

The Structure of Mn and Co Nanoparticles Obtained in Direct Surfactant Micelles

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The article deals with synthesis of Co and Mn nanoparticles in micellar aqueous solutions of cetyl pyridinium chloride. The nanoparticles (3-4 nm) and the spherical fractals (50, 150, 500 nm) have been identified with electron spectroscopy, dynamic light scattering, atomic absorption spectrometry, scanning microscopy. The structure of nanoparticles and fractals and localization of condensation nuclei in micelles have been discussed here.

Keywords: Co and Mn nanoparticles synthesis, Direct surfactant micelles, Characterization of nanoparticles with instrumental methods, Co and Mn nanoparticles fractals.

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1. INTRODUCTION

Cobalt nanoparticles by virtue of their magnetic properties are widely applied in visualization, sensors, microwave absorbing materials and many other spheres [1, 2]. Manganese nanoparticles are used in magnetic resonance imaging, sensors, catalytic processes [3].

Mn nanoparticles 6-20 nm in diameter are obtained by Mn grains (99.99%) heating at 1533 K in a helium atmosphere followed by condensation in a vacuum on a cooled substrate. Mn nanoparticles 50 nm in diameter are obtained via reduction of manganese acetate in aqueous solution by citrus limonium extract over curcumine stabilizer [4]. Plant extracts are mostly used for production of noble metal nanoparticles whose ion pairs have positive electrode potentials. Leaf and fruit extracts are mild reducing agents as compared to hydrazine hydrate used here. A higher negative standard electrode potential is believed to complicate the Mn nanoparticles production in an aqueous solution for Mn (-1.18 V) as opposed to that of Co (-0.28 V). Mn nanoparticles, as a consequence, are proposed to be produced via reduction by butyllithium in diphenyl ether over oleinic acid to create a protective layer [5]. It is well-known that cobalt nanoparticles are pyrophorous and are spontaneously flammable at room temperature. Formation of a protective capsule on every nanoparticle (encapsulation) is a common method for protection and stabilization of nanoparticles. Carbon is mostly used for this purpose. For example, Co particles of 120-125 nm covered with carbon were obtained with the technique as follows (to be compared to the technique suggested below). Co(OH)₂ intercalated by sodium dodecyl sulfate (SDS) was obtained from cobaltic salt on a strongly basic anion exchange resin of gel type AB-17-8 in OH-form and then solvothermally decomposed in oil.

Nanoparticles are known to be synthesized in the reverse and direct micelles of a surfactant. Synthesis in the reverse micelles is more labor-intensive as it requires more operations for separation of hydrocarbons. We suggest synthesis in direct micelles i.e. in aqueous solutions [6]. Nanoparticles in the direct

micelles were traditionally obtained in anionic surfactant solutions. According to a classical micelle model, Mn and Co ions were believed to be located at an adsorption layer and were ready for nucleation. Hence, the nanoparticles cannot be obtained at the micelles of the cationic surfactants. For agronomy, nanoparticles synthesis is required in the solutions of the cationic surfactants due to their antifungal and bactericidal properties [7, 8].

Therefore, we propose and validate a new model of a micelle of dual properties [9].

On hydrocarbon solubilization, the micelles become compacted. On hydrophilic chemicals addition (citric acid, glycerine), the micelles expand and the metal cations may be solubilized there. Such synthesis and ion flotation allow development of a technology for nanoparticles production from waste [6].

For the above-mentioned mechanism the experimental results of the nanoparticles synthesis carried in the direct micelles are contradictory. For example, during Pt nanoparticles production in the sodium dodecyl sulfate solutions by fast cooling of the solution on a cryogenic transmission microscope it is concluded that the nanoparticles are formed outside the micelles [10]. In contrast, in other work, photoreduction of Pt ion is shown to occur inside the micelles [11].

This work presents Co and Mn nanoparticles synthesis in the direct micelles of cetyl pyridinium chloride for validation of condensation centers (nanoparticles) inside the micelles. Then the micellar solutions, structures of nanoparticles and formed fractals are characterized by physical and chemical analytical methods.

2. OBJECTS AND METHODS

Reagents. Cobaltous chloride CoCl₂·6H₂O, hexahydrate, $T_{melt.} = 735\text{ }^{\circ}\text{C}$; manganous chloride MnCl₂·4H₂O, tetrahydrate $T_{melt.} = 650\text{ }^{\circ}\text{C}$; citric acid C₆H₈O₇ $T_{melt.} = 153\text{ }^{\circ}\text{C}$; hydrazine hydrate N₂H₄·H₂O (65%), transparent colorless liquid; sodium dodecyl sulfate (SDS) C₁₂H₂₅SO₄Na, $T_{melt.} = 207\text{ }^{\circ}\text{C}$; N-cetyl pyridinium chloride (CPC), C₂₁H₃₈NCl·H₂O,

monohydrate is Sigma-Aldrich reagents, double-distilled water. Purity of SDS, CPC is verified by absence of minima at CMC $8.1 \cdot 10^{-3}$, $4.7 \cdot 10^{-4}$ M, respectively, on a surface-tension isotherm built for their aqueous solutions at 25 °C.

Method of Co nanoparticles synthesis in micellar aqueous solutions of CPC. Two solutions were prepared in the bunsen beakers of 500 ml. 0.95 g of cobaltous chloride hexahydrate, 1.92 ml of 0.1 H citric acid, 0.38 g of CPC and 200 ml of distilled water were put into the first beaker. 1.92 ml of 0.1 H citric acid, 0.38 g of CPC, 20 ml of 13 M hydrazine hydrate and 180 ml of distilled water were put into the second beaker. The obtained solutions were poured into a bunsen beaker of 1000 ml, thoroughly stirred with a stirring rod and mixed in a magnetic stirrer for 150 min.

Method of Mn nanoparticles synthesis in micellar aqueous solutions of CPC. Two solutions were prepared in the bunsen beakers of 500 ml. 0.864 g of manganese chloride tetrahydrate, 1.92 ml of 0.1 H citric acid, 0.38 g of CPC and 200 ml of distilled water were put into the first beaker. 1.92 ml of 0.1 H citric acid, 0.38 g of CPC, 20 ml of 13 M hydrazine-hydrate and 180 ml of distilled water were put into the second beaker. The obtained solutions were poured into a bunsen beaker of 1000 ml, thoroughly stirred with a stirring rod and mixed in a magnetic stirrer for 150 min.

Method of Mn and Co nanoparticles synthesis in aqueous solutions of SDS. The method of Mn and Co nanoparticles synthesis is the same for the CPC solutions since CMC of SDS and CPC are almost equal ($1.07 \cdot 10^{-3}$ M) [12].

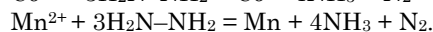
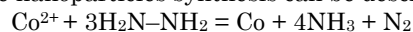
Nanoparticles characterization. During the synthesis, visible spectra of the solutions were recorded with a spectrophotometer UV-1800 (Shimadzu, Japan). The SDS aqueous solutions were studied by dynamic light scattering in an analyzer Zetasizer Nano ZS (Malvern Instruments Ltd, Great Britain). A linearly polarized (500:1) helium-neon laser of 632.8 nm wavelength was used as a light source. Intensity of an incident beam was adjusted by an automated attenuator to permit the measurement of the samples with various scattering level. An avalanche photodetector was applied as a detecting system. The NIBS technology was also implemented here to eliminate multiscattering at high concentration of particles/molecules and to optimize a signal coming from the poor scattering samples with low concentration. The scattered light was recorded at angle 173° in the process. In the frame of NIBS, adjustment/optimization of the scattering volume is available which provides a wide range of concentrations. Data of an autocorrelation function were processed by the cumulants method. Refractive index of water and water viscosity were taken as 1.330 and 0.8872 SP, respectively.

Size of nanoparticles in a powder was defined by a scanning electron microscope Quanta 650 FEG in vacuum. The powders of the nanoparticles were obtained by filtering the solutions. The precipitate on a filter paper was put into a beaker with a help of

ethanol, liquid was separated by centrifugation. Rinsing and centrifugation were repeated several times to separate the most part of CPC. Then the material was dispersed in water; a drop of a diluted suspension was topped on a glass; when water evaporated, the samples were analyzed. Percentage of Co and Mn was defined in these dry powders by an atomic-absorption spectrometer Kvant-Z.ETA (Akvilon, Russia) with argon taken as protective gas. Percentage of Co and Mn was found to be 96.1 and 94.2 %, respectively.

3. RESULTS AND DISCUSSION

Nanoparticles synthesis. Electron spectra of the disperse systems. Redox reactions proceeding in the nanoparticles synthesis can be described as follows:



Reaction mixture in a cobaltic salt solution discolours from rose, red, violet to blue. Reaction mixture of manganese salt discolours from faintly lactescence to dark rose.

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Concentration of CPC should be maintained at level 4-5 times higher than that of CMC so that the micelles of CPC could be present in the reactive atmosphere. Usually the concentration should lie in the range for spherical micelles of ionogenic surfactants. It has been found that if the surfactant concentration is lower than that of CMC, the spectrum of the reaction mixture (Fig. 1a) remains unchanged as compared to the spectrum at the start of the reaction. Formation of Co condensation centers, therefore, occurs inside the micelles when surfactant concentration is higher than that of CMC. A part of CMC, except for the micelles, participates in stabilization of the re-formed nanoparticles of metals due to adsorption on their surface.

CoCl_2 forms a series of crystalline hydrates: with 6 molecules of water (rose), 5 (red), 4 (dark-red), 2 (violet), 1 (blue-violet). Identical colour of the solutions, of crystalline hydrates and spectra (Fig. 1) indicate that there is a gradual dehydration of ions before the ions are reduced to the condensation centers of atoms during the synthesis; it assists in the incorporation of ions and atoms into the direct micelles.

An absorption band of hydrates is shifted to a short-wave spectral range (band 4). It is replaced with the bands of plasmon absorption of the nanoparticles. The plasmon absorption spectrum of the cobalt nanoparticles is less in its intensity and as in the case of other nanoparticles (Ag, Au) it depends on their size [13].

The small nanoparticles may be assumed to aggregate gradually (Fig. 1b and c). Absorption bands of such aggregates are marked as 1, 2, 3. Nanoparticles aggregation is confirmed by the results obtained with dynamic light scattering (Fig. 3) and scanning microscopy (Fig. 4). MnCl_2 is presented as tetrahydrate which has been used for nanoparticles synthesis. Its solution has no absorption bands in visible electron spectrum (Fig. 2).

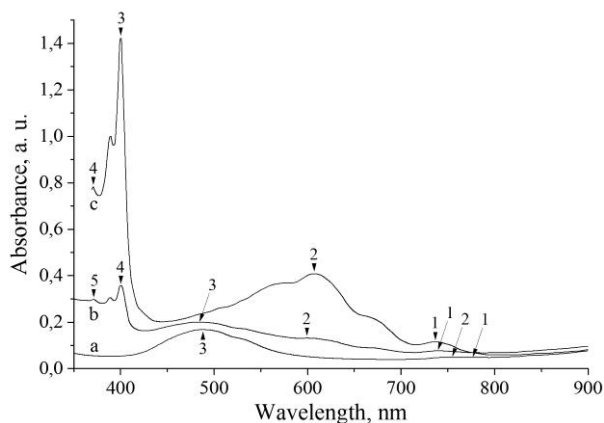


Fig. 1 – Absorption spectra of a reaction mixture (Co) in a visible part of the spectrum: a – is before hydrazine hydrate was added; b – is 30 min after hydrazine hydrate was added; c – is 150 min after hydrazine hydrate was added

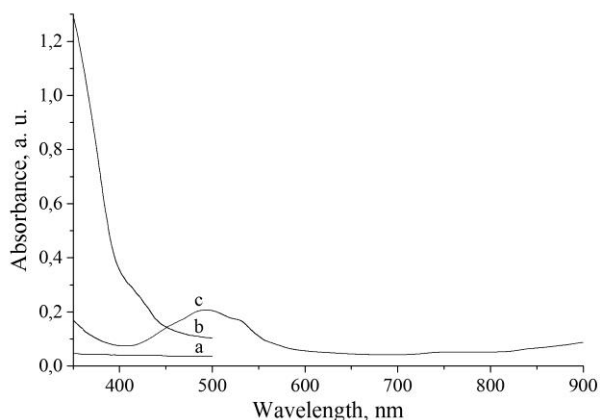


Fig. 2 – Absorption spectra of a reaction mixture (Mn) in visible part of the spectrum: a – is before hydrazine hydrate was added; b – is 150 min after hydrazine hydrate was added; c – is SDS (Co) after a synthesis and standing for 24 hours.

After the reaction mixture is stirred for 150 min, the Mn disperse system shows plasmon absorption as «an arm» on an intensive band of the electron spectrum in the range of 400-450 nm. The nanoparticles of Mn are covered with CPC more than that of Co. It is apparent from a halo around fractals of the nanoparticles on the pictures taken by the scanning microscope (Fig. 4).

On addition of SDS to Co and Mn salt solution, flakes of sparingly soluble salts $(\text{SDS})_2\text{Co}$ and $(\text{SDS})_2\text{Mn}$ are immediately formed. They will dissolve eventually and transparent solutions will be obtained. On addition of hydrazine hydrate, their spectra remain unchanged as may be seen from comparison of Figs. 1 and 2. Thus it may be concluded that the nanoparticles are not formed in the SDS miscellar solutions. Apparently it is conditioned by formation of an ion triplet which electrostatic ion interaction is amplified by hydrophobic effect and SDS hydrocarbon groups prevent hydrazine hydrate from contact with the ions.

Morphology of nanoparticles and fractals.

Different methods used for studying morphology of nanoparticles give ambiguous results. It is explained by a natural tendency of nanoparticles for aggregation to

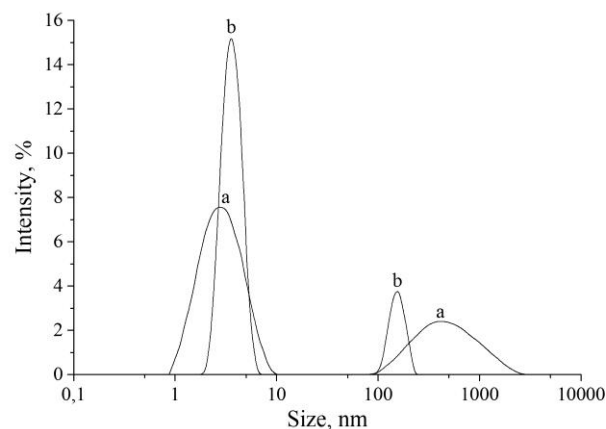


Fig. 3 – Nanoparticle size distribution based on dynamic light scattering data: a is for Co; b is for Mn

attenuate interfacial energy. Thus it is initially required to consider the experimental results obtained with dynamic light scattering (Fig. 3) which allows identification of the tiniest spherical nanoparticles.

In obtained aqueous suspension, Co nanoparticles of 3.09 ± 1.47 nm in dia and large aggregates of 580 ± 436 nm in dia are detected with a large range of size distribution. Nanoparticles of 3.64 ± 0.75 nm in dia and fractals of 155 ± 25 nm in dia are obtained for Mn. Diffusion of nanoparticles is defined by dynamic light scattering and is converted into nanoparticle diameters by the Einstein-Smoluchowski relation. The particles measured by this method are always spherical.

The diameters of Co and Mn nanoparticles are less than the CPC micelles diameter of 4.5 nm which is consistent with the hypothesis for formation of condensation centers inside the micelles. Volume of the CPC micelle is 49 nm^3 , dia is 4.5 nm [14]. It can be shown that if the nanoparticles are stabilized by a double monomolecular layer all CPC molecules are adsorbed on the surface of nanoparticles and there are no micelles in the solution.

The double monomolecular layer of CPC is poorly washed off and is obviously left in powder which has been studied by scanning microscopy (Fig. 4). Aggregates of the nanoparticles are of 50-60 nm in diameter. They have a vivid halo, i.e. «a mantle» made of a CPC stabilizer layer. A small object observed in a scanning microscope has the same shape (spherical) as a big one detected by dynamic light scattering in dispersion.

The main long-range forces responsible for particle interaction (Van der Waals forces, electrostatic forces, steric forces (due to overlap of two CPC layers of the interacting particles) are isotropic. Magnetic dipole-dipole interactions are anisotropic.

With appropriate model used, interaction energy may be expressed as a function of distance between two particles.

In many cases, structures of fractal aggregates may be interpreted in terms of a relative balance between diffusion and reactive (adhesion) results. Nature of fractal organization of Co nanoparticles obtained in the solution (Fig. 3) and on a glass after water is evaporated from the drop (Fig. 4) may be compared.

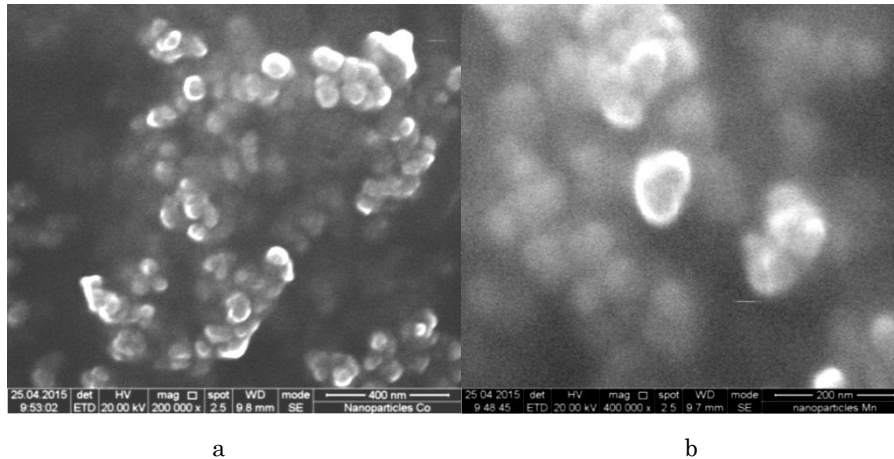


Fig. 4 – Quanta 650 FEG images of nanoparticles: a is Co, b is Mn

Fractal dimension is calculated as $D = \ln N / \ln(R/a)$, where N is number of nanoparticles in a fractal, R is diameter of a fractal, a is diameter of a nanoparticle. Fractal dimension in both dispersions is 3. Therefore, nature of fractal organization in the disperse system (Fig. 3) and in the powder on the glass (Fig. 4) is the same.

4. CONCLUSION

The disperse systems with Co, Mn nanoparticles of 3-4 nm in diameter were obtained. Before ions reduce to metal nanoparticles, they are shown to dehydrate and the condensation centers are formed inside the micelles. In dispersion the nanoparticles aggregate into the fractals.

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