The Influence of Reactant Excess and Film Flexibility on the Mechanism of Nanoparticle Formation in Microemulsions: A Monte Carlo Simulation

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In this paper we have studied by Monte Carlo simulation the influence of reactant excess (*x*) and film flexibility (*f*) on the final size of particles obtained by reaction in microemulsions. We have observed that the ripening mechanism is more significant as reactant excess and film flexibility increase because, when one of the reactants is exhausted, ripening is the only possible way of growth. This gives rise to a faster growth process. Experimental results of particle sizes for different *x* values agree with the results obtained by simulation, which provides an explanation of the growth mechanism. These results show that both parameters (*x* and *f*) are important in order to explain the final size distributions of particles obtained in microemulsions.

Introduction

Microemulsions provide good media for the preparation of relatively monodisperse small colloidal particles which, among other applications, can be used as catalysts.[1–4] The role of microemulsions is to compartmentalize reactants. From a mechanistic point of view, it is known that kinetic confinement within a water pool facilitates nucleation and limits the growth of particles. Nevertheless, a complete understanding of the process of particle formation in these restricted media has not been achieved.

The nucleation and growth processes involved in particle formation in homogeneous media are well-known.[5] According to the classical crystallization theory, the final particle size depends mainly on the ratio of nucleation to growth rates. A slow nucleation process leads to a low number of nuclei which can grow and reach a large polydisperse size. On the contrary, if the nucleation process is quick, a large number of nuclei are formed, so the final particle size will be small and monodisperse. However, particle formation in a compartmentalized medium is different because interdroplet material exchange plays an important role in the mechanism. In this paper, we will show that the kinetics and final particle size depend on the size of the channel communicating colliding droplets as well as on the ripening contribution in the whole process.

Simulation Procedure

The computer simulation of nanoparticle formation in microemulsions was run to simulate the kinetic course of the reaction. It was developed based on the model previously reported.[6,7] This model has been successfully applied to explain the experimental results of different reactions in microemulsions.[6–9] Each simulation begins with 1000 microemulsion droplets randomly located on a two-dimensional square lattice. A total of 10% of the space is occupied by droplets (volume fraction of droplets $\varphi =$ 0.1). Droplets diffuse on the lattice by performing random walks to nearest-neighbor sites, subject to the exclusion principle; i.e., we do not allow more than one droplet to occupy a given site at any one time. Cyclic boundary conditions are enforced at the end of the lattice.

Initially, 500 droplets carried c_A molecules of A and 500 droplets carried c_B molecules of B. The reactant species were distributed throughout the droplets using a Poisson distribution:

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

where $P(n)$ is the probability that a droplet contains n reactants (A or B) whose average occupancy is $\bar{n}$. The concentration of A was kept constant ($c_A = \bar{n} = 32$) in all simulations. To study the influence of the reactant excess, the concentration of B has been changed in each simulation ($4 \le c_B = \bar{n} \le 32$).

All simulations were run for 10 000 Monte Carlo steps (mcs); 1 mcs was defined as the time taken for all droplets to step to a nearest neighbor.

Microemulsions are used as microreactors as they can exchange the content of their droplets through a collision. Droplets collide when they occupy contiguous lattice sites. Because the rate of communication between droplets is very fast,[10] it is assumed that this exchange can only take place when an energetic collision between two droplets is

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able to establish a water channel between the droplets,[10] forming a transient droplet dimer.[11] This process is energetically unfavorable because it implies a change in the curvature of the surfactant film.[11,12] Therefore, the rate constant of this process is not diffusion-controlled, and only a very small fraction of the total collisions (1 in 1000 for AOT, sodium dioctyl sulfosuccinate, surfactant films) between droplets leads to reactant exchange.[10] The intermicellar exchange process, governed by attractive interactions between droplets,[13] can be modified by changing the bulk solvent used to form the micellar solution. In most cases droplet communication is the rate-determining step in particle formation.[14] This study is focused on reactions which are controlled by the inter-droplet exchange[15] (very fast chemical reactions), and we assume that each collision between reactants gives rise to the formation of products. This is a valid approximation when the reaction is very quick in comparison with the interdroplet exchange rate.

Consequently, in our simulation it is assumed that when two droplets step onto contiguous sites, they can establish a water channel, forming a transient dimer.[11] At this stage, water cores can interchange their contents. Depending on the nature of the species inside the droplet, the employed interchange criteria will be different.

1. The *interchange of reactants in the absence of products* leads to two possible situations:

1.1. If both droplets carry the same reactant, one reactant from the droplet containing a higher number of reactants will go to the droplet containing a lower number of reactants (concentration gradient).

1.2. When the two droplets containing different reactants (A and B) collide, one reactant goes through the channel from one droplet to the other one, in which the chemical reaction instantaneously takes place (A + B → P). Therefore, we assume that only one product can be obtained in each collision. Assuming again a concentration gradient, this first product will locate inside the droplet carrying a lower number of reactants. All units of products inside a single droplet are considered to form a single cluster of P units, which is called a P aggregate. These aggregates of P units grow by different mechanisms (see below), giving rise to the observed final particles.

2. The *interchange of reactants in the presence of products* allows us to simulate an *autocatalytic* reaction, which will be catalyzed by the existing P aggregates. To simulate this phenomenon, it is assumed that when one of the droplets is carrying an aggregate, the reaction always proceeds on the aggregate. When both droplets are carrying aggregates, autocatalysis takes place on the bigger one. Therefore, we consider that a larger aggregate has a greater probability of playing as a catalyst because of its larger surface. In this way, we consider that the reaction proceeds faster on an aggregate surface (auto-catalysis) than in the absence of P.

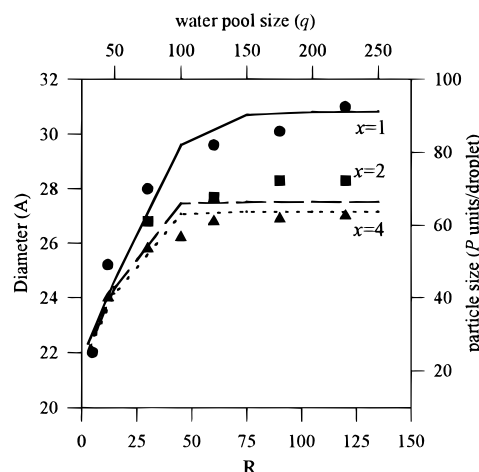3. The *interchange of aggregates* becomes more important as the reaction takes place because more and more

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Figure 1. Particle size versus droplet size. Symbols show CdS particles obtained in AOT/isooctane/water microemulsions using different ratios of $x = c_A/c_B = [Cd^{2+}]/[S^{2-}]$ (data taken from ref 19); lines show simulation results for different values of x and a fixed value of $f = 30$ (P aggregates of less than 30 units can be interchanged).

droplets carry P aggregates. At this stage, collisions between two droplets both containing aggregates are the most probable. The interchange of aggregates or reactants during the collision is allowed. To simulate the interchange of aggregates between droplets, some aspects have been taken into account:

3.1. The interchange becomes more difficult as the aggregates grow. The *flexibility of the surfactant film* around the droplets governs the ease with which channels communicating colliding droplets can form and also the size of these channels. To study the influence of the film flexibility, we have introduced the variable *f*, defined as the maximum size of the aggregate which can be interchanged: aggregates with a number of P units bigger than *f* were not allowed to transfer from one droplet to another. In this way, a highly flexible surfactant film will allow the interchange of larger aggregates than a rigid surfactant film will allow.

3.2. It is well established that larger particles grow as smaller ones disappear by means of *ripening*. This mechanism, called *growth by ripening,* implies mass transport from small particles to larger particles, and it has been introduced in the simulation in the following way: if one droplet containing an aggregate with a number of *i* units (P_i) collides with another droplet containing an aggregate with a higher number of P units (P_j), the smaller aggregate can be interchanged from the initial droplet to the droplet carrying the larger aggregate, giving rise to a bigger one ($P_i + P_j \rightarrow P_{i+j}$), provided the film flexibility and droplet size allow this interchange. To take into account the influence of droplet size, we have introduced in the simulation a parameter *q* which restricts the maximum number of products P (and therefore the maximum particle size) which can be carried by a droplet. In each simulation, all droplets have the same size.

Results and Discussion

Influence of Film Flexibility and Reactant Excess on the Nanoparticle Size. Figure 1 shows the influence of reactant excess on the final nanoparticle size using different ratios of [H₂O]/[surfactant]. Assuming simple geometrical arguments, the size of the droplet is expected to be proportional to the mole ratio $R = [H_2O]/[surfactant]$. This has been experimentally confirmed by techniques

such as small-angle neutron scattering,[16] ultracentrifugation,[17] and time-resolved fluorescence quenching.[18] Thus, the size of the water cores can be changed simply by changing R, and the compartmentalized water droplets of different sizes can then be used to control the particle growth. In Figure 1 is shown the change of the particle size with R for different reactant excess, defined as $x = c_A/c_B$, with $c_A = [Cd^{2+}]$ and $c_B = [S^{2-}]$, for the formation of CdS particles in an AOT−water−isooctane microemulsion (data taken from ref 19). Lines in Figure 1 show simulation results for different values of x. Good agreement is obtained between experiment and simulation. For all values of x, it can be observed that droplet size controls particle size; i.e., the particle grows until its size becomes comparable to the droplet size for small droplets sizes (*droplet control*). For large droplets exhaustion of reactants causes the plateau observed in Figure 1 (*concentration control*). For $x = 1$ this is a well-known result,[19] which has been previously confirmed by simulation.[8] We will focused our attention on the influence of the reactant excess ($x > 1$) on the final particle size as well as on the particle formation mechanism.

In Figure 1 it is also observed that particle size increases with droplet size for all values of x. It can be noticed that the biggest sizes are obtained for $x = 1$ and the size of CdS is always smaller when one of the two reactants is in excess ($x = 2$ or 4). Some authors[2,4,19] have explained this result by assuming that the crystallization process is faster when one of the species is in excess. However, this explanation does not take into account the spatial restrictions when the reaction takes place in microemulsions. In this case interdroplet exchange can play an important role in the final size.

The results in Figure 1 correspond to a fixed value of film flexibility. The intermicellar exchange process, related to the attractive interactions between droplets, can be modified by changing the surfactant used to form the micellar solution. Because AOT−isooctane−water microemulsions seem to correspond to a film flexibility value $f = 30$ (see Figure 3 in ref 7 and Figure 3 in ref 8), we have used this value in the simulation. When isooctane is replaced with cyclohexane as the bulk solvent, a decrease in the intermicellar potential with an unchanged value of the water pool radius is observed.[20] The micellar exchange rate constant measured by Robinson et al.[14] decreases by a factor of 10, and therefore a smaller value of f has to be employed ($f = 15$; see Figure 3 in ref 7). Although in our simulation we do not explicitly indicate that the rate constant for droplet communication depends on surfactant film flexibility, previous results[6] allow us to conclude that a rigid film would be associated with a slow interdroplet communication rate because a high flexibility implies that a larger stable channel is formed in each collision. This leads to a high exchange rate. On the contrary, a very rigid film tends to form nearly hard-sphere droplets,[21] giving rise to short lifetime channels which slow down the exchange rate. To study only the influence of film flexibility in the final particle size, we have carried out our simulation with large enough droplets (large q values).
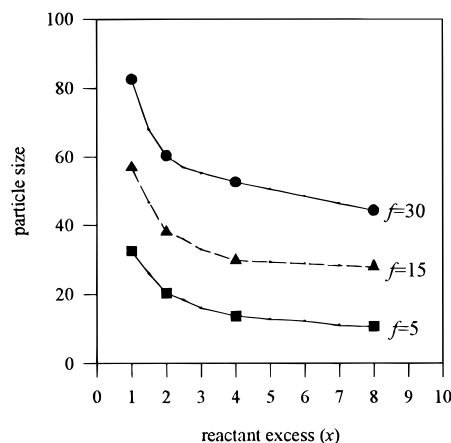
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Figure 2. Particle size versus reactant excess x ($x = c_A/c_B$) for different values of film flexibility. No restriction in droplet size. The lines are simply a guide to the eye.
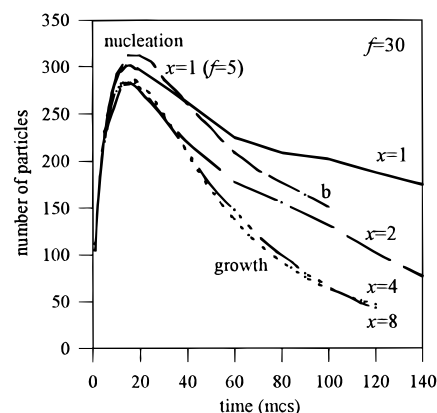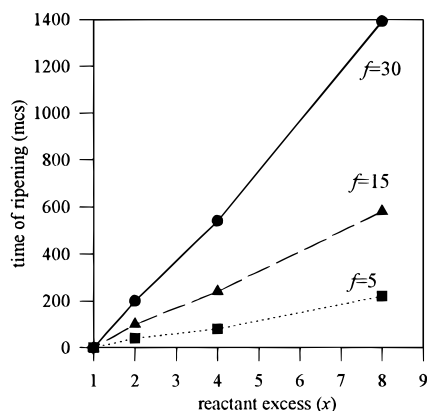

Figure 3. Time evolution of droplets carrying aggregates smaller than 10 P units for different values of x ($x = c_A/c_B$). All curves were simulated for $f = 30$, except curve b which corresponds to $f = 5$ (aggregates of less than 5 units can be interchanged) and $x = 1$ ($c_B = c_A$).

In this way the droplet size does not have any influence on the particle size. Figure 2 shows the final particle sizes obtained by simulation, using different f values, for a fixed droplet size and different reactant excesses. For the same reactant excess, it is observed that particle size increases as f increases. On the other hand and according to experimental results,[15] nanoparticle size decreases for any value of surfactant film flexibility as the excess of one of the reactants increases.

The explanation of this result is related to the particle growth mechanism. The formation of nanoparticles in microemulsions involves the existence of two well-defined processes associated with the nucleation and growth of the particles.[18] Therefore, it is important to study the influence of f and x on both nucleation and growth. Nanoparticle growth can take place via reaction on an existing product (growth by autocatalysis) or via ripening (growth by ripening).

Influence of Film Flexibility and Reactant Excess on the Nucleation Process. Figure 3 shows the initial stage of nanoparticle formation, i.e., the nucleation process. The number of small aggregates (aggregates formed by less than 10 P units), which simulate nuclei, is plotted against the initial time (the first 140 mcs), for a large value of droplet size (no restriction by droplet size). Each curve corresponds to a different value of reactant excess $x = c_A/c_B$. One can observe the existence of two well-defined processes: nucleation and growth. Nucle-

Figure 4. Ripening time versus reactant excess (x) for different values of surfactant film flexibility. Lines are simply a guide to the eye.

Figure 5. Time evolution of the number of droplets carrying aggregates smaller than 10 P units for a fixed value of reactant excess $x = 4$ ($c_B = 8$, $c_A = 32$) and different values of surfactant film flexibility. This inset shows results for the initial stage of the synthesis.

ation is associated with an increase in the number of nuclei and growth is associated with a decrease. It is interesting to note that the presence of this maximum has also been spectrophotometrically detected by Towey et al.[14] and by time-resolved SAXS by López-Quintela and Rivas[22] for the synthesis of nanoparticles in AOT microemulsions. Similar results have been obtained for different film flexibilities. It is observed in Figure 3 that both f and x hardly influence the nucleation process although they have a great influence on the growth. It can also be observed that the maximum slightly decreases when one of the reactants is in excess. This could be explained by taking into account that, for $x > 1$, one of the reactants is exhausted very early, so the reaction is more difficult and this gives rise to the formation of a smaller number of nuclei.

Influence of Film Flexibility and Reactant Excess on the Growth Process. The growth processes can be observed after the maximum in Figure 3 is reached. It must be noted that small aggregates disappear faster as the concentration excess increases; i.e., the rate of growth is higher when one of the reactants is in excess, although this effect is less important for very high reactant excess. Similar qualitative behaviors are obtained using different surfactant film flexibilities. To explain these results, we must take into account that, for $x = 1$, the two possible mechanisms of growth, autocatalysis and ripening, contribute to the growth as has been shown in previous studies (see, e.g., Figure 1 in ref 6). For $x > 1$ growth is mainly due to ripening because growth by autocatalysis ends when one of the reactants is exhausted. Growth by ripening is faster than growth by autocatalysis because by autocatalysis only one unit of P is added to an aggregate at each collision. On the contrary, growth by ripening implies that, in each effective collision, the aggregate increases by more than one P unit. Moreover, this kind of growth can take place even though there is no reactant in the medium. One can then say that the whole growth process is faster as the ripening contribution is greater. Our simulation procedure allows us to monitor the time in which the growth is only due to the ripening mechanism. For this purpose we calculate the time needed to attain the equilibrium distribution of particle sizes. The difference between this time and the time at which the last reactant disappears will be the ripening time, because the only possible way of growth in this situation is by ripening. Figure 4 shows the simulation results using
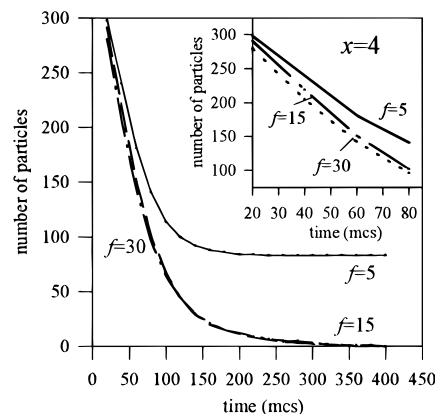
different surfactants (different f values) and different concentration ratios (x). Two conclusions can be drawn from this figure. First, the ripening time increases significantly as x increases for any f value. These results agree with the explanation given above because for the same film flexibility, when x increases, one of the reactants is earlier exhausted. Afterward, no autocatalysis can take place, and therefore the ripening contribution increases. Second, the ripening time is greater as flexibility increases for any reactant excess. This is because by ripening aggregates can grow further whenever the size of the interdroplet channels (f) allows the exchange. Therefore, one can expect nanoparticle formation to be faster as f increases, keeping the reactant excess fixed. The growth of nanoparticles for different f values and $x = 4$ ($c_A = 32$, $c_B = 8$) is shown in Figure 5. At the first stage of the synthesis, it can be observed that growth is faster as f increases, as expected (see the upper figure). For low values of surfactant film flexibility ($f = 5$), the curve falls more gradually until a constant value is reached, when the aggregate grows sufficiently and cannot be exchanged because of to the control of interdroplet channel size. For more flexible films ($f = 15$ and 30), growth is faster and more time is needed to reach a constant value, as expected. The behavior found using $f = 15$ and 30 is similar because aggregates containing less than 10 P units are observed and both values of interdroplet channels are larger than 10, so interdroplet exchange is always allowed in both cases.

It is a well-known experimental result that the intermicellar exchange process controls the nanoparticle size which increases with the efficiency of the exchange process.[15,23,24] This could be explained by our simulation results because, as the size of the channel which communicates colliding droplets is proportional to the surfactant film flexibility, the fact that large particles are favored by ripening at high f values[6,7] implies that the rate will be higher as f increases. Therefore, the effective rate constant for droplet communication will be greater.

Conclusions

Our simulation has allowed us to reproduce the experimental results about the influence of the reactant excess on the final particle size. It has been observed that the nucleation process is hardly affected by the

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reactant excess, but this has a big influence on the growth. Therefore, the explanation given in the literature about a faster nucleation when one of the reactants is in excess is not totally correct. Moreover, it can be concluded that ripening rather than autocatalysis is responsible for the faster growth observed. It has also been proved that the surfactant film flexibility may also play an important role in the final particle size.

Finally, we can conclude that the usual classical theory used to explain the crystallization process in homogeneous media has to be modified to include flexibility, droplet size, and concentration to account for the very different experimental results obtained for the production of particles in dynamic restricted media.