Effects of the reaction rate on the size control of nanoparticles synthesized in microemulsions

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Abstract

Microemulsions are very versatile reaction media which find nowadays many applications. Microemulsions have been used to control the particle size of many inorganic and organic materials because they induce drastic changes in the reagent concentrations and this can be particularly used for tuning the reaction rates. The influence of the chemical reaction rate on the final size of nanoparticles prepared in microemulsions is studied by computer simulation. We found that different chemical reaction rates lead to different final nanoparticle size. This result is explained mainly due to the ripening contribution to nanoparticle growth.
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1. Introduction

Nowadays, there is a great interest in nanotechnologies and the developing of simple and reproducible methods to synthesize nanomaterials has attracted the interest of many researchers. The microemulsion method is a good candidate for this purpose. The technique of microemulsions to produce nanoparticles has already 20 years of history behind [1,2], but the mechanisms to control the final size and the size distribution are still not well known. The knowledge of the mechanism is a crucial step in order to extend the potential applications of this technique. The nanodroplets can be used as nanoreactors to carry out chemical reactions. It was assumed that these nanodroplets could be used as templates to control the final size of the particles. However, the research carried out in the last years has shown that besides the droplet size, several other parameters play an important role in the final size distribution. As an example, microemulsions have been used to produce nanoparticles of pure metals like copper [3,4], silver and silver halides [5,6], metal sulfides [7–10] and so on. These experimental studies report the effects of various parameters on particles sizes and particle size distributions. In spite of the advantages offered by the microemulsion technique, the results vary depending on the reaction conditions employed. Therefore, much has yet to be done in order to understand the mechanism of particle formation and also to obtain a better control of its size. To gain more insight into this problem, we carried out computer simulations on the formation of nanoparticles in microemulsions to elucidate the kinetics and mechanism of formation of these particles [11–14]. In addition, the influence of different synthesis variables was also studied. The simulation model was successfully applied to explain the experimental results of different reactions in microemulsions [15,16]. This paper is focused to the study of influence of the chemical reaction rate (v_r) on the size of nanoparticles and how other synthesis parameters, like concentration, can modify the behaviour. For this purpose, we improve our previously developed simulation algorithm to introduce the chemical reaction rate parameter.

2. Simulation procedure

The computer simulation of the formation of nanoparticles in microemulsions was carried out using the model

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previously reported [13]. Briefly, each simulation begins with 1000 microemulsion droplets randomly located on a three-dimensional cubic lattice (volume fraction $\varphi = 10\%$). Droplets diffuse on the lattice by performing random walks to nearest neighbour sites, subject to the exclusion principle and using cyclic boundary conditions. The time unit base is 1 Monte Carlo step (mcs), which is defined as the time taken for all droplets to move in one step into one of their nearest neighbors. A half of droplets carried c_A molecules of reactant A and a half of droplets carried c_B molecules of reactant B. In this paper, we will discuss results using $c_A = c_B = 4$ (low concentration) and $c_A = c_B = 32$ (high concentration). At the beginning of each simulation, the reactant species were distributed throughout the droplets using a Poisson distribution:

$$P(n) = \frac{\langle n \rangle^n}{n!} \exp(-\langle n \rangle) \tag{1}$$

where $P(n)$ is the probability that a droplet contains n reactants (A or B) whose average occupancy is $\bar{n}$.

Microemulsions are used as microreactors because they can exchange the content of their droplets through a collision. Droplets collide when they occupy contiguous lattice

sites and they can establish a channel forming a transient dimer, exchanging their contents (reactants and/or products). Exchange criteria depend on the species inside the droplets (see Refs. [12,13] for details). After collision between two nanodroplets containing different reactants, reactants can be transferred and both reactants can be located inside the same droplet.

In previous researches, we considered a instantaneous reaction $(A + B \rightarrow P)$, so that the simulation procedure was only addressed to study reactions which are controlled by the interdroplet exchange. In the present study, the algorithm was improved to include different reaction rates. Only a percentage v_r of reactants inside the colliding droplets gives rise to products. The fastest reaction corresponds to $v_r = 1$ (100% reactants transform in products).

All units of products inside a single droplet were considered to be aggregated in a single particle (a cluster of P units). These aggregates of P units grow by different mechanism (see below), giving rise to the observed final particles.

As the reaction takes place, more droplets could contain products and reactants simultaneously. The reaction inside the microemulsion droplet can be catalyzed by the surface
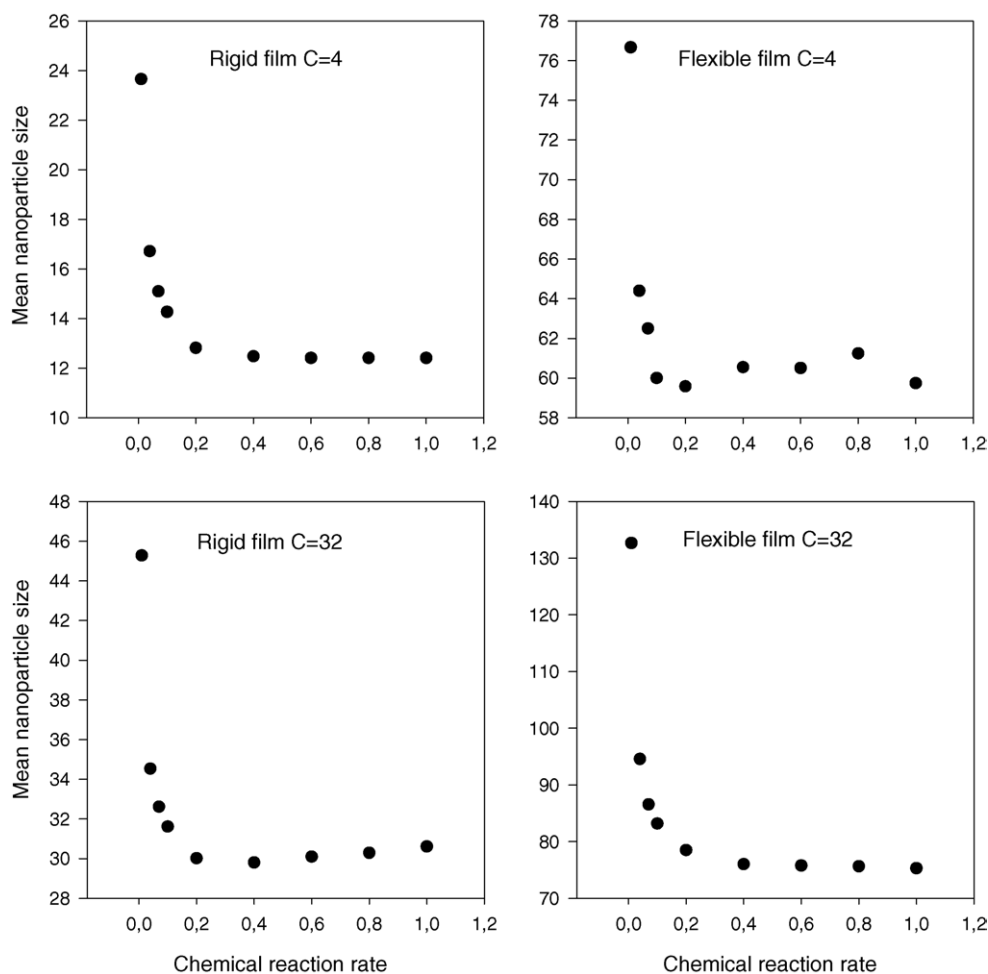

Fig. 1. Mean nanoparticle size (number of P units constituting a particle) obtained at the end of the synthesis vs. chemical reaction rate v_r (reactants fraction which give rise to products), using different combinations of the film flexibilities and reactant concentrations.

of an existing aggregate. To simulate this phenomenon, it is assumed that when one of the droplets is carrying an aggregate, the reaction always proceeds on the aggregate and the reaction rate will be double. When both droplets are carrying aggregates, autocatalysis takes place on the bigger one because a larger aggregate has a greater probability of playing as a catalyst because of its bigger surface.

The film flexibility depends on the type of surfactant, cosurfactant and oil used. From a thermodynamical point of view, the film flexibility increases on approaching the upper boundary of the microemulsion due to the increase of the dif-
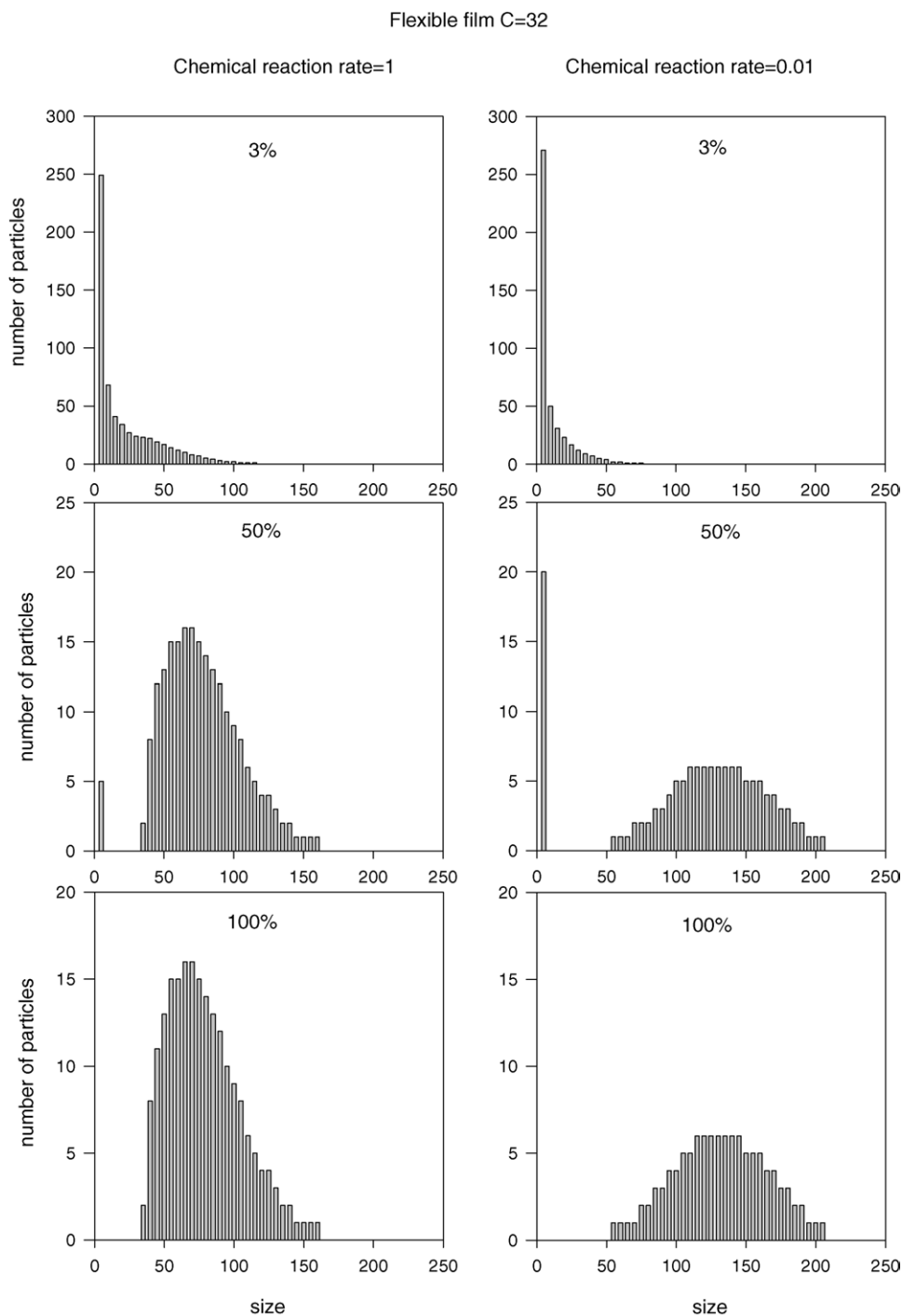

Fig. 2. Size distribution during the course of the nanoparticle formation. The size is given by the number of *P* units constituting a particle. Left column: $v_r = 1$, fast chemical reaction. Right column: $v_r = 0.01$, slow chemical reaction. The film flexibility ($f = 30$, $k_{ex} = 5$) and reactant concentration ($c_A = c_B = 32$) were kept constant. The last histogram corresponds to the equilibrium distribution and histograms A and B correspond to 3 and 50% conversion, respectively.

ference between the natural curvature and actual curvature of the surfactant film. In addition, the micellar dynamics is affected by changing length of the oil phase [5]. To introduce this phenomenon in our simulation, we can relate the flexibility of the surfactant film around the droplets and the ease with which channels communicating colliding droplets can form. Surfactant film flexibility therefore also places a limit on the size of the particles traversing the droplet–droplet channels. The influence of surfactant film flexibility is taken into account by varying a flexibility parameter (f) specifying a maximum particle size for transfer between droplets: P particles with more than f units are not allowed to pass from one droplet to another. A highly flexible film will allow the interchange of larger aggregates than a rigid film. The ripening relies on mass transport from smaller to larger particles: if a droplet containing i units of product (P_i) collides with another droplet (P_j), the smaller aggregate can be interchanged during a collision to the droplet carrying the larger particle ($P_i + P_j \rightarrow P_{i+j}$), provided the film flexibility allows this interchange.

The simulation allows also modify the droplet size. We have introduced a parameter q which restricts the maximum number of products (and therefore, the maximum particle size) which can be carried by a droplet. This influence was studied previously and in this simulation, there is no restriction by droplet size. The relation between droplet size and unit lattice is given by the collision definition; two droplets collide when they are located on contiguous lattice sites. Then, the lattice unit is two times the droplet radius.

3. Results and discussion

Fig. 1 shows the mean final nanoparticle size for different chemical reaction rates and different synthesis conditions. For all cases, larger particles sizes were obtained when the chemical reaction rate is slow ($v_r < 0.2$). Therefore, under this conditions, chemical reaction rate and particle size are case inversely related. To understand this result, it is interesting to know how the chemical reaction rate affects the nanoparticle formation process.

Fig. 2 shows the size distribution during the course of the nanoparticle formation for a fast reaction (left column, $v_r = 1$) and for a slow one (right column, $v_r = 0.01$), keeping constant the film flexibility ($f = 30$, $k_{ex} = 5$) and reactant concentration ($c_A = c_B = 32$). The last histogram corresponds to the equilibrium distribution and histograms A and B correspond to 3 and 50% conversion, respectively. One can observe that, at the beginning of the process (3% conversion), a large quantity of droplets carrying very small particles appears. By observing the size histograms at 50% conversion, one can see a very different behaviour depending on the chemical reaction rate. When the chemical reaction is fast, most of the nanoparticles have already reached the final size and a very low number of the smallest particles are appearing (see Fig. 2, left column, 50%). On the contrary, a high number of nuclei

are still forming at this stage when the reaction is slow, as one can observe in Fig. 2 (right column, 50%). At the same time, some particles have already grown to the final value. This means that in this case, nucleation and growth takes place simultaneously. This overlapping of nucleation and growth processes, which is more pronounced as the chemical reaction is slower, leads to larger and more polydisperse final nanoparticle sizes. Similar qualitative behaviours are found used different synthesis conditions (different concentrations and film flexibilities).

Chemical reaction rate directly affects the time evolution of the number of nuclei, which determines both nucleation and growth process. First, the influence on nucleation is obvious: nucleation is faster when the chemical reaction is faster. Second, growth will be strongly influenced by the nuclei number already formed at a given time. A great number of nuclei favours a fast autocatalytic growth, giving rise to a large number of small particles. Chemical reaction controls this kind of growth, being the autocatalytic growth faster as chemical reaction is faster. But in nanoparticle formation, there is another contribution to the growth: a small particle can traverse the interdroplet channel during a collision and be added to a larger particle (growth by ripening). This kind of growth only can take place if the nanoparticle can be transferred between droplets. Keeping constant the film flexibility, which determines the size of the interdroplet channel, ripening can occur if there are small enough particles. A slow chemical reaction favours a continuous nuclei production, keeping always a certain number of nuclei in the system. As a result, growth by ripening can take place during the whole process. This fact explains the bigger particle size obtained for a slow reaction. One can conclude that a slow chemical reaction rate is associated with a more important ripening contribution to the growth. Therefore, in this case (slow reactions, $v_r << 1$), compartimentalization does not play an important role and the behaviour is similar to that predicted by the classical crystallization theory in homogeneous media.

4. Conclusions

Monte Carlo simulations allow us to explain recent results concerning the influence of chemical reaction rate on particle size distributions. A decrease in nanoparticle formation rate gives rise to a larger final particle size for all the studied synthesis conditions. Chemical reaction rate affects both nucleation and growth process. It has been shown that nucleation and growth take place simultaneously when the chemical reaction is slow. In addition, the ripening contribution to the growth is larger as the chemical reaction is slower.

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