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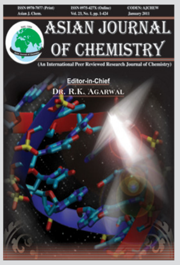

Preparation of Barium Sulfate Nanoparticles Using Semi-Batch Precipitation

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The present work aims at the investigation of different aspects on the production of barium sulfate nanoparticles. The influence of different process control parameters such as the feeding rate, temperature and initial concentrations of the reactants on the particle size has been studied to gain a deeper understanding of the important controlling mechanisms in the formation of $BaSO_4$ nanoparticles. The experiments were carried out *via* a simple precipitation reaction of sodium sulfate with barium chloride in a semi-batch reactor. Present results showed that the reaction temperature, molar ratio of Ba^{2+}-SO_4^{2-} (R) and presence of ethanol were the most important parameters for the size control of barium sulfate particles.

Key Words: Barium sulfate, Nanoparticles, Precipitation reaction.

INTRODUCTION

Inorganic powders have been widely attracted attention nowadays due to the potential to design new materials and devices in various fields. Barium sulfate has been widely used as a model system for investigating inorganic precipitation reaction or crystallization since it crystallizes only in a single phase. It is used widely because of its high specific gravity, opaqueness to X-rays, inertness and whiteness in the pharmaceutical formulations, cosmetics, paper making, offshore oil production, also, plastics, rubber and paint industries, *etc.*[1-4]. Most of previous studies were carried out under stoichiometric conditions[5-10] and little attention has been paid to non-stoichiometric precipitation. Several studies[5,10,11], confirmed the strong role of initial conditions in barium sulfate crystal formation. Aoun *et al.*[10] found that both the nucleation and crystal growth rates for $BaSO_4$ were strongly dependent on the initial reagent molar ratio, yielding minimum rates at stoichiometric conditions. Phillips *et al.*[11] carried out single-feed semi-batch experiments of barium sulfate precipitation in a stirred tank, however, they used a pitched blade turbine with dished bottom and Rushton turbine impeller in a tank, with different geometry, feed volumes, flow rates, temperature and impeller speed compared to this study. They found that the mean crystal size decreased with increasing concentration of Na_2SO_4. Furthermore, reverse micelles and micro-emulsions have been used by Hopwood and Mann[12], for the synthesis of barium sulfate nanoparticles and nanofilaments. Studies on $BaSO_4$ nano-particle precipitation in W/O non-ionic microemulsion were reported by Qi *et al.*[13] and Ivanova *et al.*[14]. Both researchers used Triton X-100 as a nonionic surfactant in a chemically pure grade, the microemulsion droplets have a controlling effect upon the size of the particles. Jia and Liu[15] synthesized nanosized $BaSO_4$ particles using a membrane reactor, in which the Na_2SO_4 solution permeated through the micropores of an ultrafiltration membrane and gradually flowed into the $BaCl_2$ solution to control the saturation ratio, nucleation and growth rates. Bala *et al.*[16] prepared a process in order to obtain $BaSO_4$ nanoparticles with self-dispersing properties by using $(NH_4)_2SO_4$ and $BaCl_2$ as raw materials and a water-ethanol solution as the reaction medium. In the present study, the effects of reactive ions, barium or sulfate, feeding rate and temperature changes, also, the effect of ethanol on the particle size distribution, mean sizes and morphology of the barium sulfate particles in a semi-batch stirred-tank reactor were investigated.

EXPERIMENTAL

Analytical grade sodium sulfate, barium chloride and absolute ethanol were purchased from Merck (Darmstadt, Germany). Distilled water was used in this study.

Preparation and characterization: In order to study the effect of different operating parameters on the barium sulfate particles production, a reactor used for this study is shown in Fig. 1 which consists of a stirred 500 mL Pyrex tank with water jacket for temperature control. The tank is equipped with 4 baffles and a four-blade propeller placed at one-third of the

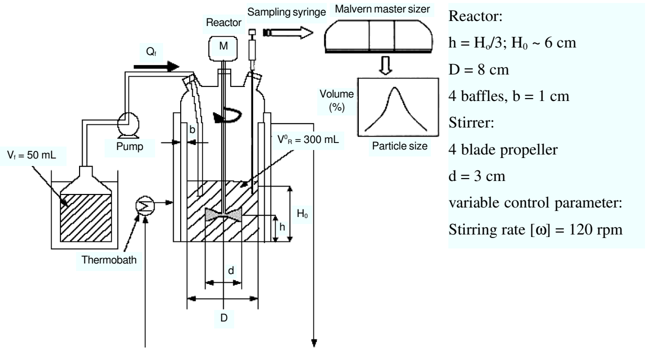

Fig. 1. Schematic diagram of single-feed semi-batch precipitation system

initial liquid height from the bottom and the feed input was located below the initial liquid level. Synthesis of $BaSO_4$ nanoparticles took place in the semi-batch mode. Series of experiment were investigated, the evolution of crystal size with respect to time at first, effect of excess ion concentration by adding Na_2SO_4 or $BaCl_2$ as feed, changing feeding rate and precipitation temperature, also, adding ethanol in the reaction medium. The experiment was initiated by adding 50 mL of Na_2SO_4 (feed solution) to 300 mL 0.1 mol/L $BaCl_2$ solution. In all the experiments stirring speed was kept constant at 1200 rpm, this was the maximum attainable speed without surface aeration, the feed (Na_2SO_4) concentration was adjusted from 0.1-1.6 mol/L (saturated) to provide the total molar ratio (Table-2). Therefore, both globally stoichiometric and non-stoichiometric precipitation conditions were investigated and the total barium to sulphate ions molar ratio was varied from 1-1/16, also, the results of using saturated (1.6 mol/L) 50 mL $BaCl_2$ as feed to 300 mL (0.1 mol/L) sodium sulfate on the mean particle size by means of a peristaltic pump were observed. In the next level the effect of changing feeding rate from 10-140 mL/s and temperature from 20-60 ºC on the finest particle size obtained from the previous step were studied. Hence, the synthesis of $BaSO_4$ nanoparticles by adding ethanol involved the following steps. 150 mL of 0.1 mol/L $BaCl_2$ solution and 150 mL of absolute ethanol were placed in the reactor. Then, 25 mL of 1.6 mol/L Na_2SO_4 solution was added into the reactor while stirring at 20 ºC and the feeding rate was 50 mL/min. In all cases barium sulfate gelatinous white precipitates were formed instantly. After 10 min, the feeding was completed, samples were taken from the reaction mixture. All precipitation experiments were duplicated at least three times to assess the reducibility of the results. The precipitates were separated from the mother liquid by centrifugation and washed with distilled water several times. The precipitates were then dried at 75 ºC. Size analysis was performed using laser diffraction equipment (Malvern Master Size 2000, UK) in the wet mode, 0.1 wt. % sodium hexametaphosphate was used as charge-stabilizing agent. The results are reported as the volume averaged mean crystal size, d (0.5). The morphology of the samples was investigated by scanning electron microscopy (LEO 1455 VP, UK) with an accelerating voltage of 10 kV. To determine the identity of any phase present in the powder a Bruker-D8 Advance X-ray diffract meter (Cu K_α radiation, λ = 1.5406 Å) were used.

RESULTS AND DISCUSSION

Effect of total ion ratio on particle size: Table-1 shows that a clear increase of crystal size and growth during the feeding period at times smaller than feeding was completed from the start of the precipitation process. When the feeding was completed, no further crystal growth was observed. Table-2 clearly shows the mean size, d (0.5), obtained at various molar ratio of Ba_2^{2+}-SO_4^{2-}(R) the mean crystal size generally decreased as the mean concentration of excess ions increased in the reactor. Bigger mean sizes and wider size distributions were obtained for the total molar ratios close to stoichiometric R = 1-1:8 and with further increase from the stoichiometric conditions R = 1:11-1:16 smaller mean sizes and size distributions were found, while using Na_2SO_4 as feed, also, feeding with $BaCl_2$ far from the stoichiometric condition (total molar ratios of 16) has the same result on mean particle size and size distribution when compared with the case of feeding with Na_2SO_4.

TABLE-1
PARTICLE SIZE EVOLUTION AS A FUNCTION OF TIME (Na_2SO_4 FED DURING 1 min)

Sampling time (min)	d (0.5) (μm)
0.5	1.441
1.5	1.663
4.5	1.664
7.5	1.665

TABLE-2
EFFECT OF TOTAL MOLAR RATIO ON MEAN PARTICLE SIZE WITH TWO FEEDING MODES

Feed	Na_2SO_4 (mol/L)	$BaCl_2$ (mol/L)	Total molar ratio ($BaCl_2/Na_2SO_4$)	d (0.5) (nm)
Na_2SO_4	0.1	0.1	1:1	1660
Na_2SO_4	0.5	0.1	1:5	532
Na_2SO_4	0.8	0.1	1:8	480
Na_2SO_4	1.1	0.1	1:11	204
Na_2SO_4	1.4	0.1	1:14	151
Na_2SO_4	1.6	0.1	1:16	152
$BaCl_2$	0.1	1.6	16:1	152

Effect of feeding rate and temperature on particle size: In order to investigate the influence of feeding rate on particles mean size and size distribution all other $BaSO_4$ precipitation parameters were kept constant (1.6 mol/L Na_2SO_4 feed, 0.1 mol/L $BaCl_2$ in the reactor, the stirring rate = 1200 rpm and T = 20 ºC) and the feeding rate was varied Q_f = 10, 17, 30, 50, 100 and 140 mL/min. The results were presented in Table-3. The effect of feeding flow rate applied had no significant effect on the mean crystal size when sodium sulfate was fed. The effect of reaction temperature on the crystallization of barium sulfate was also investigated at various temperatures (T = 20, 40 and 60 ºC), also, other operating conditions were kept constant (1.6 mol/L Na_2SO_4 feed, 0.1 mol/L $BaCl_2$ in the reactor, the stirring rate = 1200 rpm and Q_f = 10 mL/min) (Table-4). However, it was found that a change in the temperature of the system resulted in a significant change in particle size. The mean crystal size and size distributions generally increased as the system temperature increased which may be explained due to nucleation rate at different temperatures.

TABLE-3
EFFECT OF FEED RATE ON MEAN PARTICLE SIZE
(Na_2SO_4 (1.6 mol/L) AS FEED)

Feed rate, Q_f (mL/min)	d (0.5) (nm)
10	137
17	144
30	125
50	151
100	138
140	131

TABLE-4
EFFECT OF REACTION TEMPERATURE ON MEAN PARTICLE SIZE (Na_2SO_4 AS FEED)

Temperature (ºC)	d (0.5) (nm)
20	125
40	153
60	176

Effect of ethanol on particle size: The effect of ethanol on mean particle size and distribution of $BaSO_4$ particles were investigated. Precipitation took place in a liquid medium of ethanol-water. In order to investigate the influence of ethanol on the particles size, the volume of 0.1 mol/L $BaCl_2$ and 1.6 mol/L Na_2SO_4 (feed) were fixed at 150 and 25 mL, respectively. Other operating conditions were stirring rate = 1200 rpm, Q_f = 30 mL/min and T = 20 ºC which kept constant in all the experiments. After 10 min of feeding, samples were taken from the reaction mixture. The precipitates were centrifuged and washed several times with distilled water. Additionally, powder samples were dried at 75 ºC and were slightly grained for analysis. Present results showed that the mean size of $BaSO_4$ particles were significantly decreased [d (0.5) = 69 nm] compared with particles obtained in the absence of ethanol [d (0.5) = 125 nm]. Ethanol directly influenced the environment of the reaction, which, in turn, led to the initial nucleation and growth of the particles. Fig. 2 shows the XRD pattern of $BaSO_4$ powders. The samples display the typical orthorhombic structure of $BaSO_4$ (JCPDS No. 02-1199) and no impurity peaks were detected. As shown in Fig. 2 the intensity of the diffraction peaks for products obtained in the presence of ethanol (2b) was obviously lower than that of the diffraction peaks for products obtained in the absence of ethanol (2c). This suggested that precipitates of the $BaSO_4$ powders synthesized in ethanol contained crystal grains that were much smaller than those in water, which might be related to reduction of the dielectric constant of the reaction medium and adsorption of the ethanol on to the surface of the $BaSO_4$ particles. The ethanol therefore improved the reaction conditions by favouring the formation of small particles and by restraining particle growth during the precipitation. Fig. 3 shows the SEM picture of the products in the absence of ethanol (2a), rod-like barium sulfate particles and the products obtained in the presence of ethanol with more spherical and rod-like particles (2b), also, in none of the pictures traces of agglomeration were observed.

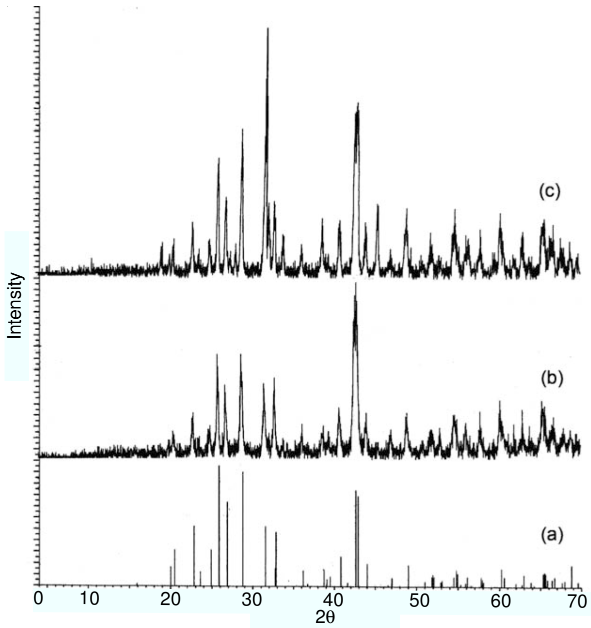

Fig. 2. XRD pattern of $BaSO_4$ powders

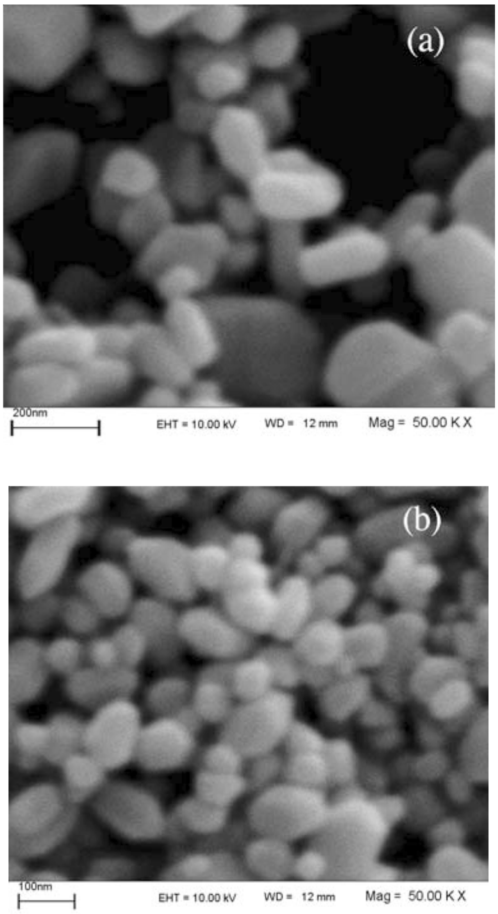

Fig. 3. SEM photography of $BaSO_4$: (a) from products in pure water and (b) from products obtained in the presence of ethanol

Conclusion

In this paper, different process control parameters were investigated and their effects on product properties such as particle size, size distribution were elucidated. It can be concluded that molar ratio of Ba^{2+}-SO_4^{2-}(R), the reaction temperature and presence of ethanol, proved to be the most significant parameters in controlling the particle size and may also influence nucleation and growth rates. It was also found that the crystal size increases with increase in temperature. Feed initial molar ratio significantly influences the particle size distribution and the smallest precipitate particles are obtained by feeding with barium chloride or sodium sulfate at high total molar ratios. The ethanol added during the preparation system impedes the growth of the particles more than pure water, also, barium sulfate particles with morphologies, such as sphere or rod-like could be fabricated *via* a simple precipitation reaction of sodium sulfate with barium chloride in the absence and presence of ethanol.

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