МОДЕЛИРАНЕ ФОРМИРАНЕТО НА НАНОСТРУКТУРИ ОТ $CaCO_3$ В ОБРАТНА (W/O) МИКРОЕМУЛСИОННА СИСТЕМА

Адриана Георгиева*, Краси Панайотова, Желчо Стефанов, Богдан Богданов
Университет "Проф. Д-р Асен Златаров"-Бургас
Факултет по Технически науки, Катедра"Химично инженерство"
8010 Бургас, България
e – mails: adrianaslavova@yahoo.com; krasi2520@yahoo.com; zhstefanov@abv.bg; bogdanov_b@abv.bg*

MODELING THE FORMATION OF NANOSTRUCTURES OF $CaCO_3$ IN REVERSE (W/O) MICROEMULSION SYSTEM

Adriana Georgieva*, Krasi Panayotova, Zhelcho Stefanov, Bogdan Bogdanov
University "Prof. D-r Assen Zlatarov" – Bourgas
Faculty of Technical Sciences, Department of Chemical Engineering
8010 Bourgas, Bulgaria
e – mails: adrianaslavova@yahoo.com; krasi2520@yahoo.com; zhstefanov@abv.bg; bogdanov_b@abv.bg*
** - author for correspondence*

ABSTRACT

Recently, microemulsions have shown their potential as an interesting alterntative reaction medium for the production of relatively monodisperse small colloidal nanoparticles. The water-in-oil microemulsion (W/O) can be regarded as specific microreactor which allows: realization of chemical reactions, synthesis of different by nature nanostructures and control synthesis parameters. The aim of this article is to model the formation of nanostructures of $CaCO_3$ in the reverse microemulsion system. Studied model is water/oil (inorganic solution $Ca(OH)_2$/n-hexane/Aerosol-OT) system. A mathematical model is carried out of the preparation of nanoparticles of $CaCO_3$ in the microemulsion by a chemical reaction. Determined the distribution of particle size in the microemulsion in one drop.

Key words: *W/O microemulsion systems, particle synthesis, carbonate nanoparticles, mathematical model*

INTRODUCTION

Nanotechnologies are of fundamental importance in modern chemical industry and the study of their laws is a major preblem for their optimal design and control.

The synthesis and processing of ultrafine solid particles at the nanometer scale (characteristic length 1–100 nm) is of interest for a great number of existing and upcoming technological applications. Beside their use as active compounds in heterogeneous catalysts they are processed, for instance, as semiconductors, for enhanced magnetic and optical devices or for the production of advanced bulk materials. Because the special physical and chemical properties of nanoparticles are strongly size dependent, the major challenge for a synthesis process is to control particle size, shape and particle size distribution (PSD) [1, 3].

Nowadays, a variety of existing methods provide the know-how of defined nanoparticle synthesis of very different materials at the laboratory scale. Recently calcium inorganic particles in micro- and nanosize are prepared by various methods for the various applications. Several synthetic procedures have been designed for control of the formation of naoparticles of metal carbonates. Two routes seem important: precipitation from homogeneous solution and synthesis in microemulsion (reversed micelles) [3].

And since the demand of tailored nanomaterials for industrial applications is permanently increasing, the research on scaling-up approaches of developed and proved laboratory methods are becoming more and more important. A successful technique for the controlled preparation of very small and narrowly distributed nanoparticles is the use of w/o-microemulsions.

Recently, microemulsions have shown their potential as an interesting alternative reaction medium for the production of nanoparticles. The nanodroplets in these microemulsions are filled with different reactants and act as small reactors where the fusion–fission phenomena between the droplets lead to a controlled uniform micromixing. This has been evidenced by a number of groups during the last decade for different nanomaterials and a variety of microemulsion systems [1÷4]. However, the usability of the suggested microemulsion components (costs, availability), a key issue with respect towards a technical scale realization, was neglected in most scientific investigations.

In order to use a microemulsion system in a production technology one has to study a multitude of process parameters in order to find suitable variables to control and adjust the properties of the particles. This research can be very costly and time consuming. Appropriate computer simulations will help to reduce both experimental research time and costs.

The aim of this article is to model the formation of nanostructures of $CaCO_3$ in the reverse microemulsion system. Studied model is water/oil (inorganic solution $Ca(OH)_2$/n-hexane/Aerosol-OT) system.

EXPERIMENTAL

1. Microemmulsions, Reactor and Modus Operandi

The method for preparation of carbonate microstructures is based on the use of a single microemulsion system, namely the colloid dispersed system of W/O type: aqueous solution/n-hexane/Aerosol-OT. The corresponding alkali suspension is inorganic phase while the organic phase is n-hexane, with the inorganic microdrops being dispersed in the organic substance. The substances composing the three-component reverse microemulsion system are comparatively low by price, easily available and easily separable.

The microemulsion samples were prepared by mixing with n-hexane and 0.01M solution of Aerosol-OT (AOT ($C_{20}H_{37}NaO_7S$)) in a glass reactor followed by addition of the particular inorganic solution (Ca(OH)2). The experiments were carried out at temperature of 25°C. Further, the ratio $R = [H_2O]/[AOT]$ was kept 20 for all reversed micelle solutions.

A method for preparation of carbonate nanostructures by microemulsion technique was developed and the equipment necessary for process studied was supplied. The synthesis of ultrafine $CaCO_3$ particles was carried out in an installation containing a laboratory glass reactor with stirrer. Its design, performance and specific method for the preparation of nanostructures based on alkali carbonates are as described earlier (for details see) [2÷4].

The advantages of the technology for nanosynthesis developed are as follows: the initial materials are easily available and at comparatively low price, use of small amounts of raw materials; easy control of the microemulsion system during the nanostructure synthesis process; comparatively simple installation and this is a clean and non-contaminating technology.

2. Precipitation reaction of anionic system (one particle in one droplet)

Precipitation a process in which a solid phase is formed as a result of a chemical reaction of two or more components contained in the liquid phase [1]. Ex : $A(L) + B(L) \rightarrow C(S)$.

2.1. Studied model system

Studied model is water/oil microemulsion system (inorganic solution $Ca(OH)_2$/n-hexane/Aerosol-OT). These ternary mixtures, usually consisting of water, a nonpolar solvent (oil phase) and a surfactant, are thermodynamically stable, optically clear and isotropic one-phase solutions. In case of w/o microemulsions (also named reverse micelles) nanometer sized water droplets are stabilized by a surfactant monolayer and segregated by a continuous oil phase.

Only one microemulsion system of the type W/O was used, i.e. a particular case of the microemulsion method was realized whith only one colloid-dispersed system containing one of the reagents is prepared while the other is fed into the reactor in the form of gas or liquid.

Schematically the formation of a nanoparticle in a single drop is shown in Figure 1.

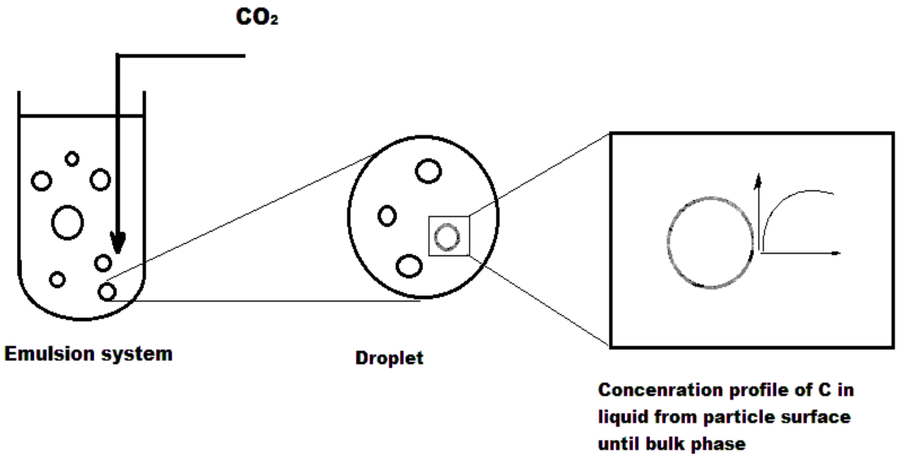

Figure 1. Important population dynamic mechanisms

2.2. Chemistry of the reaction

The chemical interaction between $Ca(OH)_2$ and CO_2 can be described by the following general equation:

$$Ca(OH)_2 + CO_2 \rightleftharpoons CaCO_3\downarrow + H_2O$$

Within the drop the probable chemical reactions can be described as follows:

$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3\downarrow$$

2.3. Kinetics of formation of carbonate nanoparticles in W/O microemulsion (mass balance)

$$A(L) + B(L) \rightarrow C(S),\ r_C = kc_Ac_B \qquad \textbf{(2.3.1)}$$

$$\frac{dc_A}{dt} = -r_C \qquad \textbf{(2.3.2)}$$

$$\frac{dc_B}{dt} = -r_C \qquad \textbf{(2.3.3)}$$

$$\frac{dc_C}{dt} = r_C - \frac{1}{V_{drop}} \frac{dm_C}{dt} \qquad \textbf{(2.3.4)},$$

where:

$\frac{dm_C}{dt}$, [kg/s] - mass transfer rate of $C_{(s)}$ to particle interface;

$\mathbf{V_{drop}}$, [m^3] - volume of the droplet.

Assume that **ρ** is constant and particle **C** is spherical, then eq. (2.3.4) becomes:

$$\frac{dc_C}{dt} = r_C - \gamma r^2 \frac{dr}{dt} \qquad \textbf{(2.3.5)},$$

where: $$\gamma = \frac{4\pi\rho}{M_C V_{drop}}$$

Growth rate of particle is defined as:

$$\frac{dr}{dt} = G = k_G\left(c_C^L - c_C^{sat}\right)^g \qquad \textbf{(2.3.6)},$$

where:

$\mathbf{k_G}$, [(m/s)/(mol/m^3)^g] - growth rate constant;

$\mathbf{c_C^{sat}}$, [mol/m^3] - C saturation concentration;

$\mathbf{c_C^L}$, [mol/m^3] - concentration of C in liquid.

The distribution of the concentration of all the reagents over time is presented us Figure 2.

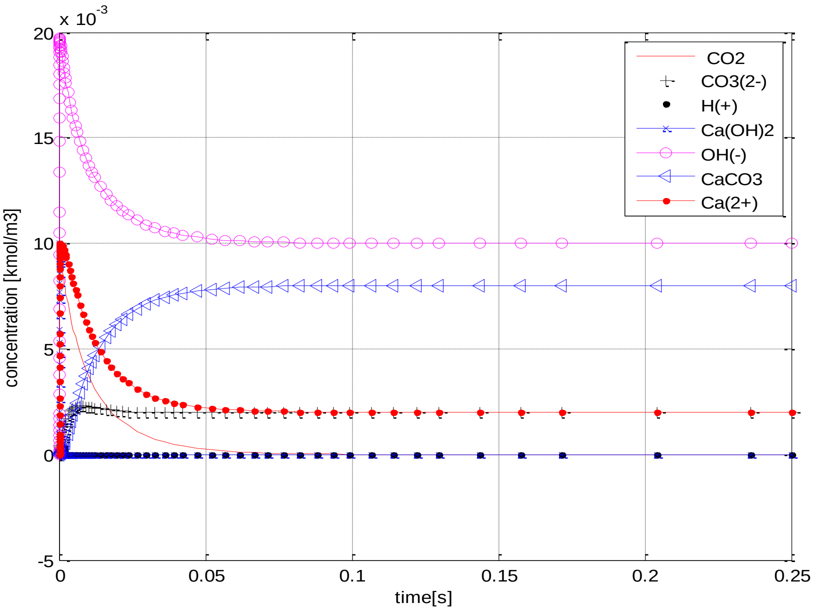

Figure 2. Concentration of all reactants over 0.25 (s)

The concentration of the A, B and C (kmol/m^3) over time τ (s) for the investigated system and the process is expressed graphically in Figure 3.

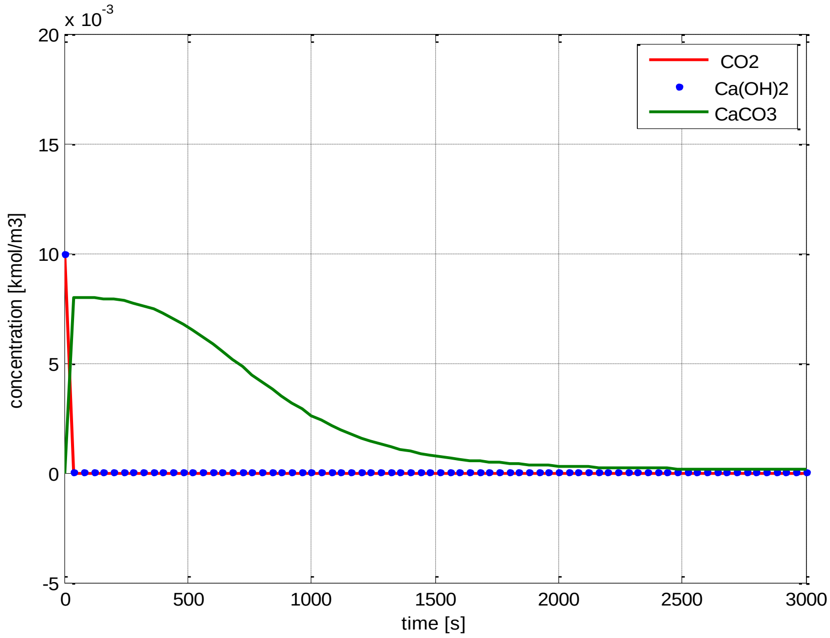

Figure 3. Concentration of A, B, and C (kmol/m^3) over time τ (s)

The increase of the amount of formation was nanostructures over time by a chemical reaction is presented in Figure 4.

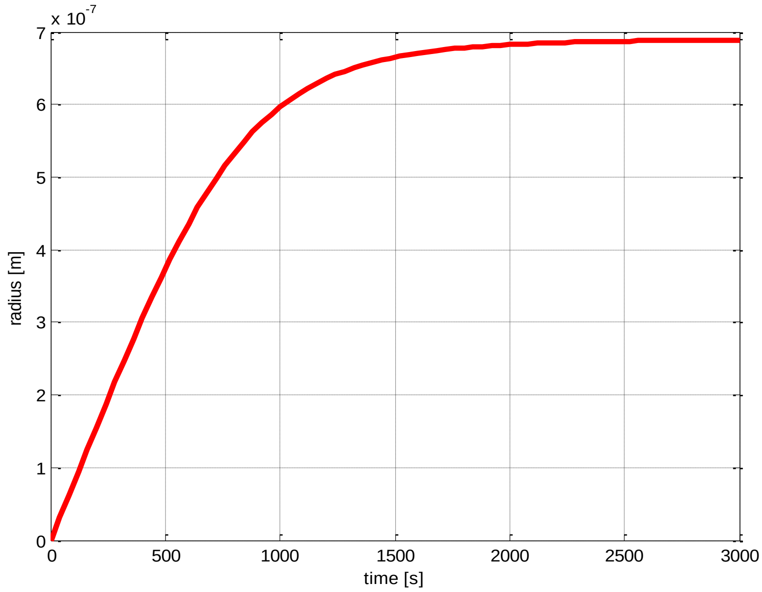

Figure 4. Size of particle r (m) over time τ (s)

CONCLUSION

Studied model is water/oil (W/O (inorganic solution $Ca(OH)_2$/n-hexane/Aerosol-OT)) microemulsion system as the reaction medium for the preparation of carbonate nanostructures. Modeling is done on the formation of nanoparticles of $CaCO_3$ in the reverse microemulsion. Are described chemistry and kinetics of the sampled reaction and graphically interpreted results. Determined the distribution of particle size in the microemulsion in one drop.

ACKNOWLEDGMENT

The authors want to acknowledge the support of the project by the National Science Fund of Ministry of Education and Science – Bulgaria.

REFERENCES

1. Voigt, A., D. Adityawarman, K. Sundmacher, 2005, Size and distribution prediction for nanoparticles produced by microemulsion precipitation: A Monte Carlo simulation study, Nanotechnology, 16, p. 429-434.
2. Slavova, A., Chr. Karagyozov, J. Ulrich, B. Bogdanov, 2009, 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, 1 (4), p. 324 - 328.
3. Georgieva, A., Chr. Karagiozov, J. Ulrich, B. Bogdanov, Y. Denev, 2010, Nano-sized $BaCO_3$ particles - a study the effects of the physico - chemical conditions on the systhesis in a water in oil microemulsion systems, Asian Chemistry letters, 14 (2), p. 141-148.
4. Георгиева, А., Б. Богданов, 2011, Разработване на методика за получаване на карбонатни наноразмерни частици в обратна микроемулсионна система, “Химични, биохимични технологии и опазване на околната среда, Сборник доклади, Школа 10.11 – 12. 11. 2011г. Бургас, стр. 1-5.