

Supersaturation controlled morphology and aspect ratio changes of benzoic acid crystals



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ARTICLE INFO

Article history:

Received 7 July 2016

Received in revised form 7 December 2016

Accepted 5 January 2017

Available online 17 January 2017

Keywords:

Supersaturation

Crystal growth

Aspect ratio

Molecular dynamic simulation

Benzoic acid

ABSTRACT

Supersaturation is a factor of great industrial importance to the crystal growth by affecting the final aspect ratio and morphology of organic compounds. In this work, the qualitative relationship between aspect ratio and supersaturation of benzoic acid (BA) was elucidated for the first time by experimental and simulative study. Experimentally, it was found that the crystal shape of BA changes from needle-like crystal to rectangular sheet and then to hexagonal particles with the increasing supersaturation ranging from 1.029 to 2.941. The increment of supersaturation decreases the average aspect ratio of crystallized particles from ~20.5 to ~1.3. Furthermore, a higher supersaturation ($\sigma = 1.618$) leads to more isotropic hexagonal crystals due to less face discrimination at high crystallization rates. Additionally, we predicted the supersaturation-dependent crystal habit by the modified attachment energy (MAE) model, which yield good agreement with the experimental observed crystals at medium and high supersaturations.

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1. Introduction

Crystallization from solution, as a typical separation and purification process, has been widely used for the manufacture of pharmaceutical compounds. (Fujiwara et al., 2005) Optimization and control of crystal shape and size is an important objective in crystal preparation as different crystal shapes can induce both chemical and physical properties. (Liu et al., 2013; Lovette et al., 2008; Ma et al., 2002) Hence, it is necessary to understand factors that affect crystal shape and control approach during the crystallization process in order to obtain products with desired characteristics, which has driven intensive research toward this direction. Many factors, such as solvent, (Karunanithi et al., 2009) supersaturation, (Jung and Kim, 2011a,b) seed, (Liu et al., 2010) and impurities, (Yang et al., 2012) have effects on product qualities in terms of crystal morphology, crystal forms, and crystal size distribution. Supersaturation, as a driving force to determine the nucleation process and crystal growth, affects growth kinetics for each crystallographic facet so as to the formation of different morphologies in crystallization processes. (Kang et al., 2011) The

supersaturation is important not only in controlling crystal morphology but also in designing strategy for particle size, (Jim et al., 2013) especially in industrial crystallization process. (Larsen et al., 2006)

Over the past decades, computer simulation provides a helpful approach for crystallization solvent design, crystal morphology prediction and crystal habit evaluation in solvents to have a better understanding of the crystal growth. (Karunanithi et al., 2006; Schmidt and Ulrich, 2012a) Many models were reported and applied to predict the crystal habit by considering the supersaturation, which is a very crucial factor in crystallization. Deij et al. (2005) predicted the crystal morphology for a yellow isoxazolone by using Monte Carlo (MC) simulation dye depending on the supersaturation. Lovette and Doherty (2012) proposed a first-principles model to predict steady-state crystal shapes of naphthalene at different supersaturations. Schmidt and Ulrich (2012b) predicted the crystal morphology of benzoic acid (BA) by using the modified attachment energy (MAE) model in supersaturation solution. Recently, different solvent controlled crystal growth morphology of BA at the infinitely low supersaturation (saturated solution) has been studied by combining experimental crystallization and MAE simulation (Liang et al., 2014a,b). Among these methods, the MAE model has been considered as an effective model to predict the crystal morphology in supersaturated solution.

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Additionally, the supersaturation controlled morphology evolution has attracted numerous attentions. For example, Ristic et al. (2001) described the morphology of paracetamol crystals grown from water at different level of supersaturations. Lu and Ulrich (2005) studied the crystal habit of caprolactam from water at low and high supersaturations. Schmidt et al. (2011) calculated the crystal morphology of BA from aqueous solution with different water models. However, it is worth noting that the relationship between supersaturation and the resulting aspect ratio of crystal morphology still requires further clarification both in experiments and theoretical explanations. For example, the aspect ratio of naphthalene crystal from cyclohexane increases with the increase of supersaturation (Tilbury et al., 2016). In contrast, the aspect ratio of L-alanine crystal decreases with the supersaturation increasing (Tan et al., 2016). Therefore, highly effective method and supersaturation controlled aspect ratio are required for better understanding the nucleation and crystal growth process.

Herein, BA crystals at different level of supersaturations in aqueous solution were prepared via natural cooling method. The modified attachment energy (MAE) method was used to predict the crystal habit in different supersaturations to confirm the crystal shape evolution. Furthermore, the adsorption of water molecule on the most exposed surfaces was evaluated. The key aim of this work is to achieve a better understanding of supersaturation determined crystal growth habit and quantify aspect ratio changes of BA with the increasing supersaturation.

2. Experimental

2.1. Preparation of crystals

Benzoic acid (BA) samples were purchased from Sinopharm Chemical Regents Co., Ltd. Deionized water (DIW) was obtained from purification system (RO-DI plus, Hitech, PRC). In a typical experiment, a certain amount of BA compound (0.35 g–1.0 g) was added in 100 mL DIW and the solution was heated to 60 °C to completely dissolve BA samples. Then, the solution was cooled down naturally. The cooling rate was measured by monitoring the temperature with time. As the temperature was decreased, the nuclei of BA were observed. We recorded the temperature of BA in water when nucleation occurs. This preparation method is similar with the literature published by Nguyen et al. (2014). The formed crystals were observed with a polarizing optical microscope (Olympus BX-41) connected to a CCD camera, and crystal shape images were taken to analyse the effects of supersaturation. We also obtained the supersaturation after nucleation occurs by weighting the crystals when they grow for 24 h. Here, the supersaturation (σ) of the BA solution is defined as:

$$\sigma = C/C^*, \quad (1)$$

where C is the initial solution concentration and C^* is the solubility of BA. The solubility in water was measured at ~25 °C. The value of C^* was 0.34 g/100 mL, which is similar with that measured by Ward & Cooper (Ward and Cooper, 1929). Therefore, the supersaturation σ is in the range of 1.029–2.941. Here, σ values are upper bounds – assume cooled to 25 °C without crystallization.

2.2. Computation method

All the computations were carried out in the Material Studio 6.1 software. (Accelrys Software Inc.: San Diego, CA, 2012). The initial unit cell of BA is shown in Fig. 1, which belongs to the monoclinic crystal system with space group $P2_1/c$ and has four molecules in a unit cell with parameters $a=5.50$ Å, $b=5.128$ Å, $c=21.95$ Å, $\alpha=\gamma=90^\circ$, and $\beta=97.37^\circ$ (Sim et al., 1955). First, we optimized the initial BA crystal structure by running the Geometry Optimization

Crystal system	monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$, $b/\text{\AA}$, $c/\text{\AA}$	5.50, 5.128, 21.95
α° , β° , γ°	90.00, 97.37, 90.00

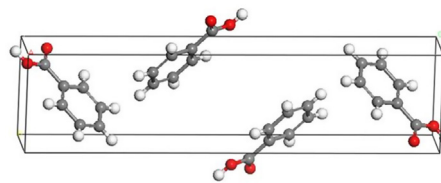


Fig. 1. The benzoic acid unit cell structure.

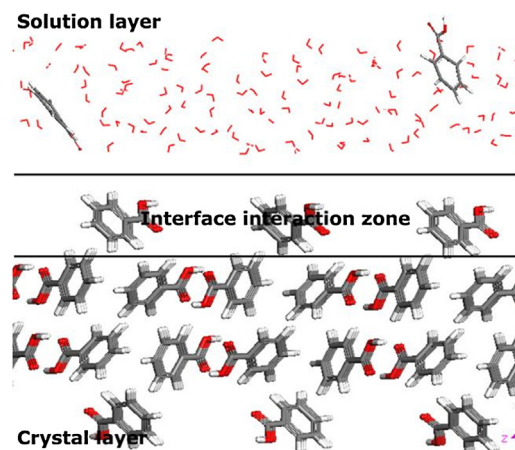


Fig. 2. A schematic diagram showing crystal growth occurs at the interface with its solution.

task in the Forcite model under different forcefields. The forcefield assigned charges were applied during simulations. According to the resulting unit cell parameters shown in Table S1, the COMPASS forcefield was selected. The ideal crystal habit of BA was calculated by the growth morphology method in the Morphology module. This method is based on the attachment energy (AE) model, which assumes the growth rate R of each crystal face is proportional to its absolute value of AE E_{att} in vacuum (Hartman and Bennema, 1980). However, the external environment, especially solvent effects, has not been considered. When considering the effect of solution, the modified attachment energy (MAE) model was established (Chen and Trout, 2010). Eight main exposed faces including (002), (10-2), (100), (011), (012), (102), (013), and (110) were considered in subsequent molecular dynamic (MD) calculations. The modified attachment energy E_{mod} can be calculated by introducing the solvent interaction E_s and correction factor S :

$$E_{mod} = E_{att} - SE_s. \quad (2)$$

The E_s is defined as the energy removing a solvent layer before the solute molecule is deposited on the surface (Bacchi et al., 2011), while S is defined as the correction factor that reflects the roughness of the crystal face (Yi et al., 2013). The S is calculated by the following equation:

$$S = \frac{A_{acc}}{A_{hkl}}. \quad (3)$$

Here, A_{acc} is the accessible solvent surface of an (hkl) slice and A_{hkl} is the corresponding area of an (hkl) slice. To calculate the solvent/crystal interaction energy E_s , the interface model was constructed, as illustrated in Fig. 2. The interface model contains three parts: crystal layer, solution layer, and interface interaction zone.

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