ВОДА/МАСЛО (W/O) МИКРОЕМУЛСИЯ – АЛТЕРНАТИВНА РЕАКЦИОННА СРЕДА ЗА ПОЛУЧАВАНЕ НА МОНОДИСПЕРСНИ КАРБОНАТНИ НАНОЧАСТИЦИ

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WATER- IN- OIL (W/O) MICROEMULSION - AN ALTERNATIVE REACTION MEDIUM FOR PREPARATION OF MONODISPERSED CARBONATE NANOPARTICLES

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ABSTRACT

The use of an inorganic phase in water-in-oil microemulsions has received considerable attention for preparing metal particles. This is a new technique, which allows preparation of ultrafine metal particles within the size range 5 nm<particle diameter<50 nm. The nano-sized particles of alkaline carbonates have specific characteristics and they are important materials for the industry. The aim of this work is to investigation the water/oil microemulsion as an interesting alternative reaction medium for the formation and synthesis of monodispersed carbonate nanoparticles. The nano-sized particles were obtained at various ratios of the phases forming the microemulsion and were studied by electron microscopy. By TEM to determine their shape, size and structure. Their sizes vary from 20 to 30 nm. A probabilistic mechanism of nanostructures forming was proposed.

Key words*: W/O microemulsion systems, particle synthsis, nanoparticles, carbonate nanoparticles*

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INTRODUCTION

The significance of nanosciencse for the future development of electronics, mechanics, medicine etc. is acknowledged all over the world. Products based on nanotechnology are already in use and the analysts expect markets to grow significantly during present decade. The creating of new products based on improved knowledge will contribute to appearance of new generation products and services in respective applied areas.

Over the last years the researchers are interested mostly in the synthesis of nanosized particles in microemulsion. They study the chemical techniques and the optimal conditions for syntheses in microemulsion systems. Taking into account the large area and the activity of the ultrafine particles synthesized in microemulsion systems, the latter can be successfully used for preparation of selective adsorbents and catalysts for a number of chemical processes. The Bulgarian scientists carry out researches on the preparation of monodisperse carbonate nanoparticles under such microemulsion conditions, the influence of suitable process control parameters like the initial concentrations of the reactants and their possible application as partially nanostructured catalysts [1-6].

Microemulsions are known to be an alternative reaction medium for preparation of fine monodispersed colloid particles. Microemulsions may be classified as water-in oil (w/o) or oil-in-water (o/w) depending on the dispersed and continuous phases. Water-in-oil (w/o) microemulsions are transparent, isotropic, and thermodynamically stable with nano-sized water droplets that are dispersed in a continuous oil phase and stabilized by surfactant molecules at the water/oil interface. The w/o microemulsion (also named reverse micelle) can be regarded as special microreactor where controlled chemical reactions can be carried in order out to obtain ultradispersed particles of desired size and shape. The shape of the microreactor depends on reaction conditions [1-6].

This method increases the homogeneity of the chemical composition at nano-level and facilitates the preparation of nanoparticles with comparatively equal sizes. Figure 1 gives the types of colloidal systems with their typical particles size and clearly visible in the band which fall microemulsions [6].

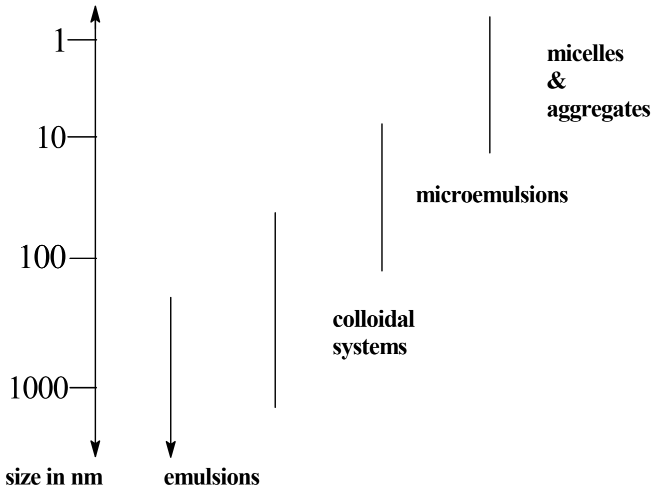

Figure 1. Types of colloidal systems

Numerous reports have been published on the synthesis of ultrafine particles if metals and oxides like Au, $BaCO_3$, Fe_3O_4 and ZnS, Pt, Pd, Rh, Fe, Cu, etc., in micelles medium [6]. The use of microemulsion systems on industrial scale, however, requires studying many parameters of the synthesis to find the best combination of variable values which would allow control and regulation of nanoparticles properties.

The aim of this work is the use and studies of water / oil (w/o) microemulsion for synthesis of monodispersed nanoparticles of alkaline carbonates ($BaCO_3$, $CaCO_3$).

MATERIAL AND METHODS

The experimental methods involve preparation of aqueous solutions of $Ba(OH)_2$ and $Ca(OH)_2$. The concentration ($C = 2.10^{-2}$ mol/l) of which was controlled by volume-analytic titration. The microemulsion used was a colloid-dispersed system of water/n-hexane/Aerosol-OT (AOT) type. The components of the used ternary microemulsion system are inexpensive and easy to separate.

The microemulsion samples were prepared by mixing n-hexane and Aerosol-OT in a glass reactor and adding subsequently water or aqueous salt solution. The aqueous solution of $Ba(OH)_2$ ($Ca(OH)_2$) was the inorganic phase and n-hexane was the organic phase (oil). The inorganic microdrops are distributed in the organic medium. The working volume of the reversed micelle system is 50 ml. The volumes of the two phases were varied from 10 to 40 ml, respectively. The volumes of both organic and inorganic phases of the system for each experiment are shown in Table 1.

The reaction conditions used for the synthesis of carbonate nanoparticles were:

- Initial concentration of aqueous solutions of $Ba(OH)_2$ and $Ca(OH)_2$ ($C.10^{-2}$) – 2 mol/l.

- Stirring speed (n) – 800 min^{-1}.
- Time for mixing the two phases (without chemical reaction) (t_1) – 60 min.
- Time for mixing and chemical reaction (t_2) – 60 min.

Table 1 **Ratio of volumes of organic and inorganic phases**

Experiment no.	Inorganic phase	Organic phase	Volume of inorganic phase V_1, ml	Volume of organic phase V_2, ml	V_1 / V_2
1	2	3	4	5	6
1	$Ca(OH)_2$	n - C_6H_{14}	5	45	0.111
2	$Ca(OH)_2$	n - C_6H_{14}	10	40	0.250
3	$Ca(OH)_2$	n - C_6H_{14}	15	35	0.429
4	$Ca(OH)_2$	n - C_6H_{14}	20	30	0.667
1	$Ba(OH)_2$	n - C_6H_{14}	30	20	1.5
2	$Ba(OH)_2$	n - C_6H_{14}	25	25	1
3	$Ba(OH)_2$	n - C_6H_{14}	20	30	0.667
4	$Ba(OH)_2$	n - C_6H_{14}	15	35	0.429
5	$Ba(OH)_2$	n - C_6H_{14}	35	15	2.333
6	$Ba(OH)_2$	n - C_6H_{14}	40	10	4

The synthesis of ultrafine $BaCO_3$ particles was carried out in an installation containing a laboratory glass reactor with stirrer. Its design and performance have been described earlier (for details see) [4]. Since the w/o microemulsion contained one of the reagents, the other was fed into the reactor in gaseous form (CO_2) at constant flow. In the case the gas is dissolved in the oil phase and reaches the water core of the droplets via mass transport phenomena. As a result, chemical interaction between the gas and the inorganic solution dispersed in the organic phase takes place, i.e. a chemical reaction occurs the products of which are slightly soluble substances. The experiments were carried out at temperature of 20–23 °C. After each experiment, the microemulsion phases undergo separation and analyses in order to prove presence of bonded carbonate ions.

RESULTS AND DISCUSSION

Solid nano-sized particles of $CaCO_3$ and $BaCO_3$ were obtained from the experiments carried out using chemical reaction in a “microemulsion” of type water in oil. The qualitative analyses of the organic and inorganic phases for all the experiments showed the presence of calcium or barium carbonate. The shape and size of the particles were determined by electron microscopy. Photographs of nano-sized particles of $BaCO_3$ are presented in Figure 2. The nano-particles synthesized were with spherical shape and almost equal sizes varying from 20 to 30 nm.

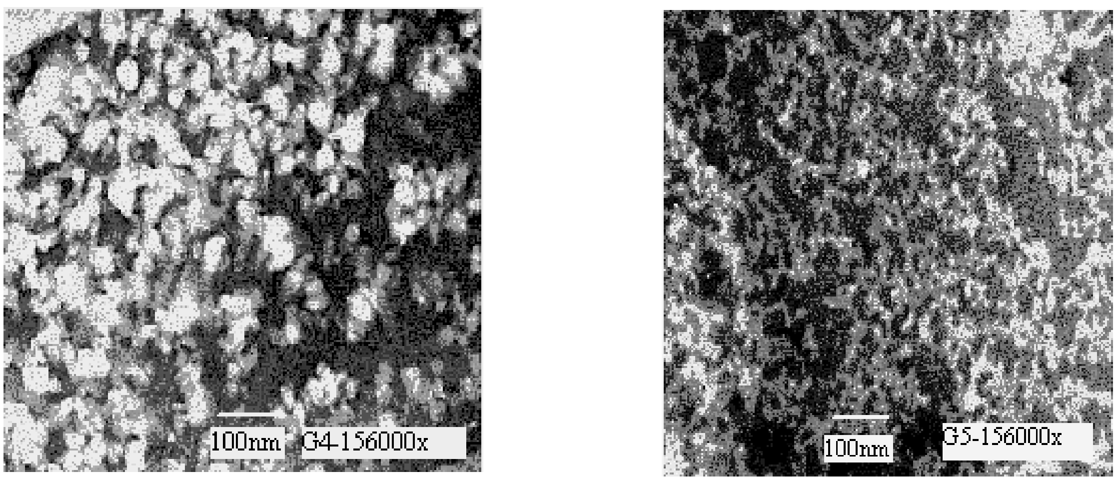

Figure 2. Electron microscopy photographs of nanoparticles of $BaCO_3$.

The electron-microscopy analysis (Fig. 2) revealed that processes of particles agglomeration took place. Since the opalescence observed with the organic phase from the experiments was not very good, the agglomeration was supposed to occur during the electron microscopy analysis itself. It may result from the irradiation of the samples by the high-energy electron beam used for the analysis.

The results sustained the opinion that the synthesis of nano-particles in microemulsion (w/o) is to be preferred. In common emulsions, both phases spontaneously separate from each other while microemulsions are thermodynamically stable, do not segregate and appear to be transparent. This can be explained with the size of the water droplets [4-511. J. Shmidt, Reaktionstechnishe Untersuchungen zur Herstellung von Nanopartikeln in Mikroemulsionen, Dissertation, TU Berlin, 2000.].

Microemulsions are also characterized by the so called "dynamic exchange process". The emulsion droplets in such emulsions constantly integrate and disintegrate, thus exchanging substance between each other. The substance dissolved in the emulsion droplets was quite small amount, i.e. the reagent concentration in the droplet was low so it could be expected to obtain small particles with almost equal sizes. In the case studied, the following physical model was suggested. The microemulsion water solution/organic phase were formed preliminarily. It contained only one of the reagents (in this case solution of $Ca(OH)_2$ or $Ba(OH)_2$). The second reagent was added in the form of a gas (CO_2). The gas passed through the organic liquid, diffused through the interphase surface oil/water solution in the drops and then interacts with the inorganic phase present in them. Thus, a chemical reaction was initiated which gave slightly soluble products ($CaCO_3$ and $BaCO_3$). This hypothesis can be schematically represented as follows (Figure 3):

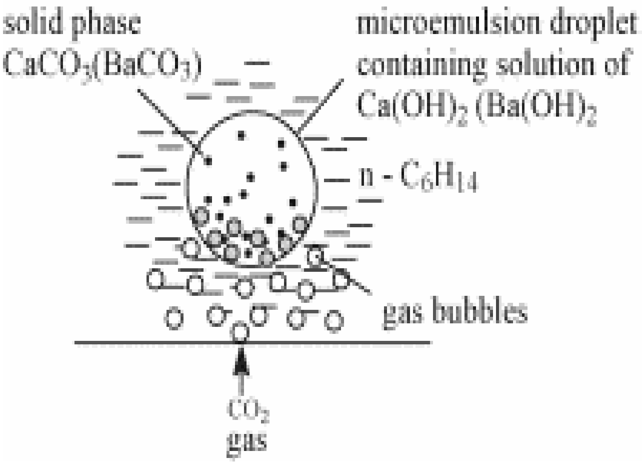

Figure 3. Probable mechanism of contact of reagents

The summarized equation of the chemical reaction proceeding between the corresponding hydroxide and CO_2 is:

$$Me(OH)_2 + CO_2 \rightarrow MeCO_3 + H_2O$$

where Me = Ca, Ba.

CONCLUSIONS

The following conclusions can be formulated on the basis of the results obtained

1. A technique and process for preparation of nano-sized particles from alkali carbonates was developed on the basis of the method of reversed micelles and a probable mechanism was suggested.
2. Nano-sized particles of barium and calcium carbonate were obtained by a chemical reaction in a w/o microemulsion. The particles were studied by electron microscopy and were found to possess spherical shape and diameters from 20 to 30 nm.
3. The nano-sized particles were obtained at various ratios of the phases forming the microemulsion. They were about the same size, which confirmed the advantage of the method selected.
4. The particles synthesized were observed to agglomerate, probably due to effects induced by the electron microscopy analysis.

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