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SYNTHESIS OF CaCO$_3$ NANOPARTICLES BY CARBONATION OF LIME SOLUTIONS IN REVERSE MICELLAR SYSTEMS

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Application of reverse micelles for the synthesis of nano-sized calcium carbonate particles in different solvents (cyclohexane, decane and heptane) has been investigated. The effect of the mole ratio of water-to-surfactant (R) and type of solvent has been studied on the size and nature of the carbonate particles. The results indicate that an increase in water-to-surfactant ratio results in a larger particle size.

Keywords: nanoparticles; calcium carbonate; reverse micellar systems; Ca-OT.

INTRODUCTION

Particulate products possessing specific characteristics are very important in the chemical process industry. Reverse micelles or water-in-oil microemulsions are being explored as a medium for the synthesis of nanoparticles because individual micelles act as nanoreactors/precipitators. The size of the precipitated particles is profoundly affected by the inherent physico-chemical properties of the micellar system as well as by the exchange of material between micelles.

The recipe for obtaining such fine particles usually involves conducting the precipitation in the cores of reverse micelles formed by the dissolution of a surfactant moiety (with and without co-surfactants) in an oil (solvent) phase. In these systems, nanodrops (3–30 nm) of the aqueous phase are trapped within aggregates of surface-active molecules dispersed in an external oil phase. The micellar core contains water plus the dissolved reactant, and the type/concentration of the surfactant, co-surfactant and amount of water present determine the characteristics of the precipitated product. It is necessary for the gaseous solute to enter the micellar core, via the continuous oil phase, in order to react with the aqueous reactant. The reverse micelles provide a cage-like effect that can control nucleation, growth and agglomeration. The solubilized reactant species are effectively distributed in separate nanoreactors at the molecular level. In addition, the ability to vary the size of the micellar core, by simply altering the water to surfactant ratio provides a very convenient handle to control the particle sizes. Ideally, the particles should not grow larger than the polar cores of the reversed micelles,

i.e. the micelle acts as a cage, preventing unlimited growth. However, under real conditions intermicellar exchange of material may lead to formation of particles larger than the core micellar volumes.

Many experimental studies have been undertaken using a reverse micellar system to precipitate nanoparticles. Copper nanoparticles (Pileni, 1997), silver and silver halides (Manna *et al.*, 2001; Dirk *et al.*, 1998; Bagwe and Khilar, 1997; Pileni, 1997), gold (Arcoleo and Liveri, 1996), BaCO$_3$ (Kandori *et al.*, 1988b), Fe$_3$O$_4$, Pt, Pd, Rh, Cu, Fe and Ir (Boutonnet *et al.*, 1982; Blanco *et al.*, 1994), CdSe (Stigerwald *et al.*, 1988), Ni, FeNi (Rivas and Lopez-Quintela, 1990), CdS, ZnS, PbS and Ag$_2$S (Khiew *et al.*, 2003; Cheng *et al.*, 1998; Hirai *et al.*, 1995; Suzuki *et al.*, 1996; Motte, 1996; Petit *et al.*, 1990; Lianos and Thomas, 1987), metal oxides like ZnO, TiO$_2$ (Chhabra *et al.*, 1995; Lal *et al.*, 1998; Wang and Li, 1999; Hingorani *et al.*, 1993) have been prepared by such means.

Calcium carbonate particles produced by carbonation of lime solutions or lime slurries are industrially important and find uses in diverse areas such as in the manufacture of toothpastes, lubricants, paints, textiles, plastics, adhesives, waste water treatment, rubber, ink and ceramic materials. Preparation of calcium carbonate particles has been reported in various types of reactors, e.g. stirred bubbling tank or column, rotating packed bed reactor (RPBR), Couette-Taylor reactor (Swinney *et al.*, 1982; Yagi *et al.*, 1984a,b; 1988 Wachi and Jones, 1991a,b; Jones *et al.*, 1992; Hostomsky and Jones, 1995; Wei *et al.*, 1997; Jung *et al.*, 2000). Many of these processes apply the concept of gas–liquid reactive precipitation. The particle size using these methods is restricted to the micrometer range. Of special interest is the production of nanoparticles of CaCO$_3$. Although such particles have been known for a very long time, their preparation has only received some attention in the last two decades, on account of special properties associated with them.

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Limited information is available in the literature so far for the synthesis of nanoparticles of calcium carbonate particles using reverse micelle technique (Kandori *et al.*, 1987; Kandori *et al.*, 1988a,b; Roman *et al.*, 1991). Kandori *et al.* (1988a,b) absorbed carbon dioxide into swollen reverse micelles of Ca-OT [calcium 1,2-bis-(2-ethylhexyl-oxycarbonyl)-1-ethane sulphonate], whose cores contained predissolved calcium hydroxide. They obtained mean particle sizes of calcium carbonate of 50–125 nm and found that the number of particles to the number of micelles was about 10^{-8}. Micrometer-sized calcium hydroxide particles suspended in reverse micellar solutions were carbonated by Roman *et al.* (1991) to finally obtain carbonate particles of about 6 nm size. Both these experimentally significant studies have given rise to speculations about the mechanism of formation of the carbonate particles. Apart from the usual phenomena of nucleation and growth of the product particles, other mechanisms that are likely to be important in gas–micellar systems are: intermicellar collisions driven by the Brownian motion of the micelles, the subsequent exchange of the contents of the colliding micelles and, for the case of suspended reactant, the solubilization of the reactant into the micellar core by micelle–particle collisions.

There has been some progress in the modelling of these precipitation systems. Nagy (1989) proposed one of the earliest models for the formation of nanoparticles. Hatton *et al.* (1993) have proposed a population balance approach to model the population dynamics of reverse micellar precipitation systems. A more complete modelling of the formation of nanoparticles in reverse micelles was done using population balances (Ramesh *et al.*, 2004; Natarajan *et al.*, 1996) and many experimentally observed trends have been reproduced. Li and Park (1999) carried out Monte Carlo simulations to construct particle size distributions for the synthesis of nanoparticles using reverse micelles assuming instantaneous nucleation and reaction in their model. Tojo *et al.* (1997) also carried out Monte Carlo simulations, using the random walk approach, for systems where the reaction rate is very fast. They have shown the influence of autocatalysis and ripening on the final size distribution of the nanoparticles formed, using film flexibility as a parameter. Bandyopadhyaya *et al.* (2000) removed some of the aforementioned limitations by incorporating a finite nucleation rate in the Monte Carlo models.

Thus, there are very few experimental studies available on gas–liquid and gas–slurry systems. Hence, the present investigation deals with the generation of extensive data for the production of nano-sized particles of CaCO₃. The effect of operating variables such as water-to-surfactant ratio and type of solvent on the particle size distribution has been investigated experimentally.

METHODS AND MATERIALS

Sodium bis-(2-ethylhexyl)-sulphosuccinate or Aerosol-OT (AOT) was purchased from Acros Organics and was used without any further processing. Calcium chloride, calcium hydroxide, methanol, cyclohexane, diethyl ether were used without any further purification. Water used was distilled and deionized. N₂ and CO₂ were supplied by AGA BV, The Netherlands.

Preparation of Surfactant

Ca-OT [calcium 1,2-bis-(2-ethylhexyl-oxycarbonyl)-1-ethane sulphonate] was prepared by the metathesis reaction of methanolic Aerosol-OT and aqueous CaCl₂ as described in the literature (Kandori *et al.*, 1988a,b).

Preparation of the Reverse Micellar Solution

A representative example for the preparation of a reverse micellar solution in cyclohexane is as follows: 0.835 ml of a Ca(OH)₂ solution (0.02 mol l⁻¹, 1.67×10^{-5} mol Ca²⁺, 3.34×10^{-5} mol OH⁻) was added to a solution of Ca-OT (8.82 g, 0.01 mol) in cyclohexane (100 g) at room temperature and stirred well until a clear solution was obtained. This resulted in an R value of 4.64 (R = [H₂O]/[Ca-OT]). Water was added to the system to set R to the desired value. A molar ratio of 1.67×10^{-3} was maintained for Ca(OH)₂ to Ca-OT for each experiment.

Samples of the reverse micellar solution were analysed using dynamic light scattering (DLS) to measure the diameter of the reverse micelles before the carbonation. A Zetasizer 5000 from Malvern Instruments, UK, was used for the measurements. The He–Ne laser operated at 633 nm was used as a light source.

Carbonation Procedure

A volume of 0.1×10^{-3} m³ of the reaction mixture [surfactant + solvent, i.e. cyclohexane–heptane–decane+ aqueous Ca(OH)₂] was transferred into a cylindrical bubbler as shown in Figure 1 (capacity = 0.15×10^{-3} m³). The solution was bubbled with N₂ through a metal filter for 20 min to generate an inert atmosphere. The particles of CaCO₃ were prepared by bubbling CO₂ into this reaction mixture for 3 min at 4×10^{-5} m³ min⁻¹. The reaction was stopped by replacing the CO₂ flow with N₂. The amount of CO₂ used was sufficient to obtain a theoretical yield of 100% of CaCO₃ particles in any experiment.

Identification and Size of CaCO₃ Particles

The shape and size of the CaCO₃ particles were measured by a Philips XL30 PEG scanning electron microscope
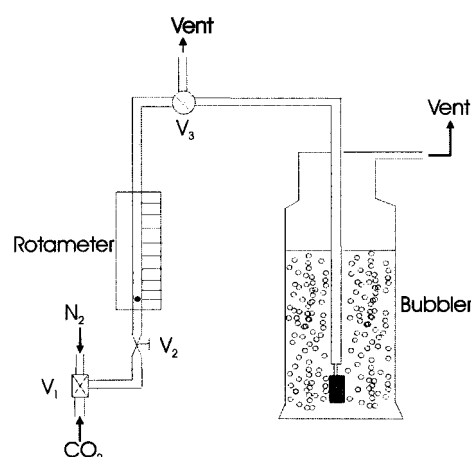

Figure 1. Experimental set-up for the carbonation experiments (V_1, V_2, V_3 are manually operated valves).

(SEM). The procedure for preparation of the sample is as follows. The reaction mixture was sprayed on a thin film of methanol on a glass plate and was dried under atmospheric conditions until all the solvent was evaporated. The residue was washed with methanol several times to remove the surfactant. The sample was dried again under atmospheric conditions till all the solvent was evaporated. The glass plate was then inserted in the SEM to obtain the images.

SEM-EDAX was applied to determine the elemental composition of the particles. The molar ratio of oxygen to calcium for these samples was found to be about 3:1, suggesting that the particles are indeed composed of $CaCO_3$. The presence of calcium carbonate particles was further confirmed by transmission electron microscope (TEM) using a Jeol 2010F field-emission gun. It was operated at 200 kV and was equipped with an EDAX detector with a super ultrathin window for an energy-dispersive X-ray spectrometry and a Gatan imaging filter model 2000 for energy-filtered imaging. The carbonated sample was sprayed onto a glass surface with a carbon grid and then dried under atmospheric conditions. It was then washed several times with methanol and dried again under atmospheric conditions before analysing with TEM.

The size distribution of the particles was determined using a scanning probe image analyser (SPIA). The analyser gave the results in form of the particle number, length, width and the surface area of the particle. The diameter of the individual particle was calculated from the surface area assuming the particles to be spherical. The particle size distribution is based on an average of 100 particles measured during the analysis.

RESULTS AND DISCUSSION

Micellar Solubilization of Ca(OH)₂

To prepare nano-sized $CaCO_3$ particles, it is essential to have some insight into the factors which determine the solubility of aqueous $Ca(OH)_2$ in the micellar solutions. Therefore, a small quantity of aqueous $Ca(OH)_2$ of 0.02 mol kg^{-1} was added to the solvent containing 0.10 mol kg^{-1} Ca-OT. Water was further added to the systems to adjust the molar ratio of water to Ca-OT ($R = [H_2O]/[Ca-OT]$). The solubility of water was measured from the transparency of the solvent at room temperature as a function of amount of water added to the systems. The maximum amount of solubilization of water was found to be dependent on the type of solvent. The value of R at which the solution became turbid was $R = 30$ for cyclohexane and $R = 40$ for heptane and decane. Thus it can be concluded that the operating window for heptane and decane is higher than for cyclohexane.

Formation of Water-in-oil Microemulsions

The size of the reverse micelles is expected to be an important parameter in the process of making $CaCO_3$ nanoparticles. The micellar size as a function of the mole ratio R ($R = [H_2O]/[Ca-OT]$) was measured in the range $R = 5–30$ using cyclohexane as the solvent. These experiments were carried out in the presence of $Ca(OH)_2$. Figure 2 shows the changes in the average diameter of micelle (as calculated from the dynamic light scattering)

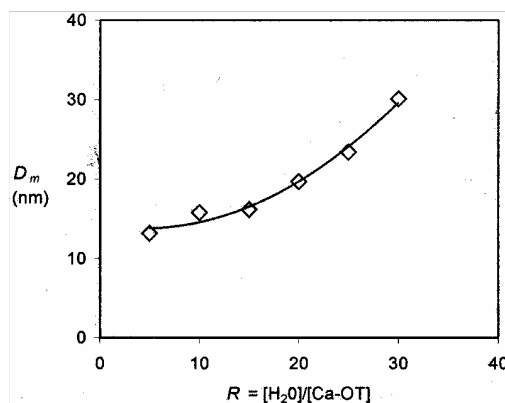*Figure 2.* The change in D_m with R for CaOT–cyclohexane systems ($T = 298$ K, $P = 1$ atm, $[Ca-OT] = 0.10$ mol kg^{-1}, $[Ca(OH)_2]/[Ca-OT] = 1.67 \times 10^{-3}$).

with R using cylohexane as a solvent. It is evident that the average micellar diameter increases with the increase in R value. Thus, it is clear that the initial size of the reverse micelle core may be tuned with the R values. This is in accordance with the results provided by Kandori *et al.* (1988a).

Formation of Particles

The actual precipitation reactions were carried out in reverse micellar solutions consisting of a continuous hydrocarbon phase (cyclohexane, heptane or decane) and a dispersed phase consisting of an aqueous $Ca(OH)_2$ solution stabilized with a surfactant Ca-OT. The precipitation reaction was started by introduction of gaseous CO_2 to the system. All experiments were carried out at room temperature, atmospheric pressure, in a set-up as given in the experimental section (Figure 1). After an experiment, the resulting solution was analysed using SEM.

Typical SEM micrographs of $CaCO_3$ particles formed are shown in Figures 3 and 4 ($R = 15$ and 30, respectively), using cyclohexane as a solvent. The particles had an average size of 62 nm for the lowest value of R. When the R value was increased, the particle size also increased.
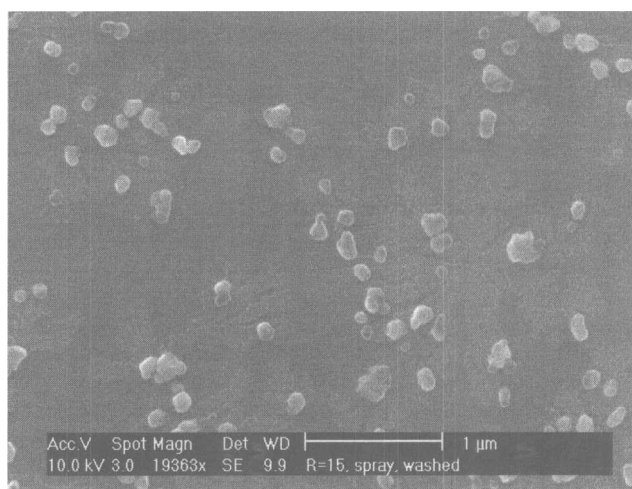

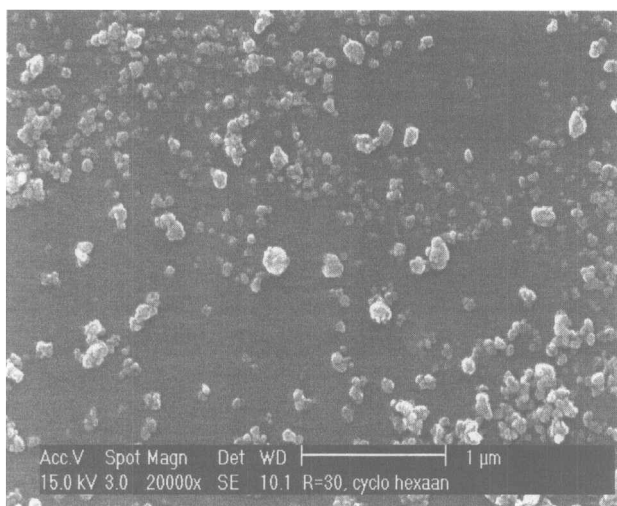*Figure 3.* SEM micrograph for Ca-OT–cyclohexane system at $R = 15$.

Figure 4. SEM micrograph for Ca-OT–cyclohexane system at $R = 30$.

At $R = 30$, particles of an average size of 194 nm were formed. Also at $R = 30$, particle agglomerates of the carbonate particles can be seen. The average diameters of the particles are summarised in Table 1 together with the values of the micellar diameter. The graphical illustration is presented in Figure 5.

It is of interest to compare the size of the initial micelle with the particle size at the end of the experiment. It can be concluded that the size of the particles is much larger than the initial size of the reverse micelle. Various explanations are possible for these observations, such as intermicellar exchange of material and/or agglomeration of already formed particles. However, more data and modeling activities will be required for a definite conclusion. Similar observations have been also reported by Kandori *et al.* (1987, 1988a). Figures 6 and 7 represent the particle size distribution of the carbonate particles at different R. The particle size distribution of the carbonate particles has not been reported elsewhere for this system and this is the first study to do so. Kandori *et al.* (1988a) have reported the values of the particle size in the range of 48–120 nm for R ranging from 5 to 30 at similar surfactant loading.

Effect of the Properties of the Continuous Phase on the Carbonation Process

The effect of the physical properties of the continuous oil phase on the formation of the carbonate particles has not been studied before. CaCO₃ nanoparticles were prepared in Ca-OT microemulsions with cyclohexane, heptane and

Table 1. Sizes of reverse micelles and CaCO₃ particles in Ca-OT–cyclohexane systems ([Ca-OT] = 0.10 mol kg⁻¹, [Ca(OH)₂]/[Ca-OT] = 1.67 × 10⁻³).

R	D_m (nm)	D_p (nm)
5	13	62
10	16	68
15	16	101
20	20	137
25	23	173
30	30	194

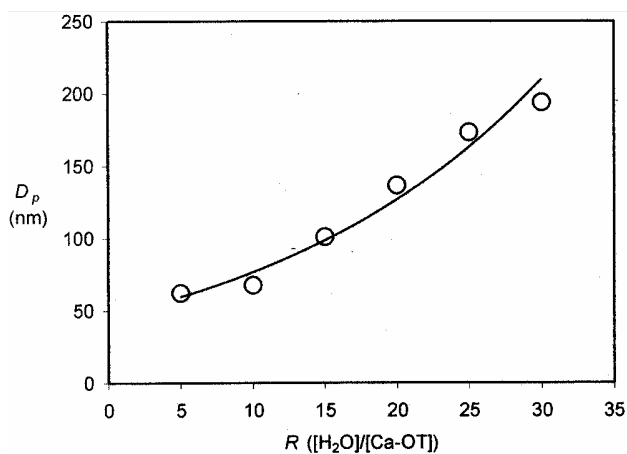*Figure 6.* Particle size distribution for calcium carbonate nanoparticles in the Ca-OT–cyclohexane system at $R = 15$.

Figure 5. Effect of the water-to-surfactant mole ratio on the size of the carbonated particles for Ca-OT–cyclohexane systems ($T = 298$ K, $P = 1$ atm, [Ca-OT] = 0.10 mol kg⁻¹, [Ca(OH)₂]/[Ca-OT] = 1.67 × 10⁻³).
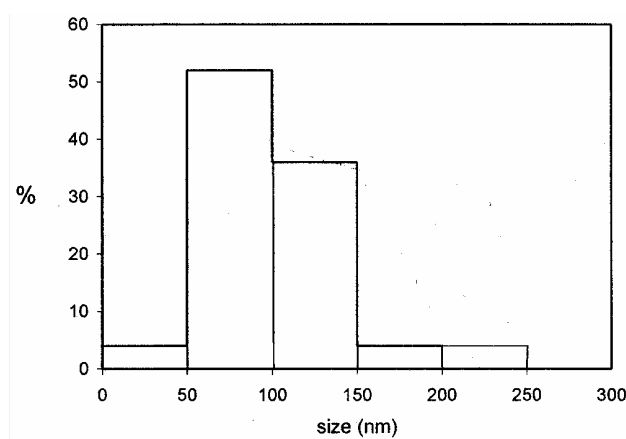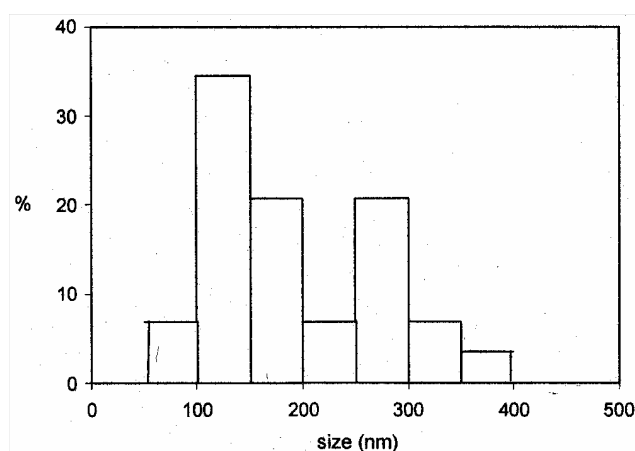

Figure 7. Particle size distribution for calcium carbonate nanoparticles in the Ca-OT–cyclohexane system at $R = 30$.

Table 2. Average particle size of the CaCO$_3$ particles at different water-to-surfactant ratio (R).

	Particle diameter (nm)		
R	Cyclohexane	Heptane	Decane
5	62	25	43
10	68	42	71
15	101	57	81
20	137	72	92
25	173	88	114
30	194	167	125

decane as the continuous oil phase. The average diameters of the particles are summarised in Table 2 for all the solvents. It was observed that the particles produced in heptane and decane were smaller in size as compared with those in cyclohexane (see Table 2). For instance, at $R = 25$, the average size of the carbonate particles was 88 nm using heptane and 114 nm using decane compared with 173 nm using cyclohexane. In all cases, it was found that the size of the particles increased with the increase in water-to-surfactant mole ratio. It was observed that agglomerates were formed at higher ranges of R and their size increased with R. The size distributions obtained for various solvents are similar in nature to the typical ones shown for cyclohexane. The experimental data suggest that particle size variation by changing the solvent is possible and is a valuable tool to tune the particle sizes of the product.

CONCLUSIONS

This work deals with the synthesis of nanoparticles of CaCO$_3$ using CO$_2$ gas and Ca(OH)$_2$ as the reactants. The reverse micellar solution was prepared using a continuous oil phase (cyclohexane, heptane or decane), a surfactant (Ca-OT) and the aqueous Ca(OH)$_2$ solution. Carbonation experiments were carried out at fixed hydroxide-to-surfactant ratio and fixed surfactant concentration. The effect of change in water-to-surfactant ratio and the solvent was studied for the synthesis nanoparticles of calcium carbonate. The size of the reverse micelles before the addition of CO$_2$ was determined and found to be about 10–25 nm using cyclohexane. An increase in the R value resulted in an increase in the particle size. Values of R higher than 30 were not attainable due to the formation of turbid solutions. The value of R depended on the solvent applied. The solutions became turbid at $R = 40$ using heptane and decane. Carbonation experiments indicate that an increase in the water-to-surfactant ratio results in an increase in the size of the for all three solvents used. The particles produced in heptane and decane were smaller in size as compared with those in cyclohexane. The experimental data obtained in this study may be used to validate theoretical models for the production of nanoparticles in reverse micellar solutions.

NOMENCLATURE

D_m	micellar diameter (nm)
D_p	particle diameter (nm)
R	molar ratio of water to Ca-OT (mol mol^{-1})

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