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MICELLAR EXTRACTION OF COPPER USING SURFACE-ACTIVE SUBSTANCES

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***Abstract.** The research proposes a method of aggregation of metallic copper particles in colloidal aqueous solutions under the action of underwater diaphragm discharge initiated in the sound frequency range. This paper considers the mechanisms of the underwater diaphragm discharge effect on a colloidal solution of metallic copper stabilised by surface-active agents (surfactants). According to the research, these mechanisms can be quite complex. They include energetic, hydrodynamic, chemical, and electrochemical effects on both copper particles and surfactant molecules. Moreover, as a result of short-term plasma exposure to the solution it is possible to increase the size of copper particles on average by 2-2.5 times. The colloidal system degrades under prolonged exposure of the solution to plasma, and in extreme cases one can even observe the formation of copper oxides.*

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Introduction

Micellar extraction is a relatively new method for the separation of substances. It is based on the use of surface-active substances (surfactants). In particular, this approach has found wide application for the isolation of metal ions (nucleates of a new phase) from aqueous solutions [1, 2]. With the development of environmentally friendly processes, micellar extraction is becoming more popular as an alternative to traditional extraction methods. Micellar extraction of metal ions has been used for analytical chemistry as well as for water and wastewater treatment due to its high efficiency and relative simplicity [3, 4]. In this study, we used micellar extraction to stabilise aqueous colloidal copper solutions. It was assumed that the effects of plasma treatment on this system can cause the enlargement of copper particles in solution. Surfactant particles are important in this technology because they reduce the surface tension of interfacial boundaries by accumulating at these boundaries. Surfactants can be divided into three main categories depending on the charge of their hydrophilic head:

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1. Anionic surfactants - the head group has a negative charge. They are the most common of all surfactants. Sodium lauryl sulphate and sodium laureth sulphate belong to this group of surfactants. They are characterised by their high activity, excellent cleaning and detergent properties. In low concentrations they are harmless to humans.

2. Cationic surfactants - the head group has a positive charge. This group of surfactants includes cetrimonium bromide, benzalkonium chloride, cetylpyridinium chloride, etc. These excellent antimicrobial agents are capable of neutralising negative charges. They are usually not compatible with anionic surfactants as can form the insoluble precipitates.

3. Non-ionic surfactants have no charge on the head group; they are neutral. Examples of such surfactants are polysorbates, ethoxylated alcohols, block copolymers (e.g. Pluronic), Triton X-100. The properties of such surfactants include emulsifying oils and fats well, being used in the food and cosmetic industries, being less prone to foam formation than other surfactants, working well over a wide pH range and being compatible with other types of surfactants.

The head group of a surfactant is considered to be the hydrophilic part of the molecule. Moreover, those surfactants consist of two main parts: a hydrophobic ‘tail’ and a hydrophilic ‘head’. In other words, the hydrophilic head group is the part of the molecule that interacts with water. Essentially, the head group determines surfactant interaction with water and other substances. Good solubility in water and the ability to interact with various surfaces make surfactants effective in a variety of applications ranging from detergents to biomedical applications [5].

It is important to understand the peculiarities of micellar extraction scheme for successful implementation of copper extraction technique from colloidal solution using surfactants. Micellar extraction is based on the ability of surfactants to form aggregates called micelles. They adsorb metal ions through various types of interactions including ionic, dipole-dipole, and hydrophobic ones. This method minimises their impact on the environment and includes the possibility of their extraction without using organic solvents. Aqueous solutions of surfactants at a concentration above the critical micelle formation concentration create micelles; they become capable of capturing metal ions. Metal ions interact with polar or charged surfactant groups located in the ‘micelle head’ region and are encapsulated within the hydrophobic part. The static and dynamic stability of micelles is determined by various factors affecting their formation and stability in solutions. These concepts refer to the thermodynamic and kinetic stability of micelles, respectively.

The static (thermodynamic) stability of micelles is determined by the equilibrium between the free energy of interaction between the molecules composing the micelles and their interaction with the solvent. The main factors affecting static stability include:

1. Critical micelle concentration (CMC) is the surfactant concentration at which micelles begin to form. The lower is CMC, the higher is the thermodynamic stability of the micelle because it is easier to form them.

2. Interactions between surfactant molecules are hydrophobic interactions, hydrogen bonding, and van der Waals forces between surfactant tails, and electrostatic interactions between head groups and solvent.

3. Temperature and ionic strength. An increase in temperature can reduce CMC and change their static stability. The ionic strength of the solution also affects the stabilisation of charged micelles by promoting charge shielding.

The dynamic (kinetic) stability of micelles is related to the temporal stability of micelles in solution and their response to changes in environmental conditions. The main factors include:

1. Surfactant concentration. At concentrations above CMC, the presence of a large number of micelles makes their formation and disintegration more possible and stable.

2. Exchange equilibrium between monomers and micelles. Micelles are in dynamic equilibrium with single surfactant molecules. The rate of exchange between micelles and monomers affects the kinetic stability.

3. Impact of external conditions. Changes in temperature, pressure, or pH can degrade micelles, alter the dynamic equilibrium, and change their static stability.

Hence, static stability is more determined by thermodynamic factors and equilibrium, whereas dynamic stability is related to the temporal stability and rate of change of micelle state under certain conditions.

Problem statement and experimental equipment description

The cationic surfactant cetylpyridinium chloride (CPC) was used to stabilise the state of the water-copper colloidal system: $C_{16}H_{33}NC_5H_5Cl$. This surfactant has been successfully used in experiments with a number of metal ions [6]. The considered colloidal system is a kind of supplier of copper in nanoform; it has unique properties compared to copper in macroform, making it interesting for various scientific and technological applications [7]. For example:

1. Copper in nanoform is characterised by an increased surface area relative to volume. It increases its reactivity and makes it useful in catalysis.

2. Copper nanoparticles have different optical properties due to plasmonic surface resonance. It can be used in sensors and biomedical applications.

3. Copper is known to be highly conductive; in nanoform it can exhibit modified conductive properties. It can be useful in microelectronics and nanotechnology.

4. Copper in the nanoform can demonstrate improved mechanical properties, such as high hardness and wear resistance, due to grain boundary hardening and other effects characteristic of nanostructured materials. At the same time, high thermal conductivity is retained.

5. Copper nanoparticles demonstrate significant antimicrobial properties and can be used in medicine (cosmetology) to kill bacteria and viruses, promoting wound healing.

The subject of this study is the last of the above mentioned properties of copper in the nanoform. Indeed, substance in nanoform can also have a toxicological effect on tissues of living organisms [8]. Therefore, the purpose was to develop a technology for enlarging the size of copper particles in their aqueous colloidal solutions to find a balance between the bacteriological activity of preparations based on them and their adverse effects on tissues of living organisms.

Preparing colloidal copper solutions was performed according to the method [9]. After preparation of the solutions, they were incubated for a day; then they were exposed to underwater diaphragm discharge (UDD). Figure 1 shows the appearance of the diaphragm discharge cell.

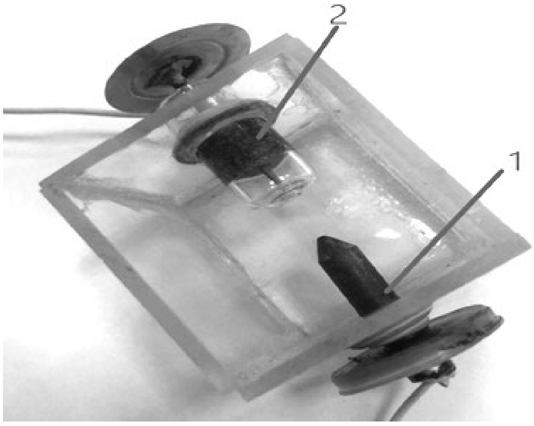

Fig. 1. Appearance of the cell for treatment of colloidal aqueous copper solution in UDD:1 - carbon cathode, 2 - anode in the form of a diaphragm

It was made of organic glass and had transparent walls. Electrodes were mounted on opposite sides of the cell: 1 - cathode in the form of a pointed carbon rod, 2 - anode in the form of a diaphragm electrode. An alternating high-voltage voltage was applied to the electrodes. The discharge was ignited directly in the solution. A high-voltage generator operating at a frequency of 75 kHz and allowing to regulate the output voltage in the range of 0.8-2.5 kV was used as a power source. The treatment time was fixed – 20 min. We selected the operating voltage due to the absence of strong fluctuations of the solution and maintaining a constant temperature. Therefore, the temperature was in the range from room temperature to 35 °C during the whole experiment on solution treatment.

Figure 2 shows the appearance of a 1 mm diameter diaphragm (*1*) and the design of an anode with a 0.5 mm diaphragm (*2*). The best results were shown by the structure shown on Fig. 2 under number ‘2’. The diaphragm was made of a glass cup with the formation of the hole with a diameter of 0.5 mm.

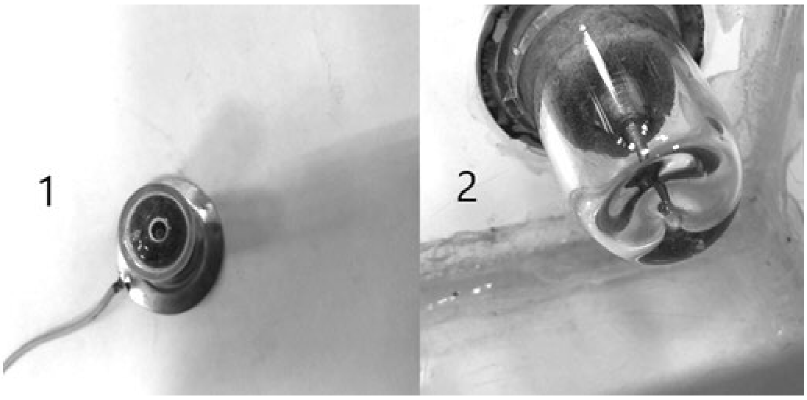

Fig. 2. Structures of a 1 mm diaphragm (1) and an anode block with a 0.5 mm diaphragm.

A thin pointed copper rod with the highest possible degree of sharpening was placed to the hole (diaphragm) from the inside. At the same time, the copper electrode did not go beyond the diaphragm.

The rod material in the anode block was chosen due to the absence of contamination of the solution with external impurities. However, slight foam formation was observed during the treatment process due to the presence of surfactants. This process was minimised but was not completely eliminated since foaming is a characteristic of cationic type surfactants [2]. Fig. 3 shows the appearance of the discharge when the solution is treated in our cell.

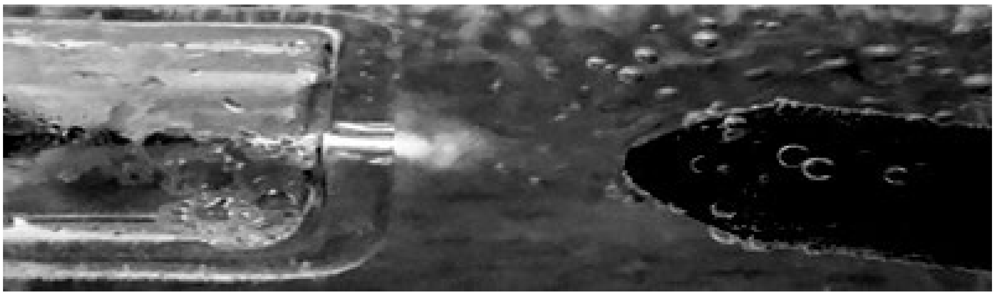

Fig. 3. Appearance of UDD in the cell (yellow-red glow was localised in the solution in the vicinity of the diaphragm)

Results and discussion

The use of plasma has shown its efficiency. In earlier studies, we used plasma to control the content of impurities in the composition of biological structures [10]. Thus, plasma technologies and plasma chemistry seem to be very promising technologies. To successfully solve this problem, it was necessary to analyse the mechanisms of the effect of UDD on the colloidal solution of metallic copper stabilised by surfactants. In general, it is necessary to consider a large number of factors, the most important are the following:

1. Energy effects. Underwater discharge generates a strong electric field and a localised temperature rise. It can cause the changes in the structure and properties of the colloidal solution. Such changes can affect the size and shape of the copper particles.
2. Hydrodynamic effects. The discharge provides shock waves and turbulent flows in the liquid. These mechanical effects can cause the aggregation or, conversely, dispersion of particles in the solution, depending on the strength and direction of the impact.
3. Chemical effects. High temperature and energetic impact can cause the changes in the chemical properties of surfactants. This can occur through the decomposition of surfactant molecules.
4. Electrochemical effects. The discharge can initiate electrochemical reactions to modify particle surfaces and affect their stability and interaction with surfactants.
5. Destabilisation of a colloidal system initially stabilised by surfactants. Surfactants play a key role in stabilising the colloidal solution by preventing aggregation of copper particles. Surfactant molecules can undergo structural changes under the impact of discharge. It can cause weakening of their stabilising properties.

These processes can occur simultaneously and affect each other. Therefore, it was necessary to take them into account when setting up the experiment and analysing the results obtained. In our opinion, modification of surfactants under the action of UDD is a rather important factor. We consider it in details.

Cetylpyridinium chloride is a cationic active surfactant containing a quaternary ammonium ion. It can be decomposed by electric discharge, in particular by UDD. Such a discharge causes the formation of active particles in aqueous media: ions (1) and radicals (2):

$$H_2O \rightarrow H^+ + OH^-, \qquad (1)$$

$$H_2O \rightarrow H^\bullet + OH^\bullet, \qquad (2)$$

which can interact with organic molecules, causing them to decompose. In addition, CPC itself dissociates in water (3):

$$C_{16}H_{33}NC_5H_5Cl \rightarrow (C_{16}H_{33}NC_5H_5)^+ + Cl^-. \qquad (3)$$

The main decomposition mechanisms of CPC can be visualised as follows:

1. Radical decomposition. Hydroxide ions can interact with the alkyl group of cetylpyridinium. This causes hydrogen abstraction and formation of a radical (4):

$$(C_{16}H_{33}NC_5H_5)^+ + OH^- \rightarrow (C_{16}H_{32}NC_5H_5)^\bullet + H_2O. \qquad (4)$$

This reaction may be part of a free-radical oxidation process or other radical mechanism. It is possible that the chain may be further broken to form smaller fragments.

2. Oxidative decomposition. $OH^\bullet$ radicals can directly oxidise the alkyl chain to alcohols or carboxylic acids. Oxidation of the nitrogen atom of the pyridine cycle is also possible. This can cause a ring breaking and the formation of amines and other fragments.

3. Reactions with reactive oxygen forms. Reactive oxygen forms produced during discharge, such as ozone (O_3) and superoxide (O_2^-), can also contribute to the degradation of surfactants, especially affecting the pyridine ring.

Hence, UDD may cause the destabilisation of the colloidal system and, as a consequence, to the enlargement of copper particles in solution. Fig. 4 shows microphotographs of copper particles deposited on the glass plate before (1) and after (2) treatment in UDD. The particles precipitated on the plate as a result of natural evaporation of the liquid at room temperature.

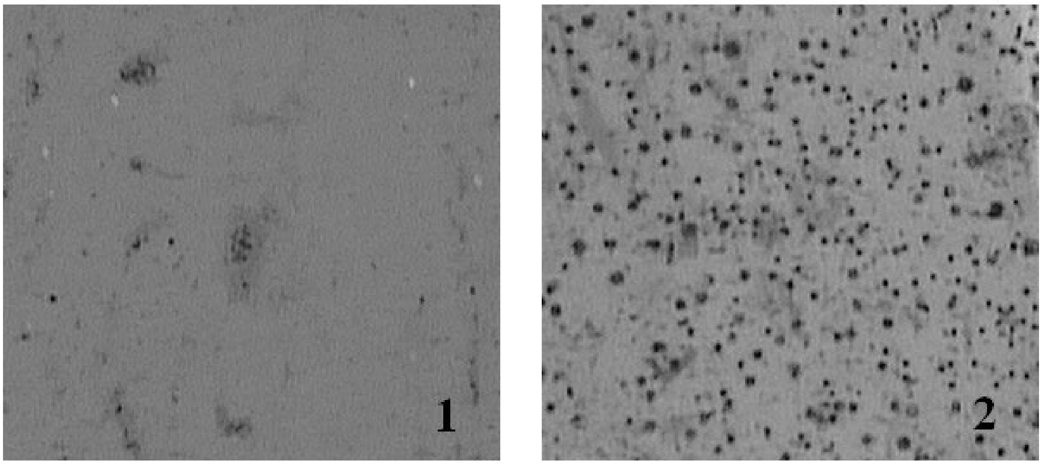

Fig. 4. Representation of copper particle sizes obtained on glass substrates: 1 - before UDD treatment; 2 - after UDD treatment (microphotographs were taken at the same magnification)

Fig. 4 shows the analysis of microphotographs: only single copper particles are visible on the glass before treatment in UDD; their number has increased dramatically after treatment in the discharge. The above are the data of optical measurements. Indeed, for the case shown in

Fig. 4 under ‘1’, the number of relatively large particles is insignificant, and the main part of copper is represented by particles in the nanometre range. In the centre of this photograph (Fig. 4, number 1) a cluster of particles can be observed. However, we consider it as the effect of aggregation of dispersed copper particles obtained by drying the glass plate. They will be represented by individual particles in solution. The slight background darkening in the images of Fig. 4 corresponds to the ‘dried’ surfactant. To reduce the amount of surfactant on the glass plates prepared for the study, they were gently washed by drip irrigation of the surface for 30 min. Copper remained on the glass surface under such washing conditions.

According to atomic force microscopy (AFM) results before plasma treatment, the average particle size was 45-60 nm, while after UDD treatment, the particles enlarged to 120 nm. Obviously, they are average particle sizes, among which larger particles were present, but multiple scans of different samples confirmed the above trends. The particle sizes were determined using the in-house software of the atomic force microscopy unit ‘Nova v.1.0.26’.

Conclusion and recommendations on the results application

Therefore, UDD might influence the size of copper particles in aqueous colloidal solution. Initially, the colloidal system was stabilised using cetylpyridinium chloride – one of the most studied and safest substances in this category [11, 12]. In micellar extraction, copper ions (Cu^{2+}) are usually involved, entering into electrostatic interaction with positively charged head groups of CPC micelles. The process can also proceed by means of complexation. Within the micellar structure, complexation between Cu^{2+} and pyridinium groups can occur. Usually micelles form rather dense structures. It effectively isolates the metal ions and prevent their aggregation. In the case of metallic copper, these mechanisms work due to the charge of small copper particles (nanostructures). The scheme of interaction of CPC with metallic copper can be shown through the mechanism of adsorption of the CPC cation on the copper surface:

$$Cu_{(s)} + (C_{16}H_{33}NC_5H_5)^+ \rightarrow [Cu(C_{16}H_{33}NC_5H_5)^+]_{ads}. \quad (5)$$

The process of copper particle coarsening in solutions is associated with the colloidal system breakdown and aggregation of copper into larger formations. This effect will ensure the development of a technology for antiseptic solutions preparation. The therapeutic effect of these solutions will directly depend on the size of copper particles in the liquid phase. Similar silver-based formulations are already available on the modern market [13]. However, replacing silver with copper in their composition will significantly reduce their cost and, consequently, the demand for these drugs on their market segment [14]. These researches are prospective and focused on optimising extraction to the development of more environmentally friendly and cost-effective technologies.

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