light scattering demonstrated that in absence of polymer big particles of selenium with radius  $\sim 100$  nm (the first day) and  $\sim 180$  nm (the second day) were formed with initial narrow unimodal distribution by dimensions. However, after  $\sim 50$  hours this distribution by dimensions became bimodal and wide. Visible aggregation of selenium occurred after two days expiration. When using PAMS as polymeric stabilizer of nanoparticles of selenium in water solutions at  $v=0.1$  the nanostructures with dimensions  $< 100$  nm (table) are formed with narrow unimodal dimension distribution without a tendency to aggregation during a week period at least.

As it follows from the data related to optical properties of PAMS polyanion in water solutions represents an non-penetrable asymmetric swelled ball with asymmetry  $p > 2$  [27]. For system PAMS-nano-  $\text{Se}^0\text{-H}_2\text{O}$  evaluation of the value of parameter  $p^*$  in approximation  $[n] \approx [n]_f$  has demonstrated that nanostructure has conformation approximating to spherical one:  $p^* = 1.5$ . It is compatible with the data related to parameter  $\rho^*$ :  $\rho^*=1.0$  that corresponds to spherical conformation [19, 22].

Assuming spherical conformation of nanostructure on the base of PAMS we determined its packing factor  $k$  [28]:

$$k = (N^* M_w^* \Sigma_l \Delta V_l) / (v^* M_0), \quad (4)$$

where  $\Sigma_l \Delta V_l$  - intrinsic (Van der Waals) volume of the repetitive link if polymer formed from increments of Van der Waals volumes of separate atoms included into this link:

$M_w^*$  - MM of the particle;

$N^*$  - number of molecules of polymers in adsorbed state

$M_0$  - MM of the repetitive link;

$v^*$  - volume of nanostructure equal to  $(4\pi/3) \times (R_{\text{sph}})^3$  where  $R_{\text{sph}} = 1.29 R_g^*$ .

Value of  $k$  made up 0.2 that is approximating to the value for globular protein ( $k = 0.6 \div 0.8$ ) by the order of magnitude.

Polarized light scattering method was used for quantitative estimation of order and micro-heterogeneity of the system PAMS - nano -  $\text{Se}^0\text{-H}_2\text{O}$ .

Compared to the system PAMS -  $\text{H}_2\text{O}$ , for which parameter  $\langle \delta \rangle^2$  is not determined in general (water solutions do not reveal anisotropic scattering), this parameter for the system PAMS -  $\text{Se}^0\text{-H}_2\text{O}$  reaches a value  $\sim 1.5 \times 10^{-7}$  that is more typical for solid bodies (Figure 4).

Sharp increase of parameter  $\langle \eta^2 \rangle$  is observed for the same system in the range of concentrations of polymer  $c < 0.05$  % (Figure 4), that verifies increase of micro-heterogeneity of the solution due to increase of scattering centers per unit volume.

In that statistic dimensions of optical dense regions  $\alpha_v$  remain invariable in the whole range of the studied concentrations (Figure 5).

A distinctive feature of the system PAMS- $\text{Se}^0\text{-H}_2\text{O}$  in the range of concentrations for polymers equal to 0.05 - 0.10 mass % is that inverse (abnormal) slope of angle dependence  $H_v$  scattering component is observed. It may be a result of nonrandom fluctuations of



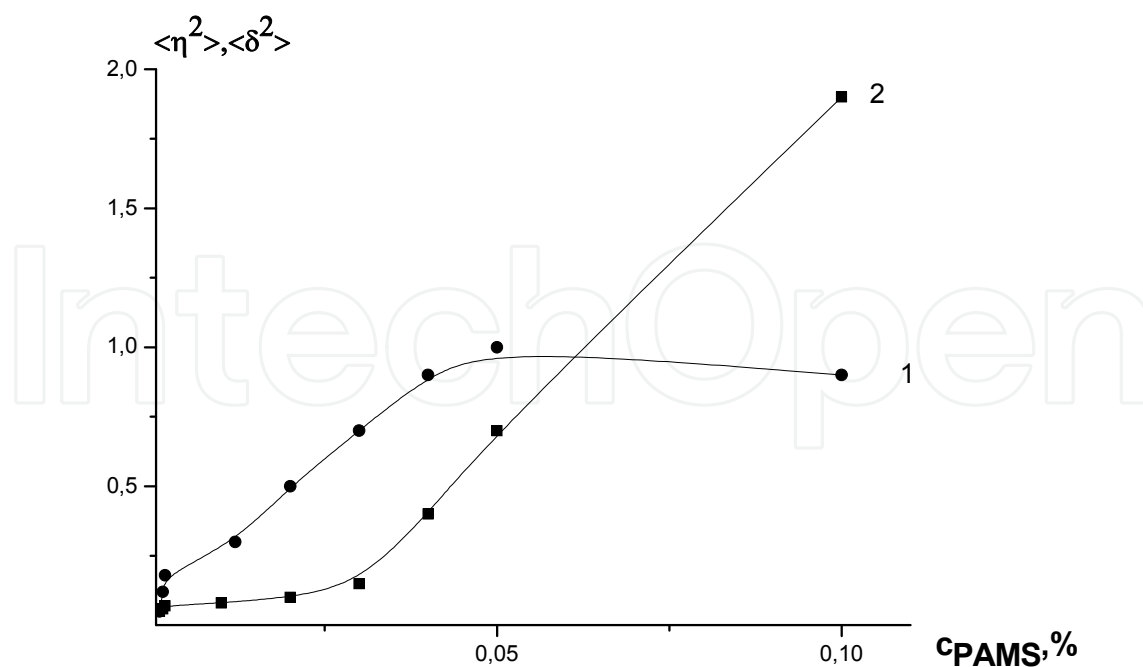


Fig. 4. Concentration dependences of mean square of polarizability fluctuations  $\langle \eta^2 \rangle$  (1) and mean square of density of optical anisotropy  $\langle \beta^2 \rangle$  (2) for a system PAMS- $\text{Se}^0$ - water.

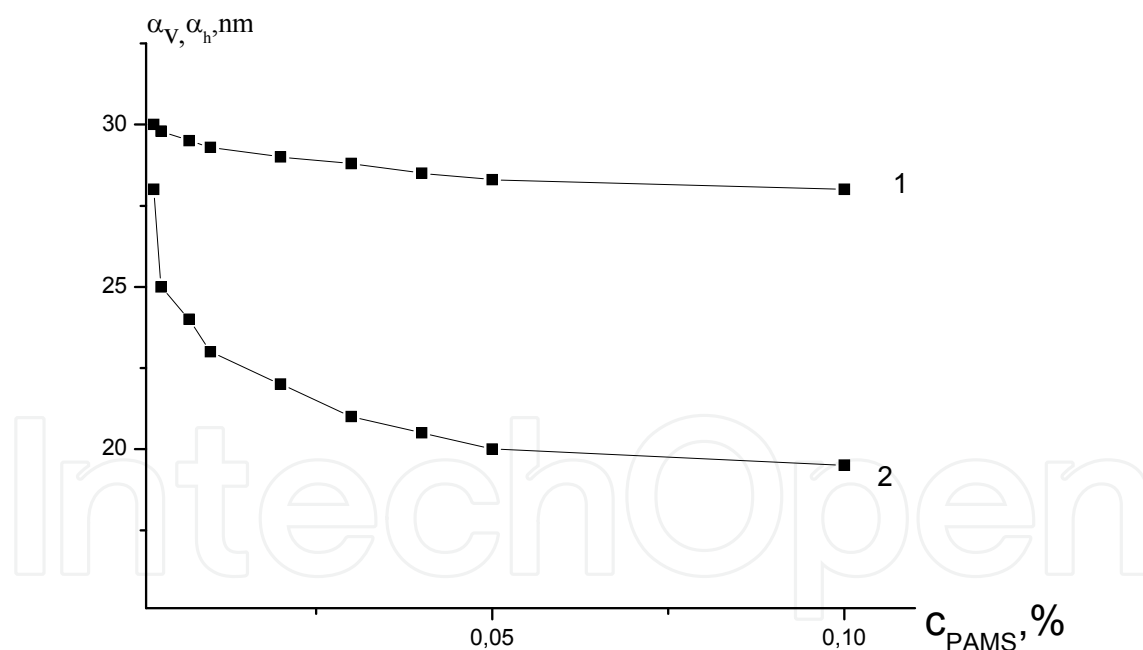


Fig. 5. Concentration dependences of correlation radius of polarizability fluctuations  $\alpha_v$  (1) and correlation radius of correlation of optical axes of scattering elements  $\alpha_h$  (2) for a system of PAMS- $\text{Se}^0$ - water.

anisotropy density for this system. Statistics processing of the data for anisotropic scattering within the angles  $40-80^\circ$  has provided a possibility to determine dimensions of the oriented regions ( $\alpha_H \sim 20$  nm) inside this system (Figure 5). Additional verification of high level of order of nanostructure is represented by the fact that value of local order factor  $F_v$

determined by relation (5) reaches the value equal to 0.7 that characterizes intermediate state of total disordering of macromolecules ( $F_v=0.33$ ) and crystal structure state of the macromolecules ( $F_v=1$ ).

$$F_v = 1/3 (1 + 2 \exp(-\alpha_v / \alpha_h)), \quad (5)$$

Since PAMS from structural point of view is N-substituted analog of polyacrylamide that is not adsorbed on nanoparticles of selenium [8] the main input into binding of PAMZZS with nano- a-Se<sup>0</sup> can be made by hydrophobic fragments as well as sulfonate groups of side links of the polymer.

According to the data of static light scattering the value of molecular mass  $M_w^*$  for nanostructure DNA-nano- Se<sup>0</sup> made up  $200 \times 10^6$  (Table) that is it was increased by 10 times ( $N^* = 10$ ) compared to free macromolecules of DNA. Statistics ( $R_g^*$ ) and hydrodynamic ( $R_h^*$ ) dimensions of the nanostructure DNA-nano- Se<sup>0</sup> coincide with each other ( $R_g^* = R_h^* = 100$  nm) and correspond to nanodimensional level (Table).

System	$k^* \times 10^{-3} \text{ s}^{-1}$	$M_w \times 10^{-6}$	$M_w^* \times 10^{-6}$	$N^*$	$A_2^* \times 10^4, \text{ cm}^3 \text{ mole} / \text{ g}^2$	$R_g^*, \text{ nm}$	$R_h^*, \text{ nm}$	$R_a, \text{ nm}$	$\Delta R, \text{ nm}$	$\Phi^* \text{ g/cm}^3$	$p^*$	$-G^* \times 10^5, \text{ J/m}^2$
DNA	0.50	20.00	200.00	10.00	-0.07	100.00	100.00	12.00	88.00	0.04	1.10	0.02
PAMS	0.4	3	75	25	0.2	90	90	9	81	0.02	1.5	0.01

Table 1. The constants of the rate of reaction of formation of nanocomposites and structural-conformation parameters of the corresponding nanostructures.

It is known that in the field of acid pH ( $\text{pH} < 4.5$ ) oxygen destabilization/denaturation of the DNA macromolecules takes place. Within the range of pH from 3.0 to 4.5 partial destabilization of twin helix is observed, further decrease of pH results in denaturation of DNA already that is verified by studies of UV absorption of DNA, circular dichroism spectra of DNA, viscosimetry data, and double refraction ( $\Delta n$ ) data in flow [29 - 32].

For the system DNA-nano- Se<sup>0</sup>-H<sub>2</sub>O at pH = 3.5 destabilization of twin helix in process of self-organization of the structure is observed: the given value of double refraction ( $\Delta n$ ) has a positive sign compared to corresponding value for negative DNA (Figure 6). If for isolated DNA macromolecule in native condition  $[n] \approx [n]_e$  [23] then for the system DNA-nano-Se<sup>0</sup>-H<sub>2</sub>O approximation  $[n] \approx [n]_e$  is fulfilled. Estimation of the asymmetry level of the form of the nanostructure resulted in the value  $p^* = 1.1$ . It agrees to the light scattering data ( $p^* = R_g^* / R_h^* = 1.0$ ).

It seems that formation of adsorbates of polymers on nanoparticles of nonmetals with the form close to spherical one is a universal phenomenon. For nanostructures, which are different from morphology point of view in the range of saturation of adsorption capacity  $v = 0.1$ , the particles with a form close to spherical one were found experimentally [8-13, 33, 34].

Calculation of average density of nanostructures at  $v = 0.1$  by formula (2) demonstrated that though the nanostructures with density  $\Phi^* = 0.02$  and  $0.04 \text{ g/cm}^3$  are formed (Table) that exceed a density of polymer ball [23] but less than for selenium containing spherical nanostructures on the base of nonionic rigid chain molecules ( $\Phi^* = (0.12 - 0.14) \text{ g/cm}^3$ ) [12].

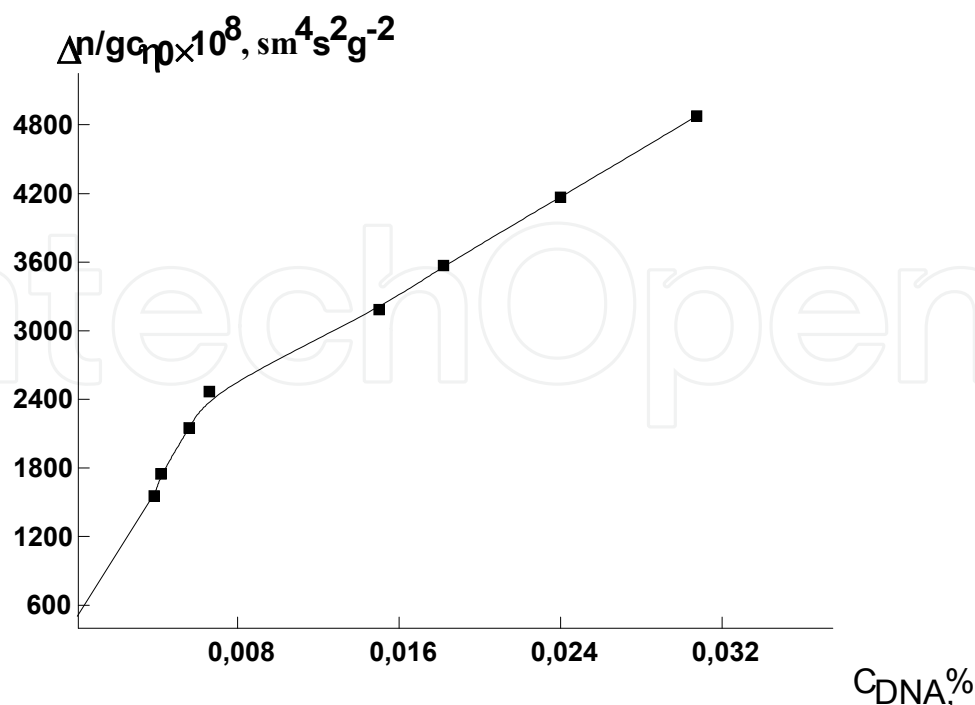


Fig. 6. Concentration dependence of the reduced optical anisotropy  $\Delta n/gc\eta_0 \times 10^8, sm^4s^2g^{-2}$  for a system of DNA- $Se^0$ - water.

Thus it was revealed that in both cases super high molecular nanostructures are formed ( $M_w^* = 200 \times 10^6$  /DNA as stabilizer/ and  $M_w^* = 75 \times 10^6$  /PAMS as stabilizer/) with close dimensions ( $R_g^*$  - statistic dimensions of nanostructure,  $R_h^*$  - hydrodynamic dimensions of nanostructure) and average densities  $\Phi^*$  (Table). The values of conformation parameters  $\rho^*$  and  $p^*$  testify a form of nanostructures approaching to spherical one:  $\rho^* = R_g^*/R_h^* = 1$  (for both systems);  $p^* = 1.1$  for system DNA-nano-  $Se^0$ -  $H_2O$  and  $p^* = 1.5$  for system PAMS-nano- $Se^0$ -  $H_2O$  (see Table).

Basing on experimental data for values of  $M_w^*$  for spherical nanostructures and assuming their mononuclear morphology we evaluated a radius of selenium nucleus that made up  $R_{nucl} = 12$  nm (DNA as stabilizer) and 9 nm (PAMS as stabilizer). Thus in water solution a width of polymer shell  $\Delta R$  on the particles of nano-  $Se^0$  stabilized by strong polyacids has small differences and makes up  $\sim 80 - 90$  nm (see Table).

With the purpose of experimental determination of the dimensions of nuclei in nanostructures PAMS- $Se^0$  and DNA- $Se^0$  their water solutions were passed through cool dehumidification, and the samples obtained in the form of pellets were studied by X-ray diffraction method. It was found that amorphous particles of nano-  $Se^0$  of spherical form for both nanocomposites had unimodal distribution by dimensions and average radius of selenium nucleus made up 10 - 15 nm. These values have good correlation with design quantity of  $R_{nucl}$  for nanocomposites.

It was shown that a complex polyanion - nanoparticle obtained under conditions of total saturation of adsorption capacity of selenium nanoparticles (mass ratio  $v$  of the components of the selenium: polymer complex was equal to 0.1) was close to its thermodynamic limit:

the second virial coefficient made up  $A_2^* = -0.07 \times 10^{-4} \text{ cm}^3 \text{ mole/g}^2$  for DNA-nano-  $\text{Se}^0$ -  $\text{H}_2\text{O}$  system and  $A_2^* = 0.2 \times 10^{-4} \text{ cm}^3 \text{ mole/g}^2$  for PAMS-nano-  $\text{Se}^0$ -  $\text{H}_2\text{O}$  system. It agrees with the data obtained at  $v = 0.1$  for selenium containing nanostructures on the base of the system of nonionic polymers and polybases [8, 12, 35].

Basing in relation [36] we have:

$$\Delta G^* = kT \ln C_e / \pi D_{\text{cp}}^2, \quad (6)$$

that is applicable in the field of stable dispersions for spherical nanostructures of arbitrary morphologies, we obtained the values of free energy  $\Delta G^*$  of interaction of macromolecule – nanoparticle per unit area of the surface of the particle (see Table). In equation (6)  $C_e$  – equilibrium concentration of polymer in molar fractions of monomeric units,  $D_{\text{sph}} = 2R_{\text{sph}}$  ( $R_{\text{sph}} = 1.29 R_g^*$ ). You may see from the Table that quantity of free energy at  $v = 0.1$  does not depend practically on structure of monomeric unit and nature of polyacids. It seems that in both cases the same mechanism of adsorption of macromolecules on selenium nanoparticles is realized. So, for ionogenic polymeric matrix (at  $\text{pH} = 3.5$  strong polyacids are in ionized state) it is observed electrosteric stabilization stipulated for by electrostatic effects from one side and entropic and osmotic effects from another side [37] appearing due to hydrophobic interactions in aqueous medium between hydrophobic fragments of organic macromolecules and energy saturated surface of selenium nanoparticles.

From totality of the presented data we can make conclusion that at adsorption of macromolecules of strong acids on selenium nanoparticles spherical nanostructures of similar morphology types with close dimensions, densities and width of polymer shell are formed.

Thus, selenium nanoparticles represent adsorption matrixes where high local concentrations of polyanions containing hydrophobic fragment can be reached.

#### 4. Conclusions

1. It has been determined by means of molecular optics that macromolecules of PAMS and DNA adsorbed on nano- $\text{Se}^0$  form high molecular nanostructures (with  $MM M_w^* = 75 \times 10^6$  и  $200 \times 10^6$ ) with dimensions equal to 90 – 100 nm including 10/25 macromolecules densely packed into its composition.
2. It was shown that polyanion – nanoparticle complex obtained under conditions of total saturation of adsorption capacity of selenium nanoparticles (mass ratio  $v$  of the components of selenium: polymer complex was equal to 0.1) is close to the limit of its thermodynamic stability. It agrees with the data obtained at  $v = 0.1$  for selenium containing nanostructures on the base of the systems of non-ionogenic polymers and polybases.
3. In saturation range of adsorption capacity  $v = 0.1$  universality of formation selenium – polymeric nanostructures of spherical form was experimentally determined.

#### 5. References

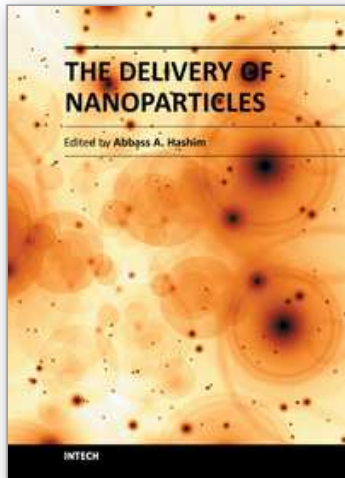
- [1] Pomogailo A.D., Rosenberg A.S., Uflyand I.E. (2000). *Metal nanoparticles in polymers*. M. Chemistry.

- [2] Kopeikin V.V., Panarin E.F. (2001). Water soluble nanocomposites of zero-valent silver with increased antiinfection activity, *J.Reports of the Academy of Science*. Vol. 380, No. 4, 497 -500.
- [3] Balogh L., Swanson D. R., Tomalia D. A., Hagnauer G. L., McManus A. T. (2001). Antimicrobial Dendrimer Nanocomposites and a Method of Treating Wounds, US 6 224 898 B1.
- [4] Connelly S., Fitzmaurice D. (1999). Programmed Assembly of Gold Nanocrystals in Aqueous Solution, *Adv.Mater.*, Vol. 11, No. 14, 1202-1205.
- [5] Yost D. A., Russell J.C., Yang H. (1990). Non-Metal Colloidal Particle Immunoassay, US Patent 4 954 452.
- [6] Ching S., Gordon J., Billing P.A. (1988). Process for Immunochromatography with Colloidal Particles, EP App. 0 299428 A2.
- [7] Zhang J.S., Gao X.Y., Zhang L.D., Bao Y.P. (2001). Biological effects of a nano red elemental selenium, *Biofactors*. Vol. 15, No. 1, 27-38.
- [8] Kopeikin V.V., Valueva S.V., Kipper A.I., Borovikova L.N., Filippov A.P. (2003). Synthesis of selenium nanoparticles in water solutions of polyvinylpyrrolidone and morphologic characteristics of the nanocomposites being formed, *High-molecular compounds*, Vol. 45 A, No. 4, 615 - 619.
- [9] Kopeikin V.V., Valueva S.V., Kipper A.I., Kalinina N.A., Silinskaya I.G., Khlebsoolova E.N., Shishkina G.V., Borovikova L.N. (2003) Study of processes of self-organization of macromolecules of poly-2-acrylamido-2-methylpropan of sulfacids and sodium dodecyl sulfate on nanoparticles of zero valent selenium, *High molecular compounds*, Vol. 45 A, No. 6, 963-967.
- [10] Valueva S.V., Kopeikin V.V., Kipper A.I., Filippov A.P., Shishkina G.V., Khlebsoolova E.N., Rummyantseva N.V., Nazarkina Y.I., Borovikova L.N. (2005). Formation of nanoparticles of zero valent selenium in water solutions of polyampholit in presence of different redox systems, *High-molecular compounds*, Vol. 47B, No. 5, 857-860.
- [11] Valueva S.V., Kipper A.I., Kopeikin V.V., Borovikova L.N., Ivanov D.A., Filippov A.P. (2005). Influence of molecular mass of polymeric matrix on morphologic characteristics of the selenium containing nanostructures and their resistance to impact of hydrodynamic field, *High-molecular compounds*, Vol. 47A, No. 3, 438-443.
- [12] Valueva S.V., Kipper A.I., Kopeiki V.V., Borovikova L.N., Lavrentyev V.K., Ivanov D.A., Filippov A.P. (2006). Studying of process of formation of selenium containing nanostructures and their characteristics on the base of the rigid molecules of cellulose derivatives, *High molecular compounds*, Vol. 48A, No. 8, 1403 - 1409
- [13] Valueva S.V., Borovikova L.N., Koreneva V.V, Nazarkina Y.I., Kipper A.I., Kopeikin V.V. (2007). Structural-morphologic and biologic properties of nanoparticles of selenium stabilized by bovine serum albumin, *Journal of physical chemistry*, Vol.81, No. 7, 1329 - 1333.
- [14] Handbook of Chemistry and Physics (2001). Ed. Lide R.D., 81<sup>th</sup> Edition, Chapman & Hill CRC.
- [15] Berezin I.V., Klesov A.A. (1976). *Practical course of chemical and enzyme kinetics*, M.: Moscow State University.
- [16] Eskin V.E. (1986). *Light scattering by polymer solutions and properties of macromolecules*, L.: Nauka, Science.

- [17] Pogodina N.V., Tsvetkov N.V. (1997). Structure and Dynamics of the Polyelectrolyte Complex Formation, *Macromolecules*. Vol. 30, No. 17, 4897-4904.
- [18] Brown W. (1993). *Dynamic Light Scattering: the Method and Some Application*. Oxford: Clarendon Press.
- [19] Meewes M., Ricka J., De Silva M., Nuffengger R., Binkert Th. (1991). Coll-globule transition of poly (N-isopropylacrylamide). A study of surfactant effects by light scattering, *Macromolecules*. Vol. 24, No. 21, 5811-5816.
- [20] Nishio I., Shao Thang Sun, Swislow G., Tanaka T. (1979). First observation of the coll-globule transition in a single polymer chain, *Nature*. Vol. 281, No. 5728, 208-209.
- [21] Konishi T., Yoshizaki T., Yamakawa H. (1991). On the "universal constants"  $p$  and  $\Phi$  of flexible polymers, *Macromolecules*. Vol. 24, No. 20, 5614-5622.
- [22] Burchard B.W. (1992). *Static and dynamic light scattering approaches to structure determination of biopolymers// Laser Light Scattering in Biochemistry* Eds. by Harding S.E., Satelle D.B., Bloomfield V.A. Cambridge : Royal Soc. Chem. Information Services.
- [23] Tsvetkov V.N., Eskin V.E., Frenkel S.Y. (1964). *Structure of macromolecules in solutions*. M.: Nauka, Science.
- [24] Stein P. (1978). *Polymer Blends*. Ed. by Poul D.P., Newman S. New York; San Francisco; London: Acad. Press.
- [25] Kalinina N.A., Kallistov O.V., Kuznetsov N.P., Batrakova T.V., Romashkova K.A., Gusinskaya V.A., Sidorovich A.V. (1990). Light scattering and structure of moderate concentrated solutions and films of polyamides, *High molecular compounds*, Vol. 32 A, No. 4, 695 -700.
- [26] Kallistov O.V., Krivibokov V.V., Kalinina N.A., Silinskaya I.G., Kutuzov Y.I., Sidorovich A.V. (1985). Structural peculiarities of the moderate concentrated solutions of polymers with different rigidity of molecular chain, *High molecular compounds*, Vol. 27 A, No. 5, 968 - 971.
- [27] Valuev S.V., Kipper S.V. (2001). Influence of ionic force on asymmetry of p form of macromolecule of poly-2-acrylamido-2-methylpropan sulfacids in diluted water-salt solutions, *Journal of applied chemistry*, Vol. 74, No. 9, 1513 - 1517.
- [28] Askadsk A.A., Matveyev Y.I. (1983). *Chemical structure and physical properties of polymers*. M.: Chemistry.
- [29] Dove W.F., Wallace T., Davidson N. (1959). Spectrofotometric study of the protonation of undenatured DNA, *Biochem. Biophys. Res. Com.*, Vol. 1, No. 6. 312-317.
- [30] Luck G., Zimmer Ch., Snatzke G. (1968). Circular dichroism of protonated DNA, *Biophys. Biochem. Acta*, Vol. 169, 548-549.
- [31] Struts A.V., Slonitsky S.V. (1983). Study of conformation of DNA molecule in water solutions of acrylamide and semicarbazide, *Bulletin of the Leningrad State University, Physics, Chemistry*, Vol. 4, No. 22, 33 - 39.
- [32] Kasyanenko N.A., Bartoshevich S.F., Frisman E.V. (1985). Study of influence of pH media on conformation of DNA molecule, *Molecular biology*, Vol. 19, No. 5, 1386 - 1393.
- [33] Storhoff J.J., Lazaorides A.A., Mucic R.C., Mirkin C.A., Letsinger R.L., Schatz G.C. (2000). DNA-linked gold nanoparticle assemblies, *J.Amer.Chem.Soc.* Vol. 122, 4640 - 4651.

- [34] Bronstein L.M., Valetsky P.M., Antonietti M. (1997). Formation of nanoparticles of metals in organized polymeric structures, *High molecular compounds*, Vol. 39 A, No. 11, 1847 - 1855.
- [35] Kopeikin V.V., Valueva S.V., Kipper A.I., Filippov A.P., Khlebosolova E.N., Borovikova L.N., Lavrentyev V.K. (2003). Study of formation of the particles of nano- Se<sup>0</sup> in water solution of cation polyelectrolyte, *Journal of applied chemistry*, Vol. 76, No. 5, 847 - 851.
- [36] Litmanovich O.E., Papisov I.M. (1999). Influence of length of macromolecule on dimension of the particle of metal reduced in polymeric solution, *High molecular compounds*, Vol. 41 A, No. 11, 1824 - 1830.
- [37] Mayer A.B.R. (2001). Colloidal Metall Nanoparticles Dispersed in Amphiphilic Polymers, *Polym. Adv. Technol.* Vol. 12, 96 - 102.

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## **The Delivery of Nanoparticles**

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Nanoparticle is a general challenge for today's technology and the near future observations of science. Nanoparticles cover mostly all types of sciences and manufacturing technologies. The properties of this particle are flying over today scientific barriers and have passed the limitations of conventional sciences. This is the reason why nanoparticles have been evaluated for the use in many fields. InTech publisher and the contributing authors of this book in nanoparticles are all overconfident to invite all scientists to read this new book. The book's potential was held until it was approached by the art of exploring the most advanced research in the field of nano-scale particles, preparation techniques and the way of reaching their destination. 25 reputable chapters were framed in this book and there were alienated into four altered sections; Toxic Nanoparticles, Drug Nanoparticles, Biological Activities and Nano-Technology.

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