

Study of the Nanoparticles Dispersions in Environmental Liquid Media

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ABSTRACT

Increasing production of nanomaterials makes study of nanoparticles behavior in the environment be of immediate interest. Nanomaterials are known to change their properties cardinally when releasing into the environment. In this work, the opportunity of nanoparticles to form stable lyosol in physiological solutions has been demonstrated. Dispersions prepared by mixing nanopowders of zinc (13.58 m²/g), copper (24.66 m²/g), aluminium oxides (54.75 m²/g), and zirconium dioxide (8.10 m²/g) with phosphate buffered saline, isotonic solution of glucose and synthetic alveolar fluid. With the help of laser diffraction method and transmission electron microscopy it was shown that in dispersions based on nanopowders and physiological media double dispersions have been formed: unstable suspensions with dispersoid size ~ 10⁻⁵-10⁻⁴ m, and lyosol's stable to aggregation with particles size ~ 10⁻⁷-10⁻⁶ m.

KEYWORDS: nanopowders, nanoparticles, dispersions, soles, environment, physiological media

1 INTRODUCTION

Nanoparticles are not new ones for the environment. Nanoparticles are formed in forest fires, volcanic eruptions, erosion of soil, water roiling, and as a result of biological objects lifecycle (pollen on plants, reproduction with fungal spores, viral infections, etc.). Also, nanoparticles are the byproducts of many anthropogenic processes: mining, boiling, melting, physical-chemical processes of various industries (Trubetskoy et al, 2006), internal combustion engines, power plants, jet engines, metal and polymer fumes, etc. (Oberdörster et al, 2005). The coming era of nanotechnology is focused on the targeted production and use of nanoparticles and products containing nanoparticles. It is obvious that extensive research and use of nanomaterials create new conditions for the inevitable entry of nanoparticles into the environment, including atmosphere, hydrosphere, lithosphere and living organisms.

In recent years there have been publications which assess ecotoxicological risks of new engineered nanoparticles in aquatic environments (Farre et al., 2009). However, so far there is lack of information about physicochemical behavior of nanoparticles in liquid biological media (saliva, sweat, alveolar liquid, etc); that does not allow predicting nanoparticles behavior and well-establish connection between cytotoxic effects and physicochemical state of nanoparticles. Determination of the ecotoxicological effects of nanomaterials upon environmental objects is based on understanding of fundamental properties of particles in the environment (Buffle, 2003). But it is clear *a priori*, that nanomaterials cardinally change their properties when releasing into the environment and because of the small size of their effect is realized at the cellular, subcellular and molecular levels.

If solid insoluble particles homogeneously distributed in the liquid phase with formation of the sol or suspension (lyophobic colloidal system), particles may aggregate spontaneously coagulation due to the high surface energy and thermodynamic instability of nanoparticles. On the other hand, under certain

conditions (the influence of ultrasound, the addition of stabilizers, the existence of repulsion between particles, etc.) nanoparticles can form dispersion with a high degree of dispersity (Handy et al., 2009). Therefore, an important characteristic of colloidal systems is known to be an aggregative stability – the ability to maintain its dispersive composition. This characteristic is most clearly determined by measuring the change in particle size distribution during the coagulation process. Also aggregative stability can be estimated with change of the precipitation kinetics (Gauptman et al., 1979), if the enlargement is a result of settlement of pretty large (able to settle) aggregates or agglomerates.

This study was focused on the assessing the possibility of formation of stable dispersions with engineered nanoparticles when they exposed to the physiological liquids.

2 MATERIALS AND METHODS

Nanopowders of zinc (NP-Zn), copper (NP-Cu), zirconium dioxide (NP-ZrO₂) and aluminum oxide (NP-Al₂O₃) were taken for the study. Nanostructured powders NP-ZrO₂ and NP-Al₂O₃ were obtained by plasma-chemical method. Such powders are promising for the manufacture of producing nanoceramic (Karban et al, 2003). Metal nanopowders (NP-Zn, NP-Cu) were obtained by electrical explosion of wires, and the technology of producing included the step of passivation for the covering metal bulk particles with the oxide film.

The phase composition of nanopowders was determined with the help of X-ray diffractometer XRD 7000, Shimadzu. The specific surface area of dry powders (S) was determined using low temperature adsorption of nitrogen (BET theory) with the device «SorbiPrep», META, Russia. The accuracy of measurements was ± 0,2 m²/g. Study of the microstructural characteristics of nanopowders was made by a scanning electron microscope (SEM) JSM-7500FA, Jeol.

To make nanoparticles dispersions several synthetic solutions were used. Phosphate buffering saline (PBS, chemical content, g/L: NaCl - 8,77; Na₂HPO₄ - 1,28; KH₂PO₄ - 1,36, pH = 6.5) was selected as a traditional solution used for testing toxicological activity of different materials in practice. Aqueous solution of glucose (Gl, C₆H₁₂O₆ - 4.5 %wt., PH = 6.5) is isotonic solution, which is used in physiotherapy to replenish fluids. Both solutions are not toxic to living organisms and their compounds are absorbed thankfully. Alveolar fluid (Alv, chemical content, g/L: MgCl₂ - 3.21, NaCl - 0.05, Na₂HPO₄ - 0.071, Na₂SO₄ - 0.039, CaCl₂·2H₂O - 0.128, C₆H₅Na₃O₇·2H₂O - 0.077, NaOH - 6.00, C₆H₈O₇ - 20.8, H₂NCH₂COOH - 0.059, C₃H₃O₃Na - 0.086, pH = 4.5) is a solution simulating pulmonary liquid in alveolars.

To prepare dispersions (suspensions and sols) nanopowders and selected media were mixed, the concentration of the solid phase was 1-5 wt.%. The dispersed phase was determined using a transmission electron microscope (TEM) JEM 2100F, Jeol. Volumetric particle size distributions in suspensions were obtained by particle analyzer SALD-7101, Shimadzu, which is based on the method of laser diffraction. The experiment was conducted when the impeller was put in for suspensions and without one for sols (in both cases without ultrasound treatment, because ultrasound helps to crush the agglomerates (Farre et al., 2009)). The results were used to calculate the average diameter of particles / agglomerates (d_{av}):

$$d_{av} = \sum d \frac{q(\%)}{100(\%)},$$

where, d is a diameter of particles in dispersions, q is a differential percentage (differential distribution), %.

Evaluation of zeta-potential at the boundary “solid-liquid” in dispersions was performed with the electroacoustic spectrometer Zeta-ASP, Matec Applied Sciences, USA. Advantage of these methods is the study of the systems under *in situ*.

3 RESULTS AND DISCUSSION

Properties of dispersions formed by solid particles in liquid medium basically depend on the phase composition of samples, with an emphasis on the surface composition, which interact with the

environment primarily. X-ray diffraction study revealed the presence of a mixture of three phases - α - Al_2O_3 (27 %wt.), γ - Al_2O_3 (29 %wt.) and δ - Al_2O_3 (37 %wt.) in nanopowder in NP- Al_2O_3 . Phase ZrO_2 (97 %wt.) was stabilized with small amounts of yttrium oxide Y_2O_3 (3 %wt.). X-ray peaks of metal powders confirmed with Zn – 74 %wt., ZnO – 26 %wt. for NP-Zn, and with Cu – 85 %wt., CuO – 15 %wt. for NP-Cu. Oxide film of metal powder was formed at the passivation and as a result of storage.

It is important to note that the kinetics of deposition and aggregation of solid particles in solutions is related to particles shape and surface structure. According to SEM data the individual particles of the powder had different morphology. Oxide powders had been made by nanostructured particles representing hollow (partially integral, partially broken) spheres. The size of the spheres was in the range 40...400 nm, and wall thickness: for NP- Al_2O_3 – 20...45 nm, for NP- ZrO_2 – 20...30 nm as shown in Figure 1a, 1b. It is necessary to underline that the initial powders were agglomerated, the size of the agglomerates belonged to the range 1 ... 6 μm (Figure1).

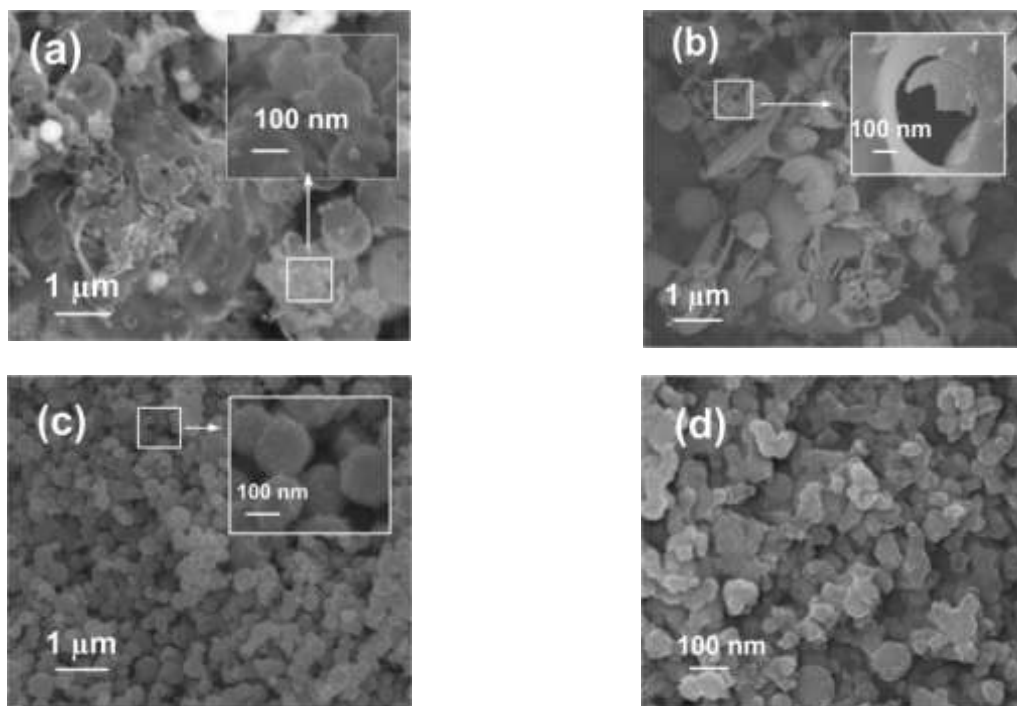


Figure 1: Morphology of nanopowders (SEM data): a) NP- Al_2O_3 , $S = 54.75 \text{ m}^2/\text{g}$; b) NP- ZrO_2 , $S = 8.10 \text{ m}^2/\text{g}$; c) NP-Zn, $S = 13.58 \text{ m}^2/\text{g}$; d) NP-Cu, $S = 24.66 \text{ m}^2/\text{g}$ (BET data).

Particles of metal powders obtained by the wire electrical explosion shaped close to spheres, see Figure 1c, 1d. In the process of wire explosion products of the material destruction fly at high speed at a temperature of 10^4 K and then rapidly cool, resulting in condensed droplets having a nearly spherical shape (Kotov, 2009). The diameters of the particles determined with SEM were larger than the diameter calculated from BET data, indicating the presence of pores and defects that increase the specific surface determined by low-temperature nitrogen adsorption. According to SEM data size of individual particles lied in the interval 20...110 nm for NP-Zn and in the interval 10...55 nm for NP-Cu; size of particle's agglomerate corresponded to 0.5...5.0 μm for the powder NP-Zn and to 0.3...3.5 μm for NP-Cu.

For the most studies specific surface area is used to assess nanopowders dispersion both and size of particles and agglomerates. This is relevant for homogeneous solid particles, since surface-average particle diameter may be calculated with the help of simplified formulas for spherical particles. Calculated diameters for the nanoparticles NP-Zn and NP-Cu were respectively 62 and 27 nm, which agrees with SEM data.

When nanoparticles enter into liquid biological matrix formed disperse systems, aggregate stability of particles depends on the composition of the powders (disperse phase) and physiological medium (dispersion phase). Analysis of dispersion formed by mixing powders and physiological solutions revealed that the processes occurring in suspensions were accompanied with aggregation of powder particles. The distribution of the disperse phase size in these systems was characterized by one or two peaks as shown in Figure 2. Despite the fact that the number of peaks for the same dispersion did not change over time, its value could vary ambiguously upon holding suspensions.

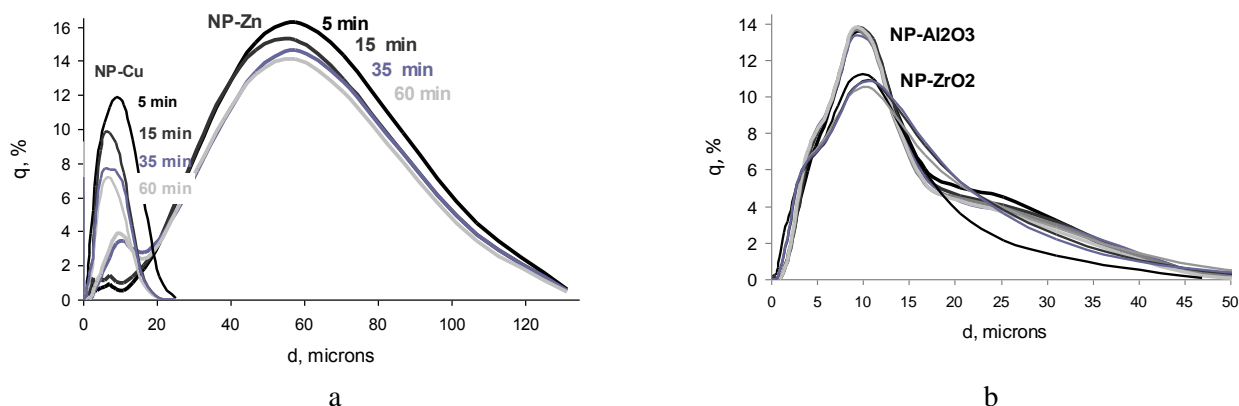


Figure 2: Size distribution of particles (data of laser diffraction): a) NP-Zn and NP-Cu in PBS-dispersion; b) NP-Al₂O₃ and NP-ZrO₂ in Alv-dispersion.

Metal nanopowders were marked by a decrease of the peak value in the curve of size distribution in time. As an example of PBS-dispersion it was shown that maximum peak value of q decreased from 12.0 to 6.5 % for NP-Cu and from 16.0 to 12.5 % (for a larger peak) and from 4 to 0.8% (for smaller one) in case of NP-Zn within 60 minutes (Figure 2a). This data may be explained with increased solubility of copper and zinc nanopowders in aqueous suspensions with similar chemical composition for the first 60 minutes of exposing. Previously the authors showed that after 60 minute-exposition of Cu and Zn electroexplosive nanopowders in aqueous suspensions system supersaturated state with respect to Cu²⁺ and Zn²⁺ was formed, that resulted in forming coarse sediments (oxides, hydroxides) with new structure (Godymchuk et al., 2010, Yunda et al., 2011). Therefore, it is quite difficult to obtain a stable dispersion in inorganic physiological media for metal powders. While in GI- and Alv-suspension particle size distribution (laser diffraction data) did not change their quantitative characteristics. For oxide nanoparticles distribution curves in all environments were characterized by constancy: the height and width of the peak in time did not change. This was most likely due to the chemical stability of the oxides system.

Table 1 Average Size of Nanoparticles Aggregates in Dispersions

Type of nanoparticles	Dry initial powder		Average size of aggregates in physiological media(μm)			
	Average size of particles (nm)	Average size of aggregates (μm)	DW	PBS	GI	Alv
NP-Zn	62.7	5.3	37.3	40.6	49.8	47.5
NP-Cu	27.0	2.2	17.7	26.0	33.6	34.2
NP-ZrO ₂	123.3	4.8	6.3	7.7	12.4	10.5
NP-Al ₂ O ₃	170.1	8.0	13.1	12.5	10.1	10.2

Comparison of laser diffraction data of powders in suspensions and microscopic data for initial dry powders allowed us to make an unambiguous conclusion that processes aggregation took place when nanopowders interacted with physiological liquids. The values the average sizes of particles aggregates in all saline are presented in Table 1. Obviously, the degree of aggregation in physiological environment containing organic compounds is higher than in aqueous inorganic one. An exception was NP-Al₂O₃ - it had a reverse trend that may explain with the increased specific surface.

Further observation formed nanopowders dispersions showed that there was a mixed system. First, suspension with a dispersoid size $\sim 10^{-5}$ - 10^{-4} m was obtained, which one was unstable and precipitated for 1...3 hours. The experimental determination of zeta-potential showed that its value varied in the range of -55 ... -30 mV (pH range 7.8...10.4). Negative values of zeta-potential were due to the formation and adsorption of hydroxyl ions on the surface of the particles. It is possible that for zinc nanoparticles on which surface an amphoteric zinc hydroxide is formed the value of zeta-potential would be with opposite sign in an acidic media.

For visually transparent solutions size distribution curves were also obtained by means of laser diffraction, and average size of agglomerates was calculated. In Figure 3a there is a comparison in average size of dispersoid for the dispersions in suspension before sedimentation and transparent solution after sedimentation. After decantation of big particles, the liosol with the size of solid particles $\sim 10^{-7}$ - 10^{-6} m remained stable over time. The value of electrokinetic potential, which characterizes the stability of the resulting dispersion, is higher in lyosol compared to the suspensions.

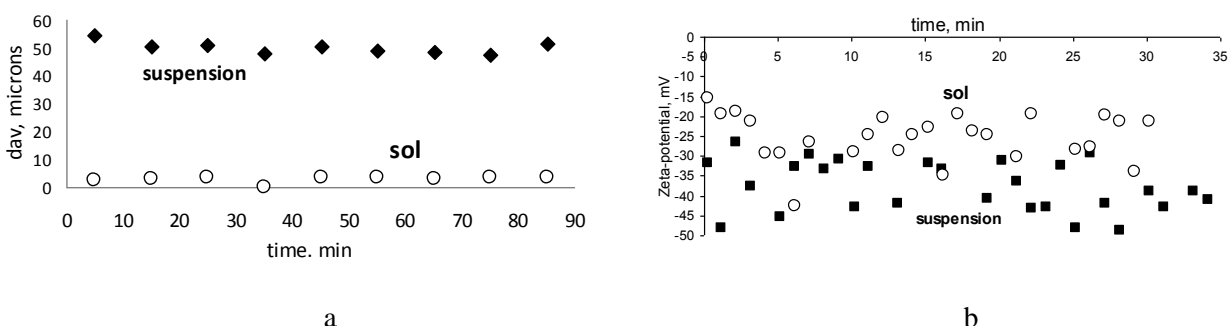


Figure 3: Characteristics of dispersions «NP-Zn + Gl-media": a) change of the average size of aggregates over 90 minutes (the method of laser diffraction); b) change of zeta-potential over 35 minutes (electroacoustic method). Sol was prepared by sedimentation of the suspension for 2.5 hours followed by decanting.

With the help of TEM it was demonstrated that nanoparticles remained in sol, which formed after decantation for several hours (Figure 4). Individual nano- and microparticles were surrounded by alcohol, proteins and organic acids molecules; nanoparticles were likely to be the core of micelle forming stable colloids. Importantly, while the existence of a stable colloid in most cases depends not only on the surface of the dispersed phase, but also the chemical properties of the dispersive medium: for example, glucose is oxidized in the presence of oxygen (aerobic decomposition) to carbon dioxide and water, while the lifetime of glucose solution (4,5 %wt.) is about 72 h.

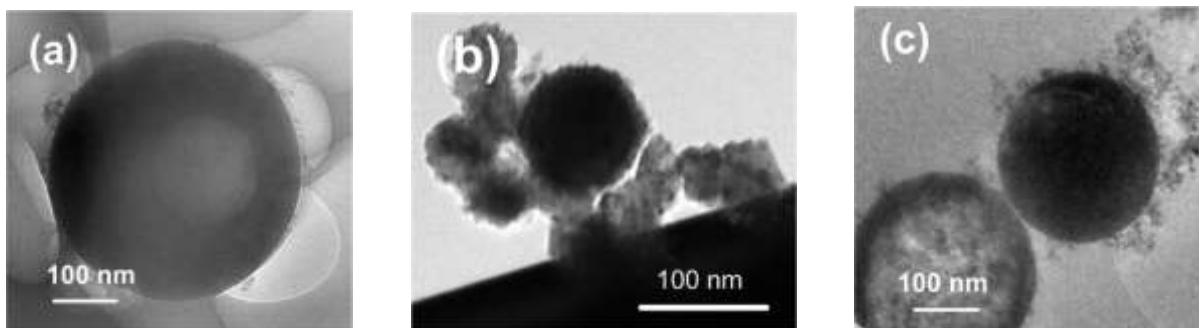


Figure 4: Nanoparticles in sols: a) NP- Al_2O_3 particles in the GI-solution; b) NP-Cu particles in AlV-solution; c) NP- ZrO_2 particles in the GI-solution (TEM data).

4 CONCLUSION

Thus, the experimental data obtained on electroexplosive metal nanopowders and plasma-chemical metal oxides nanopowders have shown when nanopowders contact with physiological liquid media stable nanoparticles dispersions can be formed there. Being stable in the environment nanoparticles can migrate through living organism ignoring the most physiological barriers. In this regard, nanoparticles demonstrate high penetration activity with respect to biological membranes that was established by other authors (Kreyling et al., 2002, Semmler et al., 2004) early. In this context obtained results confirm the potential risk of nanomaterials cytotoxic effect on the living organisms.

On the other hand, this phenomenon can be highly valued in practical application. For example, ability of nanoparticles to form stable dispersion in physiological solutions may be used in medicine for drug delivery. Moreover, toxicological study of nanomaterials in liquid environmental media (physiological solution, aquatic environment) has many analytical subtleties. One of the biggest problems in the study is tendency of nanomaterials to aggregation (Farre et al., 2009). In this respect, obtained results can be essential to prepare stable dispersions of nanoparticles used in ecotoxicological testing of nanomaterials.

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