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A systematic morphosynthesis of barium sulfate in the presence of phosphonate inhibitor

Fang Wang, Guiying Xu *, Zhiqing Zhang, Shue Song, Shuli Dong

Key Laboratory of Colloid and Interface Chemistry of Education Ministry, Shandong University, Jinan 250100, People's Republic of China

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Abstract

A systematic study of the influence of various experimental parameters on the morphology and size of $BaSO_4$ crystals after crystallization from water in the presence of diethylenetriamine penta (methylphosphonic acid) (DETPMP) was presented. Depending on the experimental conditions, there are various crystal morphologies including flowers, ellipsoids, spheres, or conjoined spheres. The results indicated that the experimental parameters, such as the concentration of the inhibitor, the pH of solution, the aging of the particle growth, and the ratio $[Ba^{2+}]/[SO_4^{2-}]$, are important for the morphology and size of $BaSO_4$. The morphogenesis of $BaSO_4$ is controlled by the chelation of DETPMP with Ba^{2+} at the nucleation and the surface adsorption inhibition of crystal growth.

Keywords: Morphology; Barium sulfate; Crystal growth; Inhibition

1. Introduction

The precipitation of sparingly soluble salts in nature, and in industrial processes, has been of much interest to chemists in recent years. In nature, the phase, structural properties, and morphology of biominerals are controlled with remarkable precision [1]. Animals and plants have learned to deal with the controlled growth of inorganic matter in the presence of structure-directing polymers, such as proteins and polysaccharides [2]. Therefore, many scientists have tried to understand the mechanisms involved with a view to the development of new synthetic routes for the manufacture of advanced materials. In industrial processes, the precipitation of sparingly soluble salts as scale is a cause for concern due to down-time required to clean equipment and the cost of possible loss of product purity due to the presence of these unwanted minerals [3]. Phosphonate molecules have been identified as compounds that strongly interact with a host of mineral phases [4–6]. Besides the suppression of crystal precipitation, phosphonates have also been used as templates for the crystallization of unusual morphologies and phases, which like functional, water-soluble polymers with the ability for ion binding control the morphology of the crystal. Depending on the strong interaction and the selectivity of molecule adsorption on different crystal faces, spherical, egg-shaped, needlelike, and plateletlike crystals are nucleated, and undergo further alignment and aggregation to form complicated superstructures, such as fiber-bundles, multifunnellike structures, peanuts or dumb-bells architectures [7–10]. So the two research fields, both natural and industrial processes, are subsummarized under the topic "biomineralization." Learning about the principle of action might also result in the development of more efficient scale inhibitor and materials synthesis.

Controlling crystallization by mimicking the biomineralization is well known. One major approach is to mimic natural biomineralization processes directly—the processes of growing an oyster shell from calcium carbonate. The proteins isolated from mollusk shells or artificially designed peptides have been used for the mineralization of calcite with controlled morphology [11–14]. Another major approach is to just mimic the principles of biomineralization.

* Corresponding author. Fax: +86 531 8564750.
E-mail address: xuguiying@sdu.edu.cn (G. Xu).

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For example, organized assemblies of surfactants or polymers have been used as effective templates for the control of crystal growth. And specific soluble additives have been shown to exert significant influence on the crystallization process [15,16]. Current design strategies of such additives have been reported by Coveney et al. [17]. These strategies are based on the rational design of a molecule which can bind all growing faces of barium sulfate, resulting in a highly active modifier of barium sulfate crystal growth in practice. Up to the present, the use of these additives as inhibitor for scale control has been researched intensely.

On the other hand, phosphonate molecules are multiprotic and their charge depends not only on the pH but also on any interactions with any cation present. Because of chelation with the cation, a number of metal phosphonate compounds have been prepared in the past decades due to their potential important applications in exchange, adsorption, catalyst, and sensor [18–28].

However, the tools for the more subtle control of the inorganic crystallization, especially the control of the inorganic morphology, are still little explored. In order to further explore the potential of phosphonates in controlling the morphology of crystals, diethylenetriamine penta (methylphosphonic acid) (DETPMP) is selected to investigate its influence on barium sulfate crystal growth. DETPMP with multiprotic can bind growing faces of barium sulfate and exert a strong influence on the external morphology and crystalline structure of the particles.

It is therefore the aim of the present paper to vary a range of accessible parameters, namely inhibitor concentration, pH, the ostward aging time, and the ratio $[Ba^{2+}]/[SO_4^{2-}]$, to shed light on the ways how the parameters influence the barium sulfate growth and systematic study morphosynthesis of $BaSO_4$ by using DETPMP.

2. Experimental

2.1. Materials

Unless otherwise noted, all reagent-grade chemicals were used as received. Diethylenetriamine penta (methylphosphonic acid) (DETPMP) was synthesized and characterized by NMR and IR. The molecular structure is shown in Fig. 1.

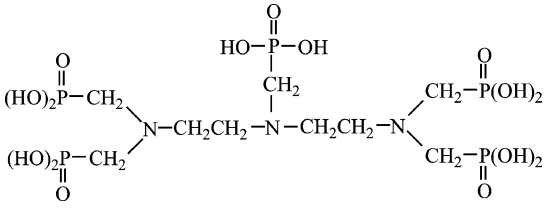

Fig. 1. Structural formula of diethylenetriamine penta (methylphosphonic acid) (DETPMP).

2.2. Crystallization of $BaSO_4$

The precipitation of $BaSO_4$ was carried out in glass vessels at room temperature (ca. 25 °C). Thrice distilled water was used throughout the experiment. Aqueous solutions of $BaCl_2$ (0.1 M) and Na_2SO_4 (0.1 M) were first prepared as stock solutions. In a typical synthesis, a solution of Na_2SO_4 (0.8 ml, 0.1 M) was injected into an aqueous solution of DETPMP (40 ml, 6×10^{-4} M) and the pH of the solution was adjusted to a desired pH by using HCl or NaOH. Then a solution of $BaCl_2$ (0.8 ml, 0.1 M) was injected quickly into the pH-adjusted solution under vigorous stirring by using a magnetic stirrer. This gave a final $BaSO_4$ concentration of 2 mM. The mixture was stirred for 1 min, and then the solution was covered by polyethylene membrane and allowed to stand under static conditions for 24 h before the product was collected for characterization. In the experiments, the concentration of DETPMP was varied from 6×10^{-4} to 6×10^{-3} M, the pH was varied from 2 to 4, the ratio $[Ba^{2+}]/[SO_4^{2-}]$ from 1:4 to 4:1.

2.3. Characterization

The morphologies of $BaSO_4$ precipitates were characterized by transmission electron microscopy (TEM, JEM100-CXII) and scanning electron microscopy (SEM, S-520, Japan). Powder X-ray diffraction (XRD) patterns were recorded on Rigaku D/Max 2200PC diffractometer using graphite-monochromatized high-intensity Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). Samples for TEM observation were prepared by placing a drop of the suspension on a TEM copper grid and dried in air. The remaining crystals were centrifugated and washed by thrice distilled water repeatedly and dried at room temperature for 48 h, then ready for SEM and XRD measurements. The apparent absorbance (which is related to the turbidity) of the systems was measured with spectrophotometer at a wavelength of 552 nm during the whole crystal growth process. The turbidity in $BaSO_4$ suspensions is caused by the presence of particles. When a beam of light passes through a $BaSO_4$ suspension, scattering reduces its intensity. The absorption of light depends on the concentration and size distribution of $BaSO_4$ particles [29]. These measurements allowed us to record the whole progress of the precipitation and locate the time range where the particles mostly formed.

3. Results and discussion

Without any additives, rectangular tablets and some distorted tablets were obtained when pH 4 (Fig. 2a). While quatrefoillike tablets were obtained at pH 2 (Fig. 2b). In present experiment, we varied pH, the ostwald aging time, and the ratio $[Ba^{2+}]/[SO_4^{2-}]$ to get a more detailed effect on the $BaSO_4$ crystal morphology in the presence of DETPMP.