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Dissolution of Zinc Nanoparticles in Pulmonary Fluid

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***Abstract* —Inhaled from the ambient air nanoparticles may reach innermost areas of respiratory tract, alveolar sacs, particularly. In this work the dissolution of electroexplosive zinc nanoparticles (62 nm) in the synthetic alveolar has been studied. The evidence of the total solubility (99 %) of metal nanopowders in the synthetic alveolar fluid had been demonstrated with the help of the stripping voltammetry. Alongside, the mechanism of zinc nanoparticles dissolution related to the electroexplosive zinc nanoparticles completely dissolving in the synthetic alveolar fluid has been proposed.**

Keywords – zinc nanopowder; dissolution; pulmonary fluid; toxicity

I. INTRODUCTION

Zinc nanopowders show great promise in science and manufacturing. For instance, zinc nanoparticles are used as catalysts at petroleum processing [1] as well as components of latex-silicate composites [2] and at phthalocyanines surface-synthesis [3]. Undoubtedly, widespread application of nanomaterials requires the growth of nanopowders production. Alongside, a large-scale production is expected to cause the increasing dispersion of nanoparticles into our environment, particularly into the ambient air. Therefore, due to the purposeful manufacturing of nanoparticles engineered nanoparticles and human body may touch more frequently.

Through the air nanoparticles are able to enter a human respiratory tract. Numerous studies have shown that owing to various mechanisms nanoparticles may not only transmit through respiratory tract, but also deposit in breathing passages of lungs [4-7]. Herewith, nanoparticles can reach the long-distance areas of respiratory system such as bronchioles and alveolar sacs [8]. What is cognitive, there are more than 600 million of alveolar sacs in human lungs and each sac reaches about 300 μm lengthways. All chemical substances reaching alveolus interact with alveolar fluid. Normally, the alveolar fluid has highly aggressive medium. That is why soluble particles can dissolve with the releasing of ions and molecules, which further can be effectively absorbed by alveolar epithelium, followed by reaching the blood-vascular system and delivering to various organs of the human body.

From the point of predicting nanomaterials toxicity the definition of nanoparticles solubility in alveolus seems to be utterly relevant. Meanwhile, the review since 1995 has shown the scarcity of data about particles solubility in physiological liquids. Hence, the present research was focused on the investigation of zinc nanopowders dissolution in alveolar fluid.

II. NANOPARTICLES TOXICITY DEPENDING ON SOLUBILITY

The solubility of nanoparticles is one of the key factors determining nanoparticles toxicity [9]. While interacting with the aqueous solutions water-soluble nanoparticles generate molecules and ions. That is why the toxicity of water-soluble nanoparticles is to be assessed not only in terms of their own composition, but also the chemical composition of the chemicals formed after dissolution.

On the one hand, it is predicted that water-soluble nanoparticles toxicity will not differ from the toxicity of bigger particles of the same composition. On the other hand, the solubility of the nanoparticles may dramatically increase [10-11]. At the same time insoluble nanoparticles remaining a free state in biological liquid for a long time may also make biological (or mechanical) damage depending on the physicochemical condition of particles surface.

What is fatefully, nanoparticles dissolution in biological fluids (blood plasma, intercellular fluid, alveolar fluid, etc.) can also take place due to the capture of nanoparticles by biomolecules such as proteins and lipids that leads to the enhancing dispersion of nanoparticles in biological media.

There are some papers demonstrating the strong dependence between nanoparticles toxicity and nanoparticles solubility. For example, the dissolution of copper oxide nanoparticles along with formation of Cu^{2+} ions promotes the formation of reactive oxygen species (ROS) being able to provoke inflammatory processes in organism, including cardiovascular diseases, as shown by A. Ivask et al in [12].

With the help of *Daphnia magna* it has been shown that the lethal dose (LD_{50}) of soluble Ag nanoparticles is 30 times less than LD_{50} of insoluble Ag nanoparticles chemically stabilized with lactate cover [13]. In another case, the particles solubility considerably enhanced the sludge antimicrobial toxicity of ZnO nanoparticles [14].

R. Yoshida et al have shown that water-soluble ZnO nanoparticles are characterized by the absence of considerable mutagenic effect on the wide range of bacteria. The authors have suggested that nanosized ZnO particles do not cause mutations and, consequently, should not be considered as a carcinogen [15]. S. Maenosono et al have showed a weakly mutagenicity of water-soluble FePt nanoparticles capped with tetramethylammonium hydroxide in mutagenicity test conducted on in a bacterial reverse mutation assay [16].

Thus, the solubility of nanoparticles may contribute to the considerable toxic effect. Herewith, molecular and ionic state of the matter speeds up the chemical reactivity of nanoparticles

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in relation to biological objects. Nevertheless, soluble substances do not cause mechanical damage of tissues and cells in living organisms and, moreover, can be easily washed away from the body without inducing any inflammatory reactions. At once, the probability of such a result may be highly low in the case of complex organisms since there is no experimental data concerning the excretion of nanomaterials from complex organisms in literature.

One way or another, the solubility has undoubtedly to be considered as a basic factor in the strategic development of sanitary regulations and standardized documents classifying nanoparticles in terms of their toxicity.

III. EXPERIMENTAL PART

The study was carried out on zinc nanopowder obtained by the wire electrical explosion in the inert atmosphere of argon (Advanced Powder Technologies, Tomsk). Before transported zinc nanoparticles were covered with thin oxide layer.

The phase composition of nanopowder was determined by an X-ray diffractometer XRD-7000 (Shimadzu, Japan).

Particles shape and size was identified with a a transmission electron microscope JEM-2100F (JEOL, Japan).

The value of the nanopowders specific surface was determined with low-temperature nitrogen adsorption (BET-theory) on the device SorbiPrep (META, Russia). The value of specific surface area (S) was used to estimate the average size of particle (d) with experimental formula:

$$d = {}^{6}\!\big/_{\rho \cdot S}, \qquad (1)$$

where d – average surface diameter; ρ – density of zinc; S – specific surface area of powders.

Chosen nanopowder was dissoluted in synthetic alveolar solution, the pH of solution was 3.7 (Table 1) [10]. It is to note, that all components of this solution are the basic partials of pulmonary fluid flooding the alveolar sacs in human lungs.

On the basis of zinc nanopowder and synthetic alveolar solution we prepared suspensions with a concentration of nanopowder no more than 0.1 wt. %. The suspensions were kept for 5, 15, 30, 60, 120, 180, 240, and 300 minutes with limited access of air. The suspensions then were separated by centrifugation (3000 rot/min) followed by filtration. Afterwards the solutions were conserved with 5% nitric acid solution. In the obtained solutions the concentration of Zn^{2+} ions was determined with stripping voltammetry. Stripping voltammetry essentially works by electroplating certain metals in solution onto an electrode. This concentrates the metal. The metals on the electrode are then sequentially stripped off, which generates a current that can be measured. The current (milliamps) is proportional to the amount of metal being stripped off.

TABLE I. THE COMPOSITION OF SYNTHETIC ALVEOLAR FLUID

Chemical Formula of the Component	**Content of the Chemical in Synthetic Alveolar Fluid, g/l**
Na_2HPO_4	0.071
$MgCl_2$	0.050
Na_2SO_4	0.039
$CaCl_2{\cdot}2H_2O$	0.128
NaOH	6.000
$C_6H_8O_7$	20.800
H_2NCH_2COOH	0.059
$C_6H_5Na_3O_7{\cdot}2H_2O$	0.077
$C_4H_4O_6Na_2{\cdot}2H_2O$	0.090
$C_3H_3O_3Na$	0.086

Determined concentration was used to calculate the dissolution degree (α) and dissolution rate (R) with formulas:

$$\alpha = \frac{m_{Zn}}{m_{NP}} \cdot 100\%, \quad R = \frac{\Delta c}{\Delta t} \cdot \frac{1}{S}, \qquad (2),(3)$$

where m_{Zn} – mass of Zn^{2+} ions in solution after exposure, m_{NP} – initial mass of the nanopowder, c – concentration of Zn^{2+} ions in the solution, t – time of the exposure, S – specific surface area.

IV. RESULTS AND DISCUSSION

Generally, the particles obtained by the electrical explosion of metal conductors have a shape close to spheres. That is explained with the thermal heating of metal particles till the state of the plasma, liquid, and gas, and condensation with the formation of drops due to Laplace pressure. The SEM data have illustrated the spherical shape of particles as shown in Fig 1.

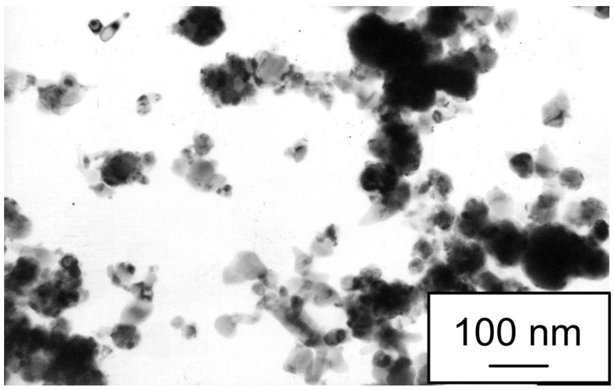

Figure 1. TEM-data of electroexplosive nanopowder

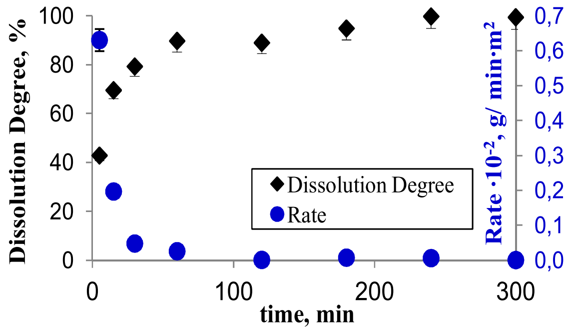

Figure 2. The dissolution rate and degree of Zn nanopowder in alveolar fluid

To reduce chemical reactivity of nanoparticles in air nanopowders had been coated with a thin zinc oxide film. The content of oxides in freshly prepared nanopowder did not exceed 5 wt.%. However, during transportation, pouring, weighing, and other manipulations nanoparticles were oxidizing. That is why, the content of zinc oxide in nanopowder by the moment of the study had reached 26 wt. %. It was assumed that due to the high degree of oxidation the dissolution degree of nanoparticles would not reach high value. Nevertheless, under chosen experimental conditions, the maximum dissolution degree of zinc nanoparticles, namely 99.4 %, achieved in 4 hours (Fig. 2). The high value of dissolution degree meant that there was the dissolution of zinc (bulk) in the alveolar solution accompanied with the dissolution of zinc oxide (coating). What is important, despite double separation of suspensions, the concentration of Zn^{2+} ions remained high in the solutions, as shown with volamperometry. In other words, both bulk zinc and zinc oxide were resolving during the exposure of nanoparticles to alveolar fluid with the formation of soluble Zn-compounds which were not separated from the solution.

As seen from the figure 2, there was a considerable growth of the dissolution rate for first 50 minutes, namely it rose up to 90 %. Subsequently, the dissolution degree of Zn nanoparticles fluctuated in the interval 90…99 %.

TABLE II. REFERENCE DATA OF ZINC SALTS SOLUBILITY

Zinc Salt	Solubility, g/ 100 g of water
$Zn(OH)_2$	$1.6\cdot10^{-4}$
$Zn(CH_3COO)_2$	30
$ZnCl_2$	367
$Zn_3(C_6H_5O_7)_2$	hardly soluble
$ZnC_4H_4O_6$	0.019
$Zn(C_3H_3O_3)_2$	the data are absent
$ZnHPO_4$	0.993 [19]

The dissolution of Zn nanoparticles may pass through several stages. First of all, it should be said that in the vessel with suspension there was a lack of air. Nevertheless the initial physiological solution had been saturated with oxygen by the moment of the study. Therefore the amphoteric $Zn(OH)_2$ ($K_{sp} = 5\cdot10^{-17}$, $Kd_{base} = 1.5\cdot10^{-9}$, $Kd_{acid} = 7.1\cdot10^{-10}$) was likely to be generated in the system according to the reaction:

$$2Zn + O_2 + 2H_2O = 2Zn(OH)_2,\ \Delta\varphi = 1{,}309\ B\ [17]\ (4)$$

The amphoteric hydroxide $Zn(OH)_2$ shows both acidic and alkaline properties related to the value of pH of the solution, as shown with the reactions (5) and (6).

$$pH > 7: Zn(OH)_2 + 2OH^- = [Zn(OH)_4]^{2-} \quad (5)$$

$$pH < 6: Zn(OH)_2 + 2H^+ = Zn^{2+} + 2H_2O \quad (6)$$

In virtue of the fact that the pH of the suspension did not exceed 3.7, it could be concluded that the dissolution of $Zn(OH)_2$ occurred with the formation of Zn^{2+}-salts at pH level less 6 [17] according to the reaction (6).

The Table 2 [18] gives the reference data of the solubility for the salts which could have been formed in the studied system.

Despite acidic media, in system containing zinc salts hardly soluble zinc citrate and zinc tartrate should had precipitated. However, there was no visual precipitation in the solution. Therefore, the complex compounds of oxyacids with Zn^{2+} ions were most likely to form. Concerning the stability of generated complexes, it depends upon the pH level. For example, the stability constant of tartrate complex is $2.2\cdot10^3$ at pH = 3.35 and the stability constant of citrate complex is $8.3\cdot10^{10}$ at pH < 6.6 [20]

V. CONCLUSION

As seen from the review done for recent years, it can be said that the increasing dispersion of nanoparticles into our environment has become a major cause for concern in the field of nanotechnology as well as environmental and occupational health. Moreover, numerous study have shown that toxicological properties of nanoparticles entered the environment are strongly influenced with the solubility of particles in environmental liquids. Since there is a scarcity of experimental data related to the mechanism of nanoparticles dissolution, to fill knowledge gap seems to be absolutely critical for the elaboration of standardized documents of nanoparticles testing in biological media.

In this work, the authors have demonstrated the dissolution of metal nanoparticles in the synthetic alveolar fluid. The dissolution degree of electroexplosive zinc nanoparticles achieved around 100 %. The evidence of total solubility of metal nanopowders in the synthetic alveolar fluid should be taken into account in terms of their respiratory toxicity.

Alongside, the mechanism of zinc nanoparticles dissolution related to the electroexplosive zinc nanoparticles completely dissolving in the synthetic alveolar fluid has been proposed. As discussed above, the dissolution was suggested to include the following stages. The first stage comprises the formation of amphoteric zinc hydroxide in the oxygenated suspension of zinc nanoparticles and the synthetic alveolar fluid. The second stage includes the dissolution of zinc hydroxide with the formation of soluble zinc salts. At the third stage the formation of citrate and tartrate complexes of Zn^{2+} ions has been proposed.

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