

PREPARATION AND PROPERTIES OF THE COLLOIDAL SOLUTION BASED ON BIOGENIC METAL NANOPARTICLES

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The aim of the work was obtaining a stable suspension based on biocompatible substances with application of biogenic metal nanoparticles encapsulated into NaCl salt matrix, as a precursor.

Water-soluble complex based on different amine derivatives with antiseptic properties was selected as a liquid for salt dissolution. The solution was subjected to dispersion using ultrasonication at elevated temperature. Dispersion is accompanied by salt shell removal with simultaneous formation of an organic shell on the surfaces of metal nanoparticles that ensures their stabilization. Study of the suspension after soaking at room temperature for 100 days showed that its characteristics remain stable.

A method for producing a stable colloidal solution based on nanoparticles of biogenic metal (Cu, Co, Fe etc.) was developed. Metal nanopowder encapsulated into salt shell was used as a precursor. It is shown that such colloidal solutions are characterized by narrow size dispersion, as well as stability to temperature impact and time factor.

Key words: electron beam evaporation, nanopowders, particle size distribution.

Over the last decades metal nanoparticles have attracted ever greater attention due to their unique properties, compared to massive metals and good prospects for application in catalysis, gas sensors and optical devices, for medical diagnostics, etc. There are a great number of commercial technologies of their manufacturing, based on the methods of vapour phase deposition, reduction, solid phase synthesis, etc. [1]. Each of the currently applied methods to produce metal nanoparticles has its advantages and disadvantages and can be used to solve certain technology problems. One of such problems is producing stable colloidal solutions of metal nanoparticles. These colloids are extensively applied in petrochemistry, organic chemistry, polymer chemistry, food industry, in agrarian and cattle-breeding complexes [2–5]. The most important characteristic of such colloidal solutions is their interaction with organic nano- and microobjects, namely, proteins, amines, nucleic acids, etc.

The work is a study of the properties of colloidal solutions produced on the bases of

metal nanoparticles (of biogenic metals Cu, Co, Fe, etc.) encapsulated into a salt matrix, together with two or more amides.

It is known that to produce colloidal solutions of nanoparticles, their stabilization by size and phase composition during their preparation is important. This stabilization can be performed both by creating protective shells on nanoparticle surface during its synthesis (encapsulation), and by introduction of synthesized nanoparticles into a stabilizing medium with additives of surfactants (SA).

The work presents an integrated approach to stabilization of metal nanoparticles based on formation of metal nanopowders (Cu, Co, Fe, etc.) encapsulated into NaCl matrix with subsequent preparation of a stable colloidal solution on their base.

Materials and Methods

Metal nanoparticles encapsulated into chemically inert medium were produced by simultaneous deposition of metal and alkali metal halogenides (NaCl) from the vapor

phase [6–8]. Schematic of the process of producing them is shown in Fig. 1. Method to produce metal nanopowders with particle encapsulation into chemically inert medium is based on simultaneous deposition of metal and alkali metal halogenide from the vapour phase. Presence of salt ions in the vapour phase, on the one hand, limits growth of metal particles, and on the other hand, ensures formation of a protective shell on their surface. Presence of a shell on the particle surface prevents the processes of their consolidation at storage and protects them from interaction with the atmosphere. Such an approach enables producing nanosized powders, in which metal nanoparticles are encapsulated into chemically-inert matrix based on sodium chloride. This composite structure allows long-term storage of encapsulated nanoparticles in regular atmosphere, and if required, removal of the salt shell, placing these powders, for instance, into liquid, in which the salt dissolves.

As an example, Fig. 2 gives composite microstructure, consisting of salt matrix and copper nanoparticles.

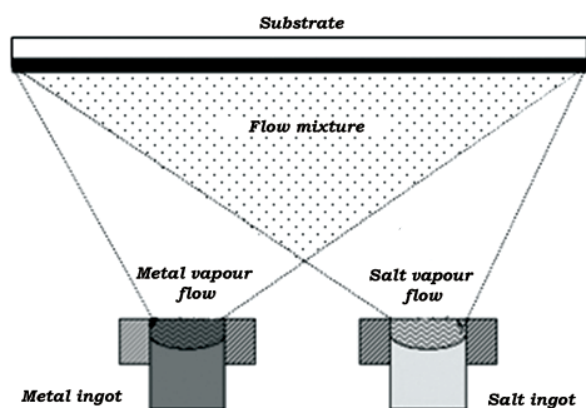


Fig. 1. Schematic of simultaneous deposition of metal and alkali metal halogenide

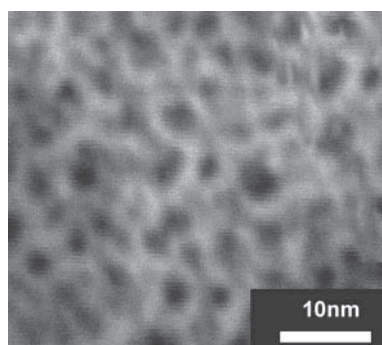


Fig. 2. Electron micrograph (light field, high resolution TEM) of a condensate formed at simultaneous deposition of vapour flows of copper and sodium chloride (darker-coloured copper particles are encapsulated into salt matrix)

Statistical processing of measurement results allowed plotting the diagram of nanoparticle size distribution (Fig. 3). It follows from the diagram that the largest number of particles is of 6–7 nm size.

At interaction with the environment, the salt shell around the particle protects it from oxidation and agglomeration. It turned out that particle size and structure remained unchanged even after storage of this nanopowder in air from more than 3 years that is indicative of high effectiveness of the shell for prevention of interaction of metal nanoparticles with the environment.

In order to produce colloidal solutions based on such particles, the salt shell should be dissolved, while avoiding nanoparticles sticking to each other. There are a large number of methods to produce stable colloidal solutions of nanoparticles [9–12]. Such solutions are, as a rule, produced by adding nanoparticles to water solution of organic molecules, which include two or more amides, with subsequent dispersion by ultrasonic treatment.

Schematic of producing colloidal solutions shown in Fig. 4, was used in the work. Different samples of metal nanoparticles encapsulated into salt matrix were placed into 20 mg bottle with backflow condenser with subsequent addition of water and amides in the quantity of two or more in a certain proportion. Obtained solution was dispersed using ultrasonic treatment for 60 min at the temperature of 60–80 °C. During dispersion the salt shell is removed with simultaneous formation of an organic shell on the surfaces of metal nanoparticle that ensures their stabilization (this method is currently being patented).

Properties of produced colloidal solutions were studied in Lavern Zetasizer Nano S instrument, Ver. 6.20 of Malvern Instruments Ltd., Great Britain, in which particle size is determined by their displacement using Einstein-Stokes relationship.

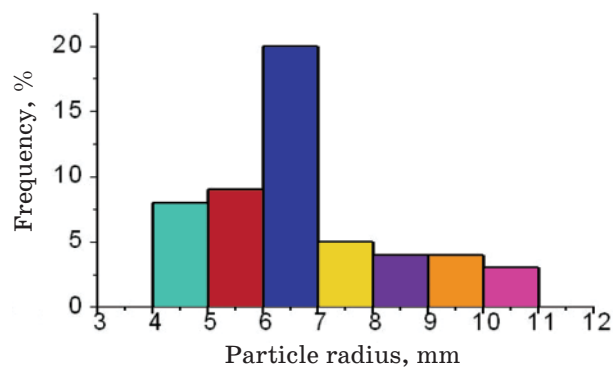


Fig. 3. Size distribution of copper particles

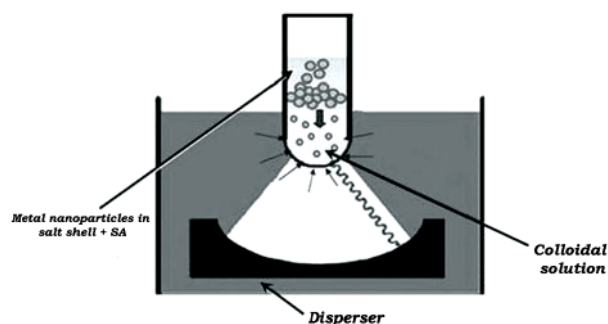


Fig. 4. Schematic of producing colloidal solutions

Results and Discussion

Fig. 5 shows colloidal solutions produced at addition of different volume fractions of encapsulated copper nanopowder to the solution.

It is seen that with increase of copper nanoparticle concentration in the colloidal solution, its colour changes from green to violet shade. It is known that solution colour depends on wave length of light scattered by dispersed particles. This leads to the conclusion that properties of scattering centers change with increase of nanoparticle concentration in the colloidal solution. This can be due, for instance, to increase of the number of complexes formed from finer nanoparticles.

Particle size distribution in the colloidal solution is given in Fig. 6. Distribution is monomodal with the mode falling within the size range from 0.5 to 2 nm.

Comparing size distribution of particles in the precursor (copper nanoparticles, encapsulated in the salt matrix; Fig. 3) and in the colloidal solution (Fig. 6) one can see that the mean size of particles in the solution



Fig. 5. Appearance of colloidal solutions with different concentration of precursor — encapsulated copper nanopowder

is smaller than in the precursor. We can assume that in the precursor the particles are agglomerates and the agglomerated particles are separated during solution formation under ultrasonic impact on it.

Aggregative stability of the colloidal solution is understood to be the ability of dispersed phase particles to resist their coalescence and, thus, maintain a certain degree of dispersion. Loss of aggregative stability leads to mutual coalescence of colloidal particles with formation of larger aggregates. Aggregative stability is attributable to colloidal particles having the same charges, which prevent them from coalescing into coarser particles. Colloid coagulation in most of the cases starts when electrokinetic potential (zeta-potential) has dropped to a certain critical value, at which coagulation starts. The smaller zeta-potential value is, the smaller the fraction of particles having such a potential preventing coagulation, and the greater the number of particle collisions resulting in their coalescence.

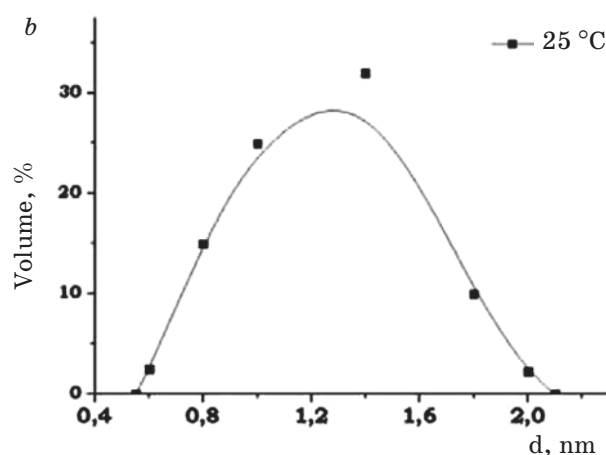
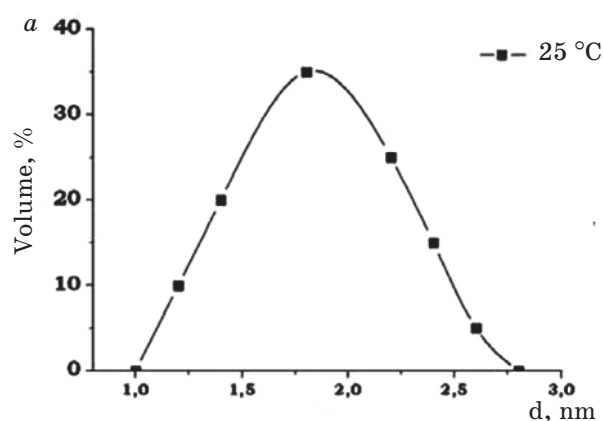


Fig. 6. Size distribution of copper (a) and iron (b) particles in amide-based colloidal solutions

Zeta-potential (particle surface charge, which determines the degree and nature of interaction of particles of the dispersed system) was determined to check the colloidal solution stability characteristics and particle ability for agglomeration. Obtained results are shown in Fig. 7.

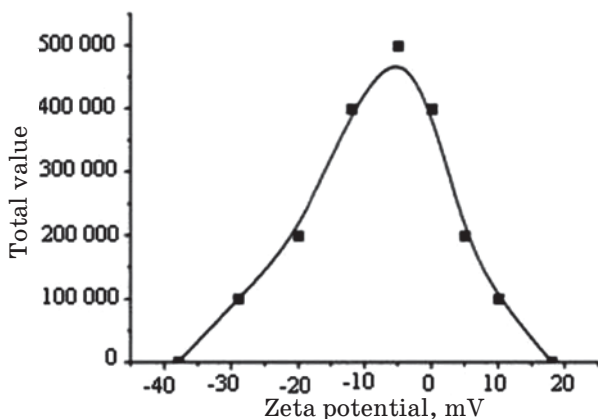


Fig. 7. Copper particle zeta potential

Such a distribution is indicative of noncompensated surface charge of particles and potentially high surface activity, respectively.

Studying the colloidal solution properties after its soaking at room temperature for a year showed that its dispersion and stability characteristics do not change.

A series of respective experiments was conducted to study the influence of temperature on colloidal solution stability. The size distribution of particles has been shown at heating of copper nanoparticle colloidal solution (Fig. 8, a) and at its subsequent cooling (Fig. 8, b). Zeta-potential change at heating and cooling is shown in Fig. 9. It is seen that particle distribution remains monomodal both at temperature rise and at subsequent cooling of the solution. Zeta potential magnitude at solution heating practically does not change that is indicative of potentially high surface activity of the particles.

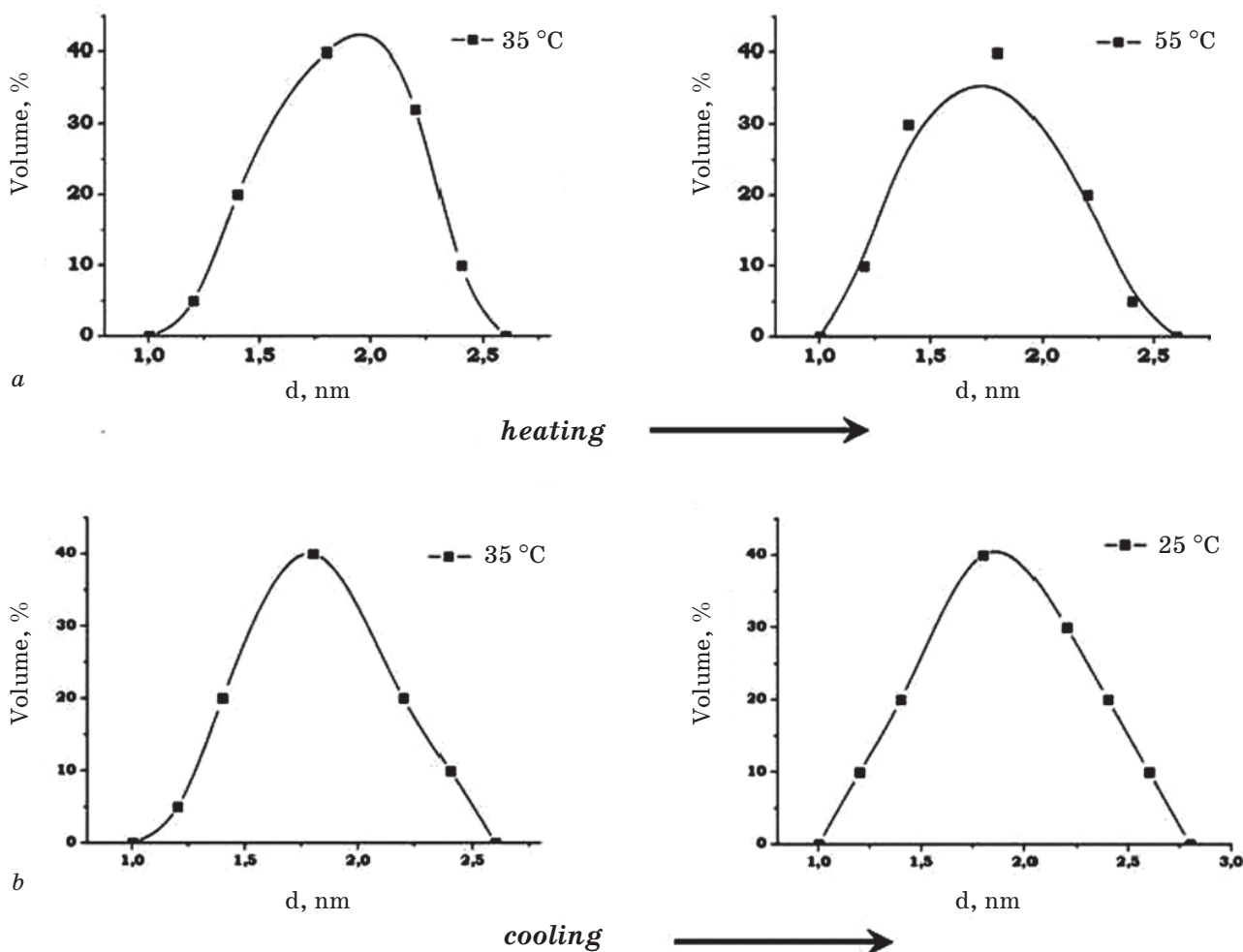


Fig. 8. Size distribution of particles at heating (a) of colloidal solution of copper from 25 °C (Fig. 6, a) to 55 °C with subsequent cooling (b)

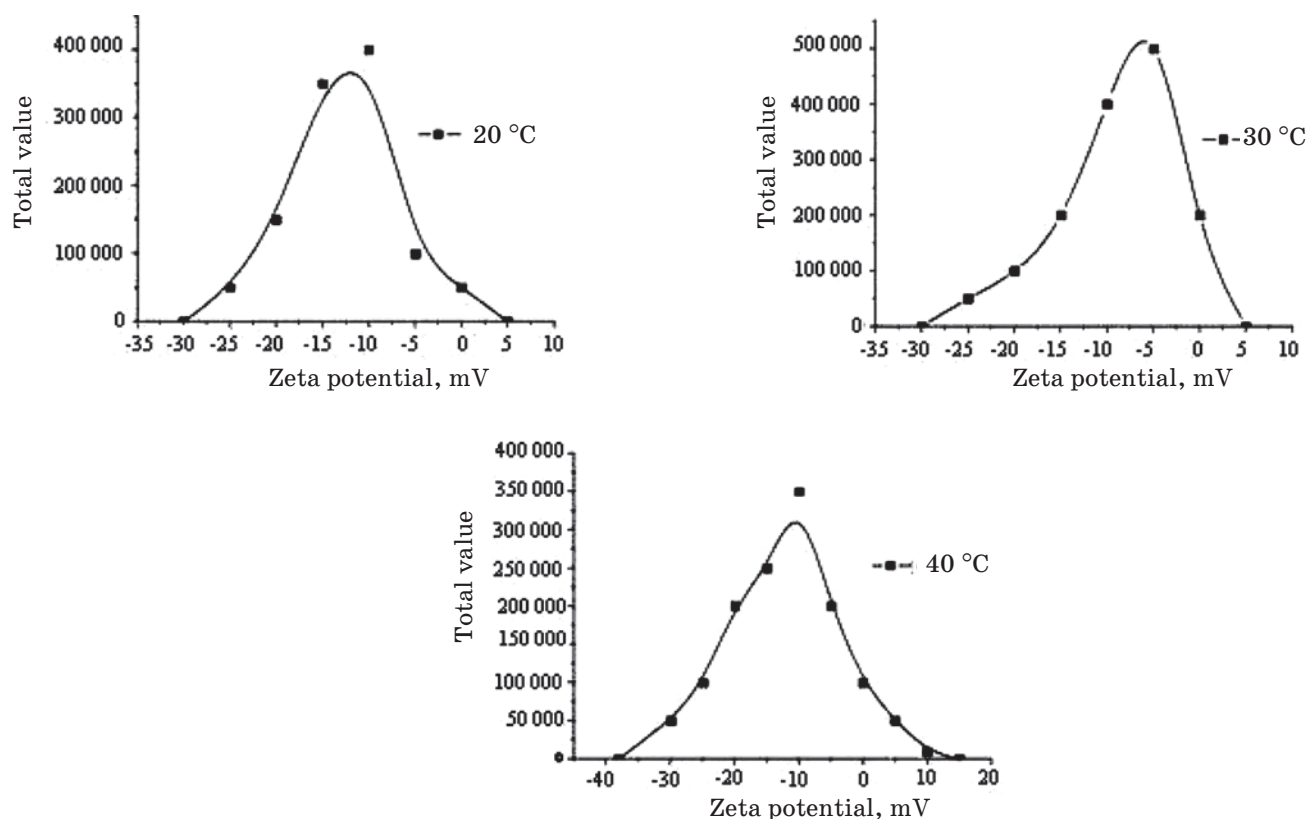


Fig. 9. Zeta-potential of copper particles at different temperatures

Thus, results obtained in the present work show that application of metal nanoparticles encapsulated into the salt matrix as a precursor, enables producing colloidal solutions of metal nanoparticles based on water solutions of amine derivatives by their simultaneous dispersion by ultrasonic

treatment. It is established that the thus obtained colloidal solutions of metal nanoparticles are characterized by a high degree of dispersion of metal nanoparticles by size, are stable for a long time and resistant to sedimentation at increase of solution temperature up to 55 °C.

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ОДЕРЖАННЯ ТА ВЛАСТИВОСТІ КОЛОЇДНОГО РОЗЧИНУ НА ОСНОВІ НАНОЧАСТИНОК БІОГЕННИХ МЕТАЛІВ

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Метою роботи було одержання стійкої суспензії на основі біосумісних речовин з використанням як прекурсора біогенних наночастинок металів, інкапсульованих у сольову матрицю NaCl.

Рідиною для розчинення солі було обрано водорозчинний комплекс на основі різноманітних похідних амінів, яким притаманні антисептичні властивості. Розчин піддавали диспергуванню з використанням ультразвукової обробки за підвищеної температури. У процесі диспергування відбувається видалення сольової оболонки з одночасним формуванням органічної оболонки на поверхнях наночастинок металу, що забезпечує їх стабілізацію. Дослідження суспензії після витримки за кімнатної температури упродовж 100 днів показало, що всі її характеристики залишаються стабільними.

Розроблено метод одержання стабільного колоїдного розчину на основі наночастинок біогенних металів (Cu, Co, Fe та ін.). Як прекурсор використовували інкапсульований у соляну оболонку металевий нанопорошок. Показано, що такі колоїдні розчини характеризуються вузькою дисперсією розмірів, а також стійкістю до температурних взаємодій та часового фактора.

Ключові слова: електронно-променеве випаровування, нанопорошки, розподіл частинок за розмірами.

ПОЛУЧЕНИЕ И СВОЙСТВА КОЛЛОИДНОГО РАСТВОРА НА ОСНОВЕ НАНОЧАСТИЦ БИОГЕННЫХ МЕТАЛЛОВ

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Целью работы было получение устойчивой суспензии на основе биосовместимых веществ с использованием в качестве прекурсора биогенных наночастиц металлов, инкапсулированных в солевую матрицу NaCl.

В качестве жидкости для растворения соли был выбран водорастворимый комплекс на основе различных производных аминов, обладающих антисептическими свойствами. Раствор подвергали диспергированию с применением ультразвуковой обработки при повышенной температуре. В процессе диспергирования происходит удаление солевой оболочки с одновременным формированием органической оболочки на поверхностях наночастиц металла, что обеспечивает их стабильность. Исследование суспензии после выдержки при комнатной температуре на протяжении 100 дней показало, что все ее характеристики остаются стабильными.

Разработан метод получения стабильного коллоидного раствора на основе наночастиц биогенных металлов (Cu, Co, Fe и т. д.). В качестве прекурсора использовали инкапсулированный в соляную оболочку металлический нанопорошок. Показано, что такие коллоидные растворы характеризуются узкой дисперсией размеров, а также устойчивостью к температурным воздействиям и временному фактору.

Ключевые слова: электронно-лучевое испарение, нанопорошки, распределение частиц по размерам.