

MICROEMULSION WATER IN OIL (W/O) - EVALUATION OF THE SURFACE TENSION FORCES AND STUDY THE INFLUENCE OF SOME FACTORS ON THE SIZE OF CARBONATE FORMED NANOSTRUCTURES

Adriana Georgieva, Krasi Panayotova, Jivko Ivanov

Department of Organic Chemical Technology and Chemical Engineering, Faculty of Technical Sciences, University Prof. Dr. Asen Zlatarov" - Bourgas, 8010 Bourgas, Bulgaria

ABSTRACT

In recent decades, microemulsions have been successfully used as reaction medium allowing the realization of chemical reactions and the synthesis of various organic and inorganic nanostructures. The aim of this work is to evaluate the surface tension forces and study the influence of some factors on the size of carbonate nanostructures formed. The values of the surface tensions of the individual phases were calculated, as well as the value of the interphase tension. The nano-sized particles of barium and calcium carbonates were obtained at various ratios of the phases forming the microemulsion and were studied by qualitative analysis and electron microscopy (TEM) to determine their shape, size and structure. Their sizes varied from 20 to 30 nm.

Keywords: W/O microemulsion systems, carbonate nanoparticles, surface tension forces

INTRODUCTION

Emulsions are widely spread type of heterogeneous dispersed systems both in nature and industry. They are usually composed of two or more immiscible liquids, the one (dispersed phase) being scattered into the other (dispersing phase) as small particles [1, 2]. The artificial emulsions are most often obtained by dispersing and vigorous agitation of the mixture. At sufficient extent of stretching

(elongation), the emulsion drops acquire unstable shape and split, thus increasing the system dispersity.

An peculiar property of the emulsions is that the stirring of two immiscible liquids can lead to dispersing either phase 1 into phase 2 or phase 2 into phase 1. For this reason, a special notation has been adopted for the type of emulsion. One of the phases and is

usually water or aqueous solution and is denoted by „W”. The other phase is denoted by “O” and it is usually non-polar liquid or one with small polarity which, in the general case, is called oil. This type of emulsions is widely spread and is object of certain practical interest. They consist of two main types of emulsions: O/W and W/O. If the organic liquid (oil) is dispersed on water, the emulsion is oil-in-water (O/W) and it is called normal emulsion. In the other case the emulsion is of the (W/O) type and it is called reverse emulsion [1÷3].

The emulsions are stabilized by emulsifying agents – surfactants (detergents). Since emulsion instability is related mainly to the excess of interphase free energy, the emulsifiers should be surfactants reducing the Tthe surface tension at the interface between the phases [2]. By nature, the surfactants are high-molecular weight substances with clearly manifested surface activity at the phase boundary. They contain hydrophilic and hydrophobic phases. Fig.1 shows the different structures forming in surfactant solutions.

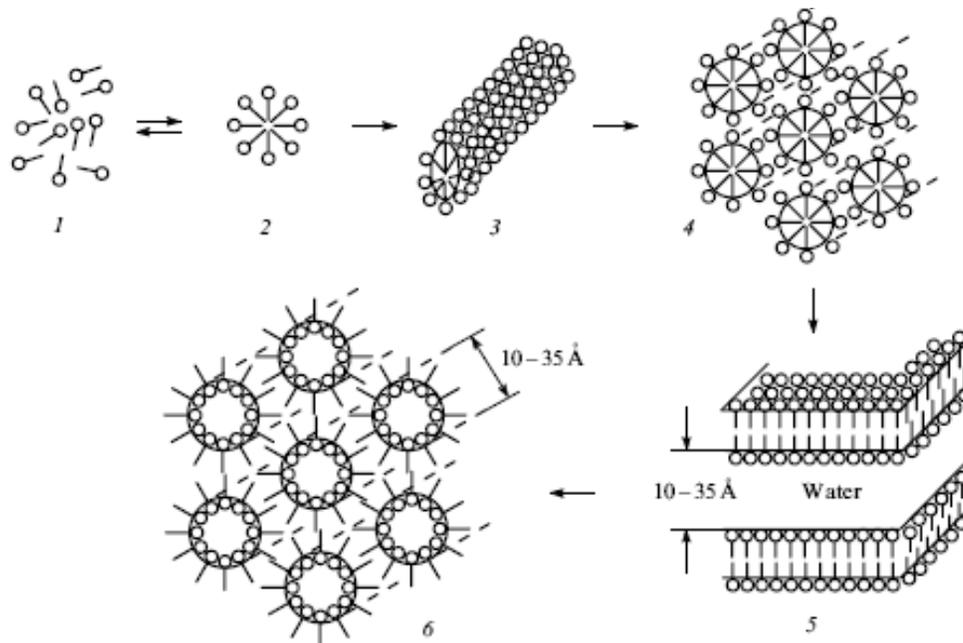


Fig. 1. Structures arising in solutions of surfactants: (1) monomers; (2) micelle; (3) cylindrical micelle; (4) cylindrical micelles as packed hexagons; (5) lamellar micelle; (6) water droplets packed as hexagons in the reverse micellar system

The microemulsions which are dispersed systems themselves are thermodynamically stable, transparent and most often comprise three components: two immiscible liquids (usually water and oil) and surfactant. They are prepared from common emulsions and are called micelles emulsions [2]. While common emulsions tend to separate spontaneously to its phases, microemulsions are stable and do not separate over time. This fact is explained with the micro-size of the water droplets which are less than 100 nm by diameter, so microemulsions are isotropic and optically translucent.

Depending on the dispersed phase and dispersing medium types, microemulsions are classified into two major classes: water-in-oil (W/O) and oil-in-water (O/W). Water droplet size can vary in wide range (from several to hundreds of nanometers)[3], depending on the conditions and stabilizer nature.

In recent decades, these dispersed systems have been successfully used as reaction medium allowing realization of certain chemical reactions and synthesis of various organic and inorganic substances. Based on their thermodynamic stability and simple structure, they are often used as model systems [5÷9, 14÷16].

A feature of the microemulsions is the so called “dynamic exchange process”. The emulsion drops in them incessantly combine and break up and exchange substance. With the development new technologies like

nanotechnology, this feature acquired the meaning of a direct approach for the preparation of ultra-dispersed particles [9, 14÷16].

The particles of nanometer size obey the laws of quantum physics which changes the fundamental approach to their mechanical, optical and electric properties. Based on their unusual properties, nano-particles and nano-materials attain great significance in microelectronics, catalysis, cosmetics, medicine, ceramics, textile industry, corrosion protection, etc.[10÷13].

The materials based on alkali carbonates have found special practical application. As nano-sized particles, calcium and barium carbonates possess some specific characteristics for many industrial materials. They are widely used as fillers in cosmetic, pharmaceutical, resin, and other industries. They are also used for the production of dyes, plastics and food additives [9, 14÷16].

MATERIALS AND METHODS

The method for preparation of carbonate nano-structures using only one microemulsion which is a colloid dispersed system of the water-in-oil type (W/O): aqueous solution of *n*-hexane/Aerosol-OT ($Ca(OH)_2(Ba(OH)_2 \cdot 8H_2O)/n-C_6H_{14}/C_{20}H_{37}NaO_7S$). The alkali suspension (aqueous solution of $Ca(OH)_2$ or $Ba(OH)_2 \cdot 8H_2O$) is the dispersed phase while *n*-hexane is the dispersing medium, with the microdrops formed being dispersed within

the organic substance. The microemulsion samples were prepared by mixing n-hexane and 0.01M solution of Aerosol-OT ($C_{20}H_{37}NaO_7S$) in a glass reactor where the specific organic solution was added afterwards.

The working volume of the water/oil microemulsion was generally $0.05 \cdot 10^{-3} \text{ m}^3$ but the ratio of the components was varied for the different experiments. In the experiments, the reverse micelles solutions were obtained at ratio aqueous solution/stabilizer $R = [\text{aqueous solution}] / [\text{Aerosol-OT(AOT)}] = 20$.

The synthesis of carbonate nano-particles was carried out in a laboratory installation comprising a batch reactor with stirring to approximate an ideal mixing reactor. A schematic diagram of the installation for preparation of nano-structures has been reported earlier [14].

During the experiments, a kind of the microemulsion method was realized where only one colloid dispersed system containing one or the reagents is prepared. The other reagent was introduced in the reactor in gaseous or liquid state.

The specific reaction conditions for the synthesis were:

- Stirring speed of the W/O emulsion with magnetic stirrer $n = 800 \text{ min}^{-1}$;

- Time to disperse microemulsion phases without chemical reaction - $t_1 = 60 \text{ min}$;
- Period of additional agitation of the microemulsion system with chemical reaction - $t_2 = 60 \text{ min}$;
- Temperature of the synthesis - $T = 25 \text{ }^\circ\text{C}$;

The sequence of operations for the preparation of ultrafine particles under microemulsion conditions by the method developed is schematically presented earlier [9, 14÷16].

After each realized experiment for preparation of carbonate microstructures, the two microemulsion phases were separated and each was subjected to quantitative analysis to prove the existence of the corresponding carbonate. The distribution of metal ions was determined complexometrically.

The identification of the ultrafine particles synthesized to determine their composition, size, shape and structure was carried out using electron microscopy analysis.

RESULTS AND DISCUSSION

As a result of the experiments carried out, solid carbonate nano-sized particles of CaCO_3 and BaCO_3 were synthesized. The nano-structures based on alkali carbonates were obtained by chemical reaction under microemulsion conditions – by

carbonization of the corresponding inorganic solution.

Both phases forming the reverse microemulsion system were subjected to qualitative analysis which showed the presence of bonded carbonate ions.

The shape, size and dispersity of the nano-structures were determined by electron microscopic methods. Electron micrographs of nano-sized particles obtained are presented in Fig.2.

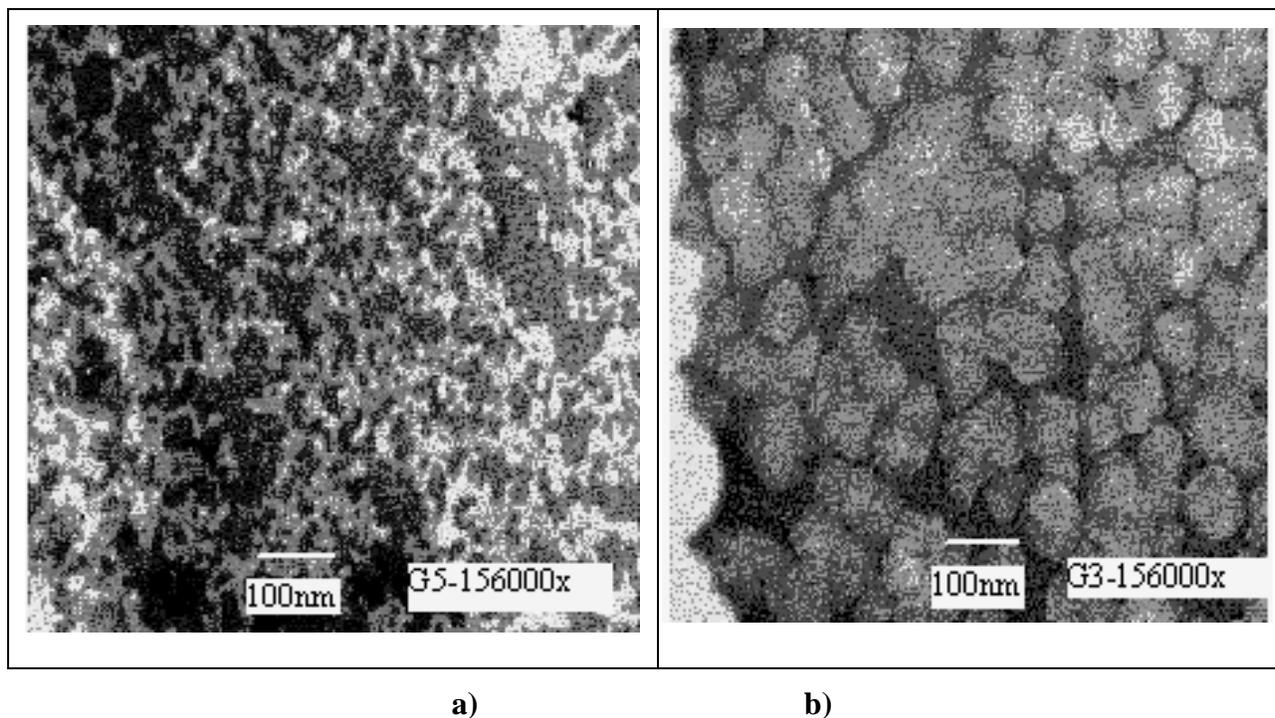


Fig. 2. Electron microscopy photographs of TEM of nano-sized particles of BaCO₃ (a) and CaCO₃ (b) obtained in W/O microemulsion system (alkali solution/n-C₆H₁₄/C₂₀H₃₇NaO₇S) and the following reaction parameters: C = 2.10⁻² mol/l; n = 800 min⁻¹; t₁ = 60 min; t₂ = 60 min; R = [H₂O]/[AOT] = 20; T = 25°C; d = 20÷30 nm

The electron microscopy analysis carried out confirmed that the nano-structures synthesized in each sample were null-sized. They were narrowly distributed by size and existed both individually and in not large aggregates (3-4 particles). The photographs

presented in Fig.2 indicated for spherical shape and size from 20 to 30 nm for the nano-particles of CaCO₃ and BaCO₃.

It was also found from the electron microscopy analysis carried out that among

the nanostructures synthesized by the method developed, these of barium carbonate had the best opalescence and were the easiest to identify. This made us carry out part of the further studies on the conditions for the formation of nanoparticles in reverse microemulsion system using a system comprising the following components: aqueous solution of $Ba(OH)_2 \cdot 8H_2O$ /n-hexane/Aerosol-OT.

I. Assessment of the surface tension forces for microemulsion system inorganic solution /n-C₆H₁₄

For the microemulsion system inorganic solution/n-C₆H₁₄($Ba(OH)_2 \cdot 8H_2O$)/n-C₆H₁₄/C₂₀H₃₇NaO₇S) studied, it was important to prove that the corresponding alkali suspension was dispersed in the organic phase as microdrops. To determine the phase distribution in the microemulsion, the surface tension forces in each of them should be determined, as well as the forces acting at the interface between the phases.

The surface tension forces act on the surface of the particles in the liquid phase. They can be expressed as the work necessary to form a unit interphase area under constant thermodynamic state parameters (temperature, pressure, chemical potentials of the components, etc.). This process is reversible and isothermal. The surface tension forces can be regarded as free energy per unit area, i.e. as specific free

energy (G_s). Therefore, per unit weight of the particle it will be

$$G_s = \bar{G}_s A \tag{1}$$

For instance, the surface tension of 0.02N solution of barium chloride was determined by the expression (Zaitsev and Aseev, 1988):

$$\sigma_{Ba(OH)_2} = \sigma_0 + 0.049(1 - a_w) \tag{2}$$

where:

- σ - the surface tension of $Ba(OH)_2$, N/m;
- σ_0 – the surface tension of water at T=25 °C. It was assumed to be $71.97 \cdot 10^{-3}$ N/m [17];
- a_w – activity of water in the solution.

The activity of water in the solution was determined using the well known equation [17].

$\ln a_w =$

$$\frac{tm_{Ba(OH)_2} M_{Ba(OH)_2}}{55510RT} \left[\begin{array}{l} B_1 + at + bt^2 + \\ \left(\frac{B_2}{1000 + M_{Ba(OH)_2} m_{Ba(OH)_2}} \right) \\ \times \left(m_{Ba(OH)_2} M_{Ba(OH)_2} + \frac{1}{E} \right) \end{array} \right] \tag{3}$$

where:

- R – universal gas constant, J/mol;
- T - temperature, K;
- m_i – molarity of the solution, g/l;
- M_i – molecular weight, g/mol;

B₁, a, b, B₂, E – coefficients calculated by mathematical processing of experimental data on heat capacities.

The barium hydroxide surface tension was calculated to be $71.88 \cdot 10^{-3}$ N/m. According to reference data, $\sigma_{n-C_6H_{14}} = 32.21 \cdot 10^{-3}$ N/m [17]. The value of the Ba(OH)₂ surface tension was close to that of water (σ_0) because the concentration of the alkali solution was quite small, i.e. the solution was highly diluted. The forces of interphase tension act on the contact areas between the two liquid phases - σ_{T_1/T_2} .

According to reference data, the interphase tension at the phase border inorganic solution/oil is $50.5 \cdot 10^{-3}$ N/m [18]. The two phases have very different polarities. The main process occurring by the contact between them is the change of contact area between the phases due to the decrease of the total surface energy of the system, i.e. conditions arise for the process of wetting to take place.

The coefficient of spreading S can be calculated from the values of the surface and interphase tensions. The coefficient is used to estimate the degree of wetting between liquid surfaces. The coefficient of spreading is expressed by the formula [19].

$$S = \sigma_{T_2/\Gamma} - \sigma_{T_1/\Gamma} - \sigma_{T_2/T_1} \quad (4)$$

$$S = -10.853$$

At values of $S < 0$, the wetting angle is determined by the equation [19]:

$$\cos \theta_0 = \frac{(\sigma_{T_2/\Gamma}^2 - \sigma_{T_1/\Gamma}^2 - \sigma_{T_2/T_1}^2)}{2\sigma_{T_2/\Gamma}\sigma_{T_1/\Gamma}} \quad (5)$$

i.e. $\cos \theta_0 = 0.3717$

Therefore, $\theta_0 = 68.18^\circ$. When $\theta < 90^\circ$, as it is in the case studied, this corresponds to the process of so called “limited wetting” or wetting with impregnation. Thus, the change of free energy per unit area can be calculated by the formula:

$$\Delta G = \sigma_{T_B/\Gamma} - \sigma_{T/\Gamma} \quad (6)$$

The interphase tension σ_{T_1/T_2} corresponds to the so called final coefficient of spreading S_k which is the value obtained after equilibrium is established at the boundary between the two liquids. The higher the coefficient of spreading is, the more rapidly spreads the wetting liquid.

In the reverse microemulsion system studied, $\sigma_{T_1/T_2} = S_k = 50.5 \cdot 10^{-3} > 0$.

Therefore, the surface tension of n-C₆H₁₄ remained lower than that of the inorganic solution, i.e. n-C₆H₁₄ wetted the inorganic solution (Ba(OH)₂).

II. Study on the effects of some factors on the size of the carbonate structures formed in the reverse microemulsion system

Under the same reaction conditions (speed of system agitation with magnetic stirrer, time for dispersing the microemulsion

phases with and without chemical reaction, etc.), the effect of the initial concentration of the inorganic solution of the reverse microemulsion $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O} / n\text{-C}_6\text{H}_{14} / \text{C}_{20}\text{H}_{37}\text{NaO}_7\text{S}$ on the size of the barium carbonate nano-particles obtained was studied. Data on the values of the initial concentrations of the inorganic solutions used are presented in Table 1.

The experiments carried out showed that the nanostructures were formed mainly in the inorganic phase which is distributed within the organic one. Using different initial

concentrations of the alkali suspension of barium hydroxide, the formation of nanostructures in W/O emulsion was studied and the average diameter of barium carbonate nano-particles was determined. The values of some basic physicochemical characteristics of the nano-structures synthesized were calculated – number of particles per unit mass (N) and specific area (A (m^2 / kg)) [20]. The data presented in Table 1 confirm the fact that the increase of particle size leads to a decrease of their number per unit mass which results in decreased specific area.

Table 1. Effect of the initial concentration of the inorganic solution of W/O microemulsion (Ba(OH)₂.8H₂O/n-C₆H₁₄/C₂₀H₃₇NaO₇S) on the size of the nano-structures obtained and values of some physicochemical properties of the particles

Initial concentration of Ba(OH) ₂ .8H ₂ O, C.10 ² , mol/l	Molarities of the inorganic solution, m, g/l	Average diameter of the nanoparticles of BaCO ₃ , d.10 ⁹ , m	Number of particles per unit mass, N.10 ⁻¹⁸	Specific area of BaCO ₃ particles, A.10 ⁻⁴ , m ² /kg	Water activity in the inorganic solution, a _w	Surface tension of water at 25°C, σ _w .10 ³ , N/m	Surface tension of the solution Ba(OH) ₂ .8H ₂ O at 25°C, σ.10 ³ , N/m
2	3.1534	10	439	13.89	0.4110	71.9350	71.9640
6	9.4600	8	858	17.8	0.1152	71.9350	71.9780
8	12.6140	15	130	9.2	0.0640	71.9350	71.9810
10	15.7700	160	0.107	0.862	0.0361	71.9350	71.9820
20	31.5340	1000	0.000439	0.138	0.0021	71.9350	71.9840

The increase of concentration was observed to have diverse effects, i.e. particle size decreased up to C_{Ba(OH)₂.8H₂O}=6.10⁻² mol/l and increased above this concentration. Besides, the increase of the concentration by an order resulted in increase of nano-structures size by three orders. This observation is sustained by the TEM

micrograph of nano-particles obtained under the following conditions:

C_{Ba(OH)₂.8H₂O}=1.10⁻¹ mol/l; n=400 min⁻¹; t₁=30 min; t₂=30 min; T=25 °C and R=20 (Fig. 3).

As can be seen from the electron microscopic analysis, the nano-structures synthesized had spherical shape and were considered to be monodispersed, as their

sizes were within the interval from $30 \cdot 10^{-9}$ to $50 \cdot 10^{-9}$ m (30÷50 nm). Obviously, particles diameters were affected simultaneously by several factors:

- The higher concentration of the initial alkali solution;
- Reduced speed of system agitation;

- Twice reduced time for phase dispersion with and without chemical interaction.

The surface tensions of water and aqueous solution of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (σ_0 and σ , N/m) were determined at temperature of 25°C , as well as the activity of water (a_w) in the inorganic solutions used. The results obtained from the studies are summarized in Table 1.

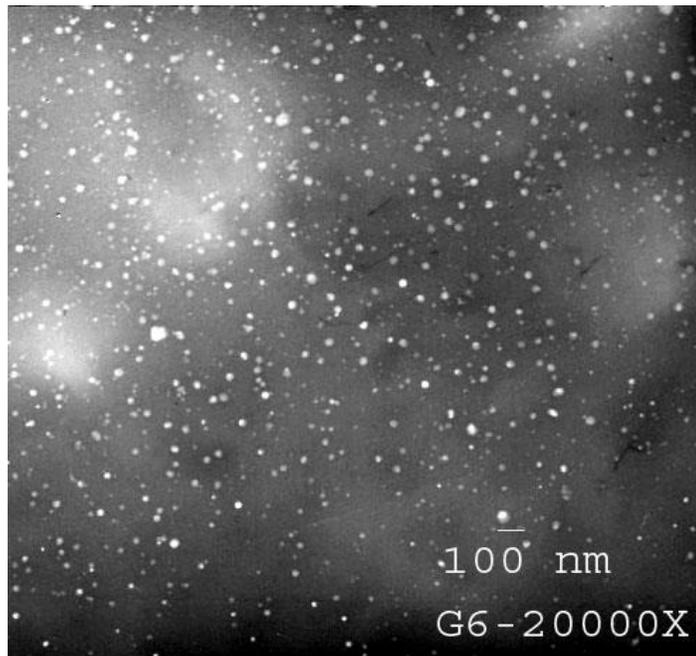


Fig. 3. TEM Micrograph of nano-sized particles of BaCO_3 obtained in W/O microemulsion system ($\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}/n\text{-C}_6\text{H}_{14}/\text{C}_{20}\text{H}_{37}\text{NaO}_7\text{S}$)

4. CONCLUSION

The following conclusions can be drawn as a result from the studies carried out:

1. A variety of the microemulsion approach for synthesis of nano-particles was realized.

In the experiments carried out, only one microemulsion system was used, which was a colloid dispersed system of the type water-in-oil (W/O) comprising: inorganic solution /n-hexane/Aerosol-OT.

2. As a result from the experiments performed, solid nano-sized particles were synthesized from calcium and barium carbonates. With these studies it was proved that:

2.1. The carbonate nano-structures were obtained by chemical reaction under microemulsion conditions and at different mass ratios between the phases forming the reverse microemulsion system.

2.2. Using the methods of electron microscopy (TEM), the nano-particles were identified and characterized. They were proved to have spherical shape and narrow distribution by size (monodispersity). The nano-structures of BaCO_3 had sizes from $20 \cdot 10^{-9}$ to $30 \cdot 10^{-9}$ m.

3. The values of some basic physical properties were calculated, e.g.: specific area (A , m^2/kg), number of particles per unit mass (N) and average diameter (d , m) of the nano-structures synthesized.

4. For the W/O microemulsion studied, the forces of surface tension of the emulsion phases were determined, as well as the forces acting at the interphase boundary.

5. The influence of the initial; concentration of the inorganic phase in the reverse microemulsion system on the size of the carbonate nano-particles obtained was studied under equal other conditions. The smallest size (diameter) of the nano-sized particles ($d=8 \cdot 10^{-9}$ m) was obtained at initial

concentration of the $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ alkali suspension of $6 \cdot 10^{-2}$ mol/l.

ACKNOWLEDGEMENTS:

The authors would like to acknowledge the financial support of the Scientific-Research Sector of University Prof. Dr. Assen Zlatarov" - Bourgas, HIX-359/16.

REFERENCES

1. Fridrisberg D. Course in Colloid Chemistry. Chemistry 1984 (in russian).
2. Mittal K. Micellization, solubilization and microemulsions. (Ed.) 1980.
3. Lide D. Handbook of Surface and Colloid Chemistry. Third Edition. CRC Press. Nov. 20 2008.
4. Hellweg T. Phase structures of microemulsions. Current Opinion in Colloid and Interface Science 2002; 7: 50-56.
5. Summ B.D, N.I. Ivanova, Colloidal - Chemical Aspects of Nanochemistry: from Faraday to Progozhin, *Moskow University Chemistry Bulletin*, 42 (5), (2001), 300-304.
6. Boutonnet M, Kizling J, Stenius P. The preparaton of monodisperse colloidal metal particles from microemulsions. *Colloids Surf* 1982; 5: (3) 209-225.
7. Fendler J.H., Colloid Chemical Approach to Nanotechnology, *Korean J. Chem. Eng.*, 18 (1), (2001), 1-13.

8. Capek I., Preparation of metal nanoparticles in water-in-oil (w/o) microemulsions, *Advances in Colloid and Interface Science*, 110 (2004), 49-74.
9. Georgieva A., B. Bogdanov, Zh. Stefanov, Water- in- Oil (W/O) microemulsion - an alternative reaction medium for preparation of monodispersed carbonate nanoparticles, "Science & Technologies", VOLUME I, Number 4, 2011, Technical studies, pp. 9-13.
10. Klabun K., Nanoscale materials in chemistry, *John Wiley & Sons, Inc.*, New York, (2001).
11. Visokov G, Nedkov I, Balabanova E. National program "Nanotechnologies and new materials". *Chemistry and Industry* 2006; 77: 20-25.
12. Karabasov Y. New materials. M.: MISAA 2002 (in russian).
13. Gusev A. Nanomaterials, nanostructures, nanotechnology. FIZMATLIT 2009 (in russian).
14. Slavova A, Karagyozov Chr, Ulrich J, Bogdanov B. Synthesis of Nano-sized Nickel Particles in Reverse Microemulsion System, and Their Use for Preparation of Partially Nano-structured Catalyst Systems. *International Review of Chemical Engineering* 2009; 1: (4) 324 -328.
15. Georgieva A., Kr. Panayotova, B. Bogdanov, Zh. Stefanov, Microemulsions – properties, application and perspectives, "Science & Technologies", VOLUME II, Number 4, 2012, Technical studies, pp. 1-5.
16. Georgieva A, Bogdanov B, Stefanov Zh, Koleva D. Microemulsion water-in-oil (W/O) – microreactor for synthesis of ultrafine carbonate nanostructures, University of Ruse “Angel Kanchev”, Proceedings, Chemical technologies 2011; 50: (9.1) 34-39.
17. Zaytsev I, Aseev G. Physical-chemical properties of binary and multicomponent solutions of inorganic substances. Chemistry 1988 Mosckow (in russian).
18. Backes H, Ma J, Bender E, Maurer G. Interfacial tensions in binary and ternary liquid - liquid systems. *Chem Eng Sci* 1990; 45: (1) 275-286.
19. Summ B, Gorunov V. Physico - chemical basis of wetting and spreading. Chemistry 1976 Moscow (in russian).
20. Tamaru K. *Interface Chemistry.* Iwanami Shoten Publ 1980.