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# Effect of additives on the morphology of calcium sulfate hemihydrate: Experimental and molecular dynamics simulation studies

Xiulong Mao, Xingfu Song *, Guimin Lu, Yanxia Xu, Yuzhu Sun, Jianguo Yu

*National Engineering Research Center for Integrated Utilization of Salt Lake Resources, College of Resources and Environmental Engineering, East China University of Science and Technology, Shanghai 200237, China*

## HIGHLIGHTS

- Additives were used to tune the morphology of calcium sulfate hemihydrate.
- The axial growth of the crystal was significantly inhibited by the additives.
- The effects of additives were investigated by molecular dynamics simulation.
- The sequence was obtained: $E_b(002) > E_b(110) > E_b(200) > E_b(1-10)$.
- The results provided a rational explanation to the experimental observations.

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## ABSTRACT

The effects of sodium dodecyl sulfonate (SDS) and sodium dodecyl benzene sulfonate (SDBS) on the morphology of calcium sulfate hemihydrate (HH) were studied by experiment and molecular dynamics (MD) simulation. It was observed that the additives significantly inhibited the axial growth of HH crystals. The binding energies ($E_b$) between the additives above and the (002) face were much higher than the ones of other faces. The following sequence was obtained: $E_b(002) > E_b(110) > E_b(200) > E_b(1-10)$, which could provide a rational interpretation to the experimental results. In addition to the additives above, the effects of other linear alkyl sulfonates (LAS) and alkyl benzene sulfonates (LABS) on the (002) face were also investigated and the binding energies were increasing with the number of carbon atoms increase. The results obtained from this study should be helpful to the performance evaluation and selection of the morphology modifiers for HH crystals.



## 1. Introduction

As the most abundant sulfate mineral in nature, calcium sulfate occurs in three major forms: calcium sulfate dihydrate (DH, $CaSO_4{\cdot}2H_2O$), calcium sulfate hemihydrate (HH, $CaSO_4{\cdot}0.5H_2O$) and calcium sulfate anhydrite (AH, $CaSO_4$). In recent decades, the crystallization process of HH has been extensively studied, including the crystallization thermodynamics in various solutions [1–5] and the crystallization kinetics in the solutions of inorganic acids [6,7] or in presence of some metal ions [8–10]. Recently, much more attention has been paid to the morphological control of HH crystals [11,12], since many physical properties, such as packing density, filtration rate, and mechanical strength of HH, are dependent on the crystal morphology [13]. To produce HH crystals with different morphologies, many methods were employed, such as adjusting the pH [14] or electrolyte concentration [15] and using crystal growth modifiers [16] to prepare HH rods, using microwave heating to prepare HH nanowires [17], and preparing HH whiskers by reactive crystallization [18]. In lastest report, the morphology and aspect ratio of HH crystals were effectively controlled by adjusting the mass ratio of cetyltrimethylammonium bromide (CTAB)/$H_2O$ and the concentration of sodium dodecyl sulfonate (SDS) during the microemulsion synthesis [19].

The previous research revealed that the presence of impuritities or additives, even at minute amounts, has a major impact on the morphology of HH. It has been suggested that the modification effect of the impurities (such as metal ions [8–12]) or additives (such as surfactants [19–22]) is due to the selective adsorption of the impurities or additives onto different crystal facets. However the interaction mechanism between the impurities or additives and the HH crystal faces at the micro level is still not accessible, partly owing to the limit of detection of the available experimental techniques [23]. Recently, many researchers have applied the

* Corresponding author. Tel./fax: +86 21 64252170.
*E-mail address:* xfsong@ecust.edu.cn (X. Song).

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molecular dynamics (MD) method to investigate the interactions between foreign substances and crystals [24–27], and their findings revealed the MD method could be used to probe into details at the atomistic level that may not be accessible by experimental techniques.

In present study, surfactants were used as additives to control the crystal size and morphology of HH crystals in aqueous systems. The effects of additives were investigated by the MD simulation to better understand the interaction between the additives and the HH crystal faces.

## 2. Materials and methods

### 2.1. Materials

Calcium chloride ($CaCl_2$, ⩾96% purity), sulfuric acid ($H_2SO_4$, 96–98 wt%), hydrochloric acid (HCl, 36–38% wt%) and anhydrous ethanol ($CH_3CH_2OH$, ⩾99.7% purity) were analytically pure (Sinopharm Chemical Reagent Co. Ltd.). Many additives are unstable or ineffective under acidic environment [20,28]. Linear alkyl sulfonates/benzene sulfonates are relatively stable in the acid solutions. In this study, two kinds of linear alkyl sulfonates/benzene sulfonates were chosen to use, namely sodium dodecyl sulfonate (SDS, ⩾97% purity) (Sinopharm Chemical Reagent Co. Ltd.), with chemical formula $C_{12}H_{25}SO_3Na$, and sodium dodecyl benzene sulfonate (SDBS, ⩾95% purity) (J&K Chemical Co. Ltd.), with chemical formula $C_{18}H_{29}SO_3Na$. Deionized water was used to prepare solutions.

### 2.2. Precipitation of HH

A 500 mL, four-neck, round bottom flask was used as the reactor equipped with a reflux condenser and a agitator. The 50 mL, 1 mol/L HCl with or without additive was firstly added into the reactor. The amount of additives added was expressed as a percentage of the total moles of calcium ions in the solution. Under stirring (200 rpm), the solution was then heated to 102 °C, the boiling point of the solution at the ambient pressure, in an oil bath. Next, the preheated, 80 mL, 1 mol/L $CaCl_2$ and $H_2SO_4$ were added into the reactor using a peristaltic pump at the same flow rate as described in a previous publication [18]. The resulting reaction mixture was refluxed for 2 h. Finally, the samples of the reaction mixture were withdrawn, rapidly filtered, washed with boiling deionized water and anhydrous ethanol successively, and dried at 60.0 °C for 5 h.

### 2.3. Characterization

The morphology of the samples was observed using a scanning electron microscope (SEM, Quanta 250, FEI Co., USA), and an optical microscope (ECLIPSE E200, Nikon Co., Japan). The crystal size was obtained by measuring 100 crystals through the optical microscope. To avoid crystal dissolution or alteration, the crystals were dispersed by anhydrous ethanol. The phase composition of the samples was identified using an X-ray diffractometer (XRD, D/max 2550, Rigaku, Japan).

### 2.4. Simulation details

All the calculations were run with the commercial molecular modeling software package Materials Studio 6.0 [29], using the COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) force field [30,31] and the Discover module. As common anionic surfactants, SDS and SDBS no longer exist as molecular form in the aqueous solution, but are dissociated into two parts: an anionic portion ($C_{12}H_{25}SO_3^-$ for SDS and $C_{12}H_{25}C_6H_4SO_3^-$ for SDBS), and a $Na^+$ ion, as shown in Eqs. (1) and (2). The anionic portion plays a crucial role in determining the surface activity of anionic surfactants. It was found that the presence of many additives caused little changes in dihydrate (DH) crystal morphology and this was attributed to the lack of ionization of the additive under acidic condition [20]. However in this study, the HH crystal morphology was indeed significantly changed in the presence of SDS or SDBS (see Section 3). Therefore it is reasonable to believe that the additives were present in their ionic forms and their models were built in the following work.

$$C_{12}H_{25}SO_3Na \rightarrow C_{12}H_{25}SO_3^- + Na^+ \quad (1)$$

$$C_{12}H_{25}C_6H_4SO_3Na \rightarrow C_{12}H_{25}C_6H_4SO_3^- + Na^+ \quad (2)$$

The HH crystal structure was obtained from Bezou et al. [32] with unit cell dimensions of $a = 12.0317$ Å, $b = 6.9269$ Å, $c = 12.6712$ Å, $\beta = 90.270°$, and $Z = 12$. The crystal form is monoclinic with the space group I121.

The pure crystal morphology was firstly calculated by means of the attachment energy (AE) method [33]. As shown in Fig. 1, there are four dominant faces predicted by AE method: (1 1 0), (1–10), (2 0 0) and (0 0 2), which could provide a good match to the one calculated with the Fourier transformation method in the previous work [34] and the experimental observation in this study. In a recent work, the morphology and structure of HH were investigated

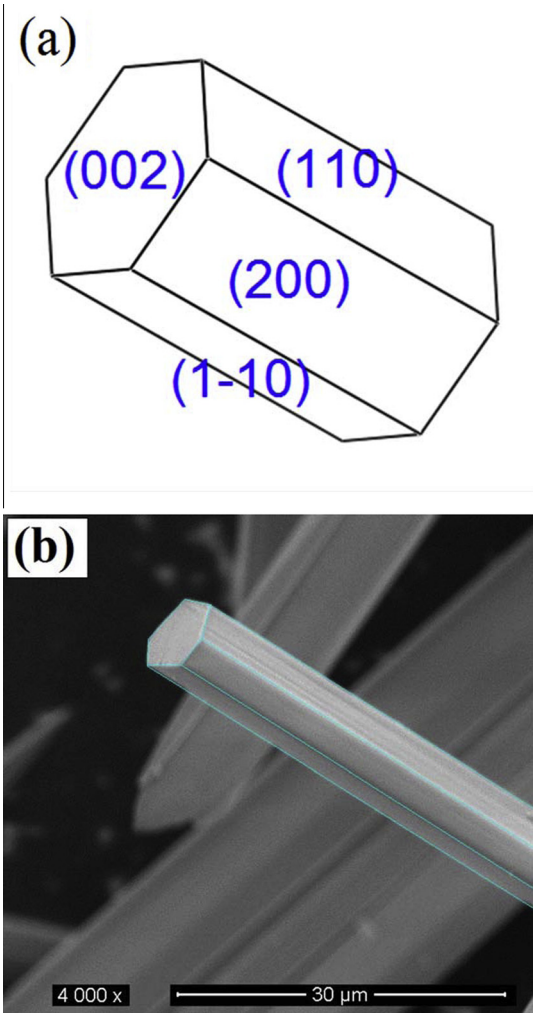


**Fig. 1.** Calcium sulfate hemihydrate crystal morphology: (a) predicted by AE method, and (b) experimental observation (without additive).