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Dissolution of Copper Nanopowders in Inorganic Biological Media

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Abstract—Electroexplosive copper nanopowders with dispersion 3.2, 5.0, 6.8, and 12.0 $m^2 g^{-1}$ were dissolved in distilled water, physiological (saline) solution, and phosphate buffer. From experimentally determined concentrations of dissolved copper and pH of the solution kinetic curves were constructed and kinetic and thermodynamic analysis was performed of the possible chemical reactions. The influence of the powder dispersion and the nature of solvents on the kinetic parameters of dissolution were considered.

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Solubility and the dissolution rate of dust and micro- and nanopowders in biological environment is an important characteristic of their chemical and biological activity. Under "biological" usually the fluids are ment, which are the products or environment of vital activity (blood, urine, plasma, alveolar fluid, gastric juice) or those used in the treatment (distilled water, saline solution on the basis of NaCl, buffer solutions based on NaH_2PO_4, etc.)

Currently, the properties of metal nanopowders (average surface size ~100 nm) are studied in laboratory under conditions of direct contact with personnel. Despite the applied personal protective equipment, the nanoparticles due to their high dispersion can in large amount get into the organism of employee. The basic ways through which the particles enter the body are the respiratory and gastrointestinal tracts [1], as well as the skin [2]. Entering into the body, the nanoparticles can be accumulated and reveal toxic effects on the body. There is evidence of functional disorders of the nervous system, abnormal liver function and kidney failure, as well as ulceration and perforation of the nasal septum associated with the accumulation of copper compounds in the body [3]. The medical experts attribute expressed allergenic properties of copper to its high ability to penetrate through the epidermal barrier into the skin [4]. The rapid development of powder technology and known data about the harmful effects, in particular, of copper, makes the study of the potential risks from the use of copper powders very urgent.

Analysis of the studies aimed at exploring the ways of admission, accumulation, and the harmful effects of metals on the biological objects allowed us to reveal a gap in the knowledge about the kinetics and thermodynamics of dissolution of metal particles. Indeed, there is only an insignificant number of publications about studying the solubility of metallic micro- and nanoparticles in biological fluids or their analogs [5–12]. Midander et al. [5] showed the influence of the environment, the method of preparation and the size factor on the dissolution of fine particles of stainless steel in saline. Later they extended their research to the study of the solubility of powders of copper and copper materials, including Cu_2O, in solutions simulating the respiratory tracts and skin [6]. In [7] are presented the experimental data on the process of dissolution of copper in a model mother liquor over a year. Sandberg et al. [8] calculated the rate of dissolution of copper specimens in sea water over a year. There are also the works on the accumulation of Cu compounds in the environment of different soils and microorganisms [9–12].

All these and other studies show a high solubility of copper in biological objects. However, these publications do not highlight the mechanism of dissolution of particles, which is one of the important fundamental problems in studying these subjects.

Since the fine powders are often in a nonequilibrium state, and the deviation from equilibrium is inversely proportional to the size of particles [13], especially relevant is the study of physicochemical mechanism of dissolution using both thermodynamic and kinetic approaches.

It should be noted that in the studies of chemical reactivity of powders in various reactions their different behavior from the compact substances is regarded as caused by both thermodynamic nonequilibrium (the concept of "stored energy" [14–15]) and morphological structure of small particles. The last factor includes the composition and properties of the surface films on the particles formed at their preparation and storage, which may affect the process both thermodynamically and kinetically [16].

The most important factor affecting all chemical processes is the solvent composition. In most studies, including present investigation, water was used as the solvent, which is the basis of most solutions including biological fluids.

In the present study we attempted to elucidate the chemical mechanism of dissolution of copper powders of different dispersity in the simplest (inorganic) biological fluids. For this purpose we obtained the experimental data on the kinetics of dissolution, compared the concentrations obtained with the tabulated data on the solubility, and performed the necessary thermodynamic calculations to substantiate the mechanism of the dissolution process under these conditions.

Objects of research. We investigated copper nanopowders differing by dispersion obtained by electrical explosion of copper wires in the Laboratory of Powder Materials of the Institute of Physics and the Strength of Materials, Siberian Branch of the Russian Academy of Sciences, Tomsk. Table 1 shows the main characteristics of the objects of research. Fine copper powders are known for their high reactivity [16]. Currently, copper powders are used extensively as additives to metal-containing grease [17–18], as material for the sensors detecting organic compounds [19–20], in electrochemistry [21–22].

Testing samples in model solutions. Metal powders (0.005±0.0001 g) were kept in 50 ml of model solution in a closed container during a period from 5 min to 72 h. The experiment was performed at a constant temperature 37°C (±0.5°C), at a constant radial stirring (90 rpm, temperature-controlled shaker BIOSAN ES-20). After storage, the suspension was slowly cooled to room temperature (21–24°C), then divided into two phases by centrifugation (2700 rpm within 5 min). After separation of the precipitate, the solution was acidified, then the copper ions concentration was determined in it. At the chosen parameters of centrifugation the particles with $d < 1$ μm were not precipitated [23]. The experimentally observed complete clarification of the suspension originated from the association of primary particles to form agglomerates of the size 8 to 25 μm as shown by electron microscopy) that were weakly consolidated and permeable to the solutions.

Preparation of model solutions. To study the behavior of powders in a synthetic biological medium, we prepared model solutions. From the analysis of published data more than 500 different formulations of synthetic biological solutions of inorganic nature are known. The base for almost any solution is sodium or potassium neutral or acidic salt of hydrochloric or phosphoric acids. Therefore for the research were chosen 0.9% aqueous solution of sodium chloride, the traditional saline solution (PS, physiological solution), which is commonly used in such studies, and phosphate buffer solution (PBS, phosphate buffer saline) providing the possibility to maintain pH close to that of blood serum, and for comparison was taken distilled water (DW). Their composition and pH value are listed below.

Table 1. Characteristics of the studied powders

Designation of copper nanopowder	Average surface particle diameter d, nm	Specific surface S, $m^2 g^{-1}$	Surface composition, wt %	
			O	Cu
Cu-50	55.8	12.0	10–15	85–90
Cu-100	98.5	6.8	10–15	85–90
Cu-150	133.9	5.0	24.13	75.87
Cu-200	209.2	3.2	20.05	79.95

Solution (Notification) DW PS PBS	DW	PS	PBS
C(NaCl), g l^{-1}	–	9.00	8.77
C(Na_2PO_4), g l^{-1}	–	–	1.28
C(KH_2PO_4), g l^{-1}	–	–	1.36
pH	7.4	7.2–7.4	7.2–7.4

The solutions were prepared on the basis of distilled water by dissolving the corresponding inorganic salts. Necessary pH in the range 7.2 to 7.4 was created by adding 0.2 M solution of NaOH. Measurement and adjustment of pH was performed with the use of a pH meter 410 Aquilon (the error ±0.01).

Determination of the copper content in solution. The copper ions concentration in solution was determined by optical density of the copper ammoniate solution at a filter wavelength 590 nm (photocolorimeter KFK-3). Calibration graph was built from the scale of the optical density of solutions of copper sulfate with copper content 5, 10, 20, 30, 40, and 50 mg l^{-1}.

Calculation of dissolution rate and degree of transformation of the samples. For comparison of the activity of the nanopowders average rate R and specific rate R_S of dissolution of the samples was calculated using the formula:

$$R = dC/dt = (\Delta C/\Delta t)\cdot(V/m). \quad (1)$$

Here R is the average rate of dissolution of metal, mg g^{-1} h^{-1}; ΔC is change in the copper concentration in the filtrate compared to the last point, mg l^{-1}; V is solution volume, l; m is the nanopowder mass, g; Δt is the time interval since the last measurement, h.

$$R_S = (1/S)\cdot(dC/dt) = (1/S)\cdot(\Delta C/\Delta t)\cdot(V/m). \quad (2)$$

Here R_S is the specific dissolution rate of samples, mg m^{-2} h^{-1}; S is the sample specific surface area, m^2 g^{-1}.

The degree of dissolution of a sample α was calculated with the formula:

$$\alpha = (m_{Cu}/m)\times 100\%. \quad (3)$$

Here m_{Cu} is the amount of copper in the dissolved form, g.

Investigation of the surface morphology and composition. Determination of microstructural characteristics of the copper nanopowder surface was carried out using scanning electron microscope Philips SEM 515 equipped with an electron spectrometer that allows analyzing the energy distribution of photoelectrons leaving the surface of the particles irradiated by X-rays and to determine the elemental composition of the surface to the depth of 50 Å (X-ray photoelectron spectroscopy, XPS).

Determination of specific surface of a sample and of the particle size. The value of specific surface S was determined using low-temperature nitrogen adsorption (the BET theory, Brunauer–Emmett–Teller) [24]. The accuracy of measurements was 4%. The value of specific surface area obtained was used to calculate by formula (4) of the conditional average size of the powder surface particles d, assuming that all particles of the same diameter and of spherical shape.

$$d = 6/\rho\cdot S. \quad (4)$$

Here d is the diameter averaged over the surface, m; ρ is the density of Cu, 8.960 kg m^{-3}; S is the specific surface area, m^2 kg^{-1}.

Characteristics of powders. Table 1 shows the characteristics of the studied samples.

Morphological examination using electron microscopy showed that the powder particles are similar in shape to spherical. However, at the time of the study the samples were subjected to agglomeration. The agglomerate size, on the average, is from 8 to 25 μm. The results obtained by electron microscopy are consistent with the calculated data of the surface-averaged diameter of particles: for the sample Cu-50 over 80% of the particles have a size 30 to 60 nm, for Cu-100 70 to 100 nm, for Cu-150 80 to 150 nm, and for Cu-200 from 100 to 250 nm.

The XPS data indicate that initially the original wire contained impurities (Mn, Al, Mo) in small amounts, no more than 2 wt %. The presence of oxygen indicates the presence of oxidized metal (CuO) formed during the sample passivation and storage. For example, in the sample Cu-150, the ratio of Cu : O is 3:1 (wt %).

Kinetics of dissolution. In all the selected solutions the change in the concentration of copper in solution for all samples is similar to that shown in Fig. 1.

In the process of dissolution, which is described by the plot in Fig. 1, one can highlight two sections. The section *1* is characterized by a very rapid increase in copper concentration in the filtrate. Then, after reaching the maximum (in 1.5–2 h) the concentration starts to decrease (Fig. 1, section *2*), therewith for the

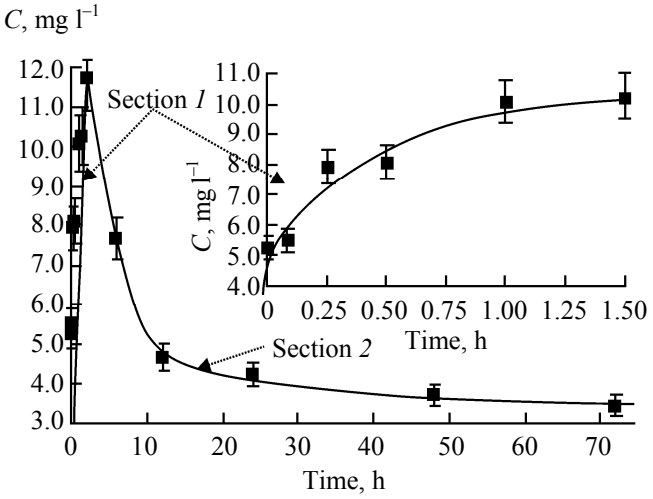

Fig. 1. Change in the concentration of copper in the filtrate after separation of the suspension for Cu-50 in phosphate buffer (PBS). (Section *1*) before maximum, (section *2*) after the maximum concentration. The inset is the enlarged 1st section.

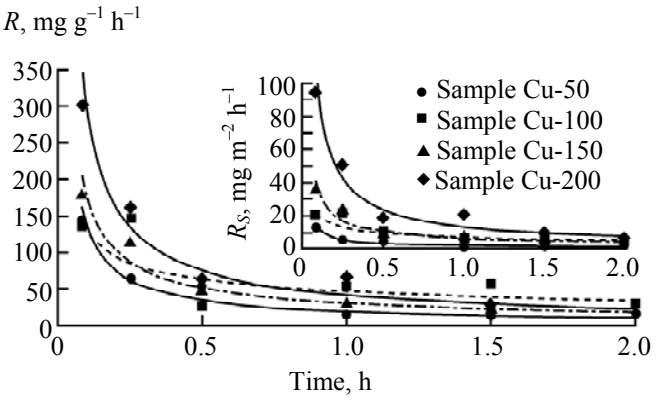

Fig. 2. Change in the average dissolution rate R and the specific dissolution rate R_S of nanopowders in phosphate buffer (PBS).

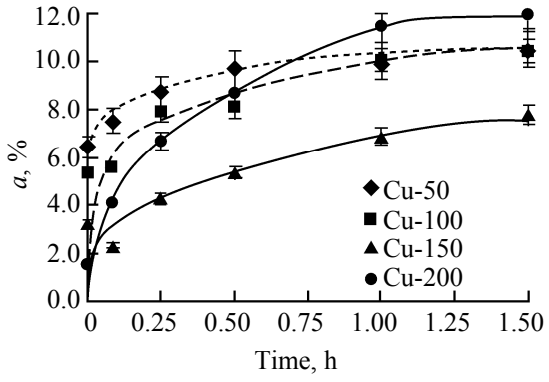

Fig. 3. Change in the degree of dissolution of nanopowders in phosphate buffer α at different dispersion.

section *2* in all the solutions used visually is observed the formation of blue precipitate of copper hydroxide, which is limitedly soluble in aqueous solutions.

Figure 2 shows the variation in the values of average (R) and specific (R_S) dissolution rates of the studied nanopowders in phosphate buffer (PBS) for the *1* section. In general, similar dependence was obtained for other solutions. It is evident that the process of dissolution of nanopowders is characterized by a decrease in dissolution rate over time, which may be associated with the expenditure of the solute and/or blocking the reaction surface by solid reaction product.

Effect of dispersion on the kinetics. Effect of dispersion of nanopowders studied on the average rate of dissolution is ambiguous. At different times of contact of samples with a solution the dependence on the dispersion may be different (Fig. 2), this is especially characteristic for the Cu-100 and Cu-150, which may be associated with the similarity of their S values (Table 2). At the same time, the dependence $R_S = f(t)$ clearly leads to the conclusion: at increase in dispersion the specific dissolution rate decreases. However, at the duration close to 2 h the values of the specific rate are aligned and are virtually independent of the particle size.

The degree of dissolution of powders. Further, to estimate the activity of nanopowders in the process of dissolution the degree of conversion α was calculated by formula (3). In general, the plots in Fig. 3 are similar for all studied nanopowders for all selected inorganic solutions. The maximum found value of α_m is rather low, 7 to 14 wt %. This can be due to the fact that the copper hydroxide particles formed in the vicinity or in the "particle-solution" interface may be strongly bound with the copper surface [25] and blocking the reaction area. It is important that there is no correlation between the content of copper oxide (Table 2) and α (Fig. 4): powders with lower oxygen content (Cu-50) have high α values. This fact speaks in favor of the view that the dissolution is not defined by the dissolution of oxide, but by the oxidation of metallic Cu.

It is evident that no certain relationship between α and the dispersion S was detected in these experimental conditions, as well as for the average rate.

At the same time, the dependence of the maximum value of α_m from S is found: with the increase of dispersion of nanopowders, in general, the maximum value of α_m increases (Fig. 4), which may be associated

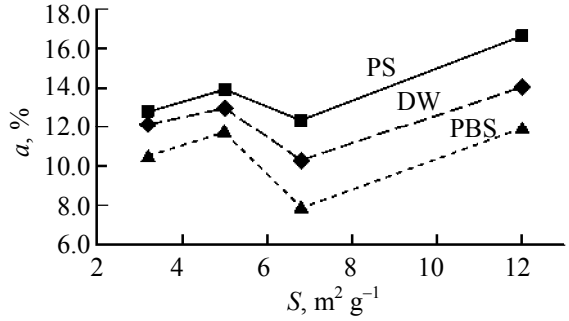

Fig. 4. The maximum degree of transformation of different nanodispersion in inorganic solutions.

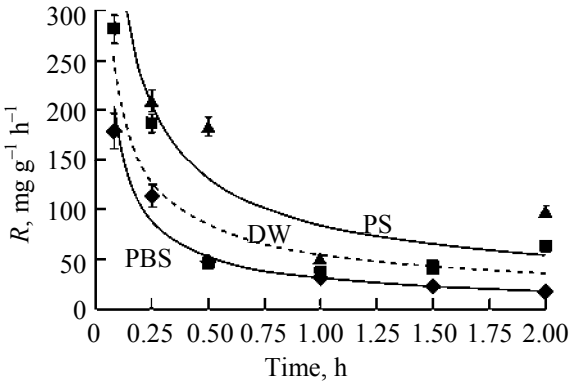

Fig. 5. Change in the average rate R of dissolution of Cu-150 in inorganic solutions.

with the increasing reaction surface. To this conclusion do not fit the values obtained for the sample Cu-150, which can be attributed to high content of oxide in this sample (Table 2) that in turn is likely due to the conditions of the sample storage.

Influence of the solvent nature. A dependence of the characteristics of dissolution, that is, the maximum degree of dissolution for all the dispersions and the average rate for one of the samples vs. the nature of the solvent are shown in Figs. 4 and 5.

It is seen that for the chosen solvent the dissolution patterns are similar, the anions Cl^- and $H_2PO_4^{2-}$ do not affect the chemical mechanism of the process, however, the kinetics is somewhat different. Thus, it is evident that the greatest values of the parameters of dissolution are achieved for all nanopowders in saline, and they decrease in the sequence of PS–DW–PBS.

The chemical mechanism of dissolution. To establish the chemical mechanism is necessary to reveal composition of the reactants and the products of dissolution. As the initial reagents, except obvious particles of copper coated with oxides (90% CuO + 10%Cu_2O [16]), the air oxygen must be taken into account. As the products, according to our experimental data, should be considered Cu^{2+} ions, solid $Cu(OH)_2$ formed on the powder after 1.5–2 h of dissolution and after keeping for 4 h the solution after separation in a centrifuge. As to the anions Cl^- and $H_2PO_4^-$, they cannot be involved in chemical reactions under these conditions. Thus, the following reactions should be considered at the dissolution of copper powder in water and in aqueous solutions:

(1) Dissolution of the oxide film:

$$CuO + H_2O = Cu(OH)_2;\ \Delta G_{298} = 7.24\ \text{kJ mol}^{-1}\ [26];$$

$$CuO + H_2O = Cu^{2+} + 2OH^-,$$
$$\Delta G_{298} = 117.44\ \text{kJ mol}^{-1},\ K_{298} = 10^{-22};$$

$$Cu(OH)_2 = Cu^{2+} + 2OH^-,\ \Delta G_{298} = 110.16\ \text{kJ mol}^{-1},$$
solubility product constant $K_{sp} = 1.2\times10^{-19}$.

It is seen that the tabulated value of solubility product (OL) lies between these values.

(2) Oxidation of copper with oxygen at the copper–hydroxide boundary:

$$2Cu + O_2 + 2H_2O = 2Cu(OH)_2;\ \Delta G_{298} = -244.32\ \text{kJ mol}^{-1}.$$

(3) Oxidation of copper with oxygen at the copper–solution boundary:

$$Cu - 2e = Cu^{2+},\ \varphi_0 = 0.34\ \text{V}\ [26],$$
$$O_2 + 2H_2O + 4e^- = 4OH^-,\ \varphi_0 = 0.401\ \text{V},$$
$$2Cu + O_2 + 2H_2O = 2Cu^{2+} + 4OH^-,\ \Delta\varphi_0 = 0.061\ \text{V}.$$

It is seen that under standard conditions the oxidation of copper with oxygen to hydroxide is thermodynamically possible. Oxidation of copper to the ion is less probable, but at the experimentally detectable low concentrations of Cu^{2+} and OH^- this probability becomes large enough (see below).

From the experimental data obtained the values of the concentration product (*CP*) in the solution separated in centrifuge were calculated (Table 2). For all powders and solvents these values significantly exceed the solubility product for copper hydroxide ($K_{sp} = 5.6\times10^{-20}$ [26]).

This means that in the separated solution occurs supersaturated state of $Cu(OH)_2$. It is clear that it can be formed by the reaction in conditions far from equilibrium.

Table 2. Experimental data and observations for the sample Cu-200 in saline

Duration	Section (Fig. 1)	Copper concentration in solution, Cu^{2+} mol l^{-1}	Solution pH	Concentration product (*CP*)[a], mol^3 l^{-3}	Visual observations in suspension	
					before separation	after separation
5 s	section *1*	$2.85\times10^{-0.5}$	7.80	1.1×10^{-17}	a precipitate on the powder is not visible	in the solution separated by centrifugation released a blue precipitate after 2–4 h
5 min		$8.71\times10^{-0.5}$	8.41	5.8×10^{-16}		
15 min		$1.26\times10^{-0.4}$	8.42	8.7×10^{-16}		
30 min		$1.62\times10^{-0.4}$	8.43	1.2×10^{-15}		
1 h		$2.07\times10^{-0.4}$	8.48	1.9×10^{-15}		
1.5 h	section *2*	$2.57\times10^{-0.4}$	8.40	1.6×10^{-15}	blue precipitate on the powder	
2 h		$9.31\times10^{-0.5}$	8.38	9.1×10^{-16}		
6 h		$7.66\times10^{-0.5}$	8.39	4.6×10^{-16}		

[a] Using the formula $CP = C(Cu^{2+})C^2(OH^{2-})$.

Table 3. Electrochemical potentials of the processes

Run no.	Reduction half-reaction [26]	φ^0, V	φ, V (by the Nernst equation)			
			pH = 7.8	$[Cu^{2+}]$ 2.4×10^{-5} mol l^{-1}	pH = 8.48	$[Cu^{2+}]$ 1.8×10^{-4} mol l^{-1}
1	$Cu(OH)_2 + 2H^+ + 2\bar{e} = Cu + 2H_2O$	0.609	0.129	–	0.087	–
2	$O_2 + 4H^+ + 4\bar{e} = 2H_2O$	1.228	0.762	–	0.727	–
3	$O_2 + 2H_2O + 4\bar{e} = 4OH^-$	0.401	0.762	–	0.727	–
4	$Cu^{2+} + 2\bar{e} = Cu$	0.337	–	0.279	–	0.306

Formation of the supersaturated solution can be explained by the dissolution of energy-saturated CuO, that is, containing the above-mentioned "stored energy" in the electroexplosive powder [14]. However, the presence of a large "stored energy" in such powders, especially in those larger than 50 nm (~100 kJ mol^{-1} [14]) has not been confirmed [15, 16].

It should be noted, however, that a change in product concentration *PC* by 5 orders of magnitude corresponds to the change of Gibbs energy by ~4 kJ mol^{-1} (calculated from the van't Hoff equation), that is, to explain our experimental data on the change in solubility is not necessary to operate the gigantic "stored energy," but enough to consider the changes in the surface energy of the order of 4 kJ mol^{-1}, which is quite realizable, also for the particle sizes of ~50 to 100 nm [27].

Availability of extra-equilibrium ion concentrations may be due to the fact that the reaction of dissolution of the copper nanopowders with the formation of Cu^{2+} itself is not equilibrium one. In the studied systems, such a reaction can only be the reaction of copper oxidation by air oxygen with participation of water. The corresponding half-reactions with the tabulated and calculated values of electrode potentials, taking into account the actual concentrations of ions, are given in Table 3. It is evident that the oxidation of copper both to $Cu(OH)_2$ and to Cu^{2+} is exoergic. For example, for reaction (2) at pH = 7.8, $\Delta\varphi$ = 0.633 V, while for reaction (3) under the same conditions at $C_{Cu} = 2.4\times10^{-5}$ $\Delta\varphi$ = 0.483 V, hence these reactions may be nonequilibrium.

Thus, analysis of the data presented suggests two possible ways of reactions. On the one hand, a dissolution of CuO nanoparticles (films) possessing a high surface energy can proceed. On the other hand, the dissolution of copper can go to the Cu^{2+} [half-reaction (3), Table 3], and then can occur a stepwise hydrolysis of copper cations with the formation of $Cu(OH)_2$. The dissolution through the formation of Cu^{2+} is kinetically preferable as compared to reaction (2), since it occurs without diffusion of ions or molecules through a solid phase, and electrochemical processes of this type proceed with a very low activation energy [28]. At the formation of hydroxide at the interface, the metal surface is blocked by the product and the rate of dissolution falls, because diffusion of Cu^{2+} ions, or OH^-, or O_2 through a layer of solid copper hydroxide is required.

In this framework the influence of dispersion is explainable: the reaction proceeds at the Cu–solution boundary, and at the increase in dispersion the fraction

of the copper surface in the total surface of the powder decreases. Therefore, the average dissolution rate increases, and the specific rate decreases.

It can be expected that the inhibition occurs the more rapidly, the greater the rate and degree of hydrolysis. Since the hydrolysis of Cu^{2+} increases in the presence of highly polarizable ions, one can expect enhanced inhibition in the series Cl^-–H_2O–$H_2PO_4^-$.

Thus, we showed that electroexplosive copper nanopowders coated with an oxide shell are soluble in biological inorganic solutions, therewith, the dissolution of nanopowders in the first phase (up to 1.5 h) proceeds with a change in the copper concentration in solution and the degree of reaction along the curve with a maximum. At the longer interaction, the experimentally detected concentration of copper in solution decreases, and a loose blue precipitate of $Cu(OH)_2$ is formed on the nanopowder particles.

Thermodynamic analysis showed that two mechanism are the most probable: (1) dissolution of the powder at the interface due to the oxidation of copper by atmospheric oxygen in the presence of water ($Cu^{2+} + 2e^- = Cu$; $O_2 + 2H_2O + 4e^- = 4OH^-$) and (2) on account of the change in surface energy at the dispergation, which is ~4 kJ mol^{-1} for the surface atoms.

The pattern of influence of the copper dispersion on the rate of dissolution is as follows: The overall dissolution rate (per unit mass of copper powder) increases with the dispersion and the specific rate (per unit surface area) is reduced. In the framework of the first mechanism this can be attributed to the influence of two opposing factors: an increase in the reaction surface and an increase in the density of surface oxide films that inhibit the copper oxidation.

The effect of the of inorganic ions Cl^- and $H_2PO_4^-$ dissolved in biological fluids correlates with their polarizability: the series of polarizability $Cl^- < H_2O < H_2PO_4^-$ is opposite to the series of solubility in solvents: physiological solution > distilled water > phosphate buffer, measured either by the degree of dissolution or by the average rate.

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