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Ultrasound assisted nucleation and growth characteristics of glycine polymorphs – A combined experimental and analytical approach

K. Renuka Devi, A. Raja, K. Srinivasan *

Crystal Growth Laboratory, Department of Physics, Bharathiar University, Coimbatore 641046, Tamil Nadu, India

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ABSTRACT

For the first time, the effect of ultrasound in the diagnostic frequency range of 1–10 MHz on the nucleation and growth characteristics of glycine has been explored. The investigation employing the ultrasonic interferometer was carried out at a constant insonation time over a wide range of relative supersaturation from $\sigma = -0.09$ to 0.76 in the solution. Ultrasound promotes only α nucleation and completely inhibits both the β and γ nucleation in the system. The propagation of ultrasound assisted mass transport facilitates nucleation even at very low supersaturation levels in the solution. The presence of ultrasound exhibits a profound effect on nucleation and growth characteristics in terms of decrease in induction period, increase in nucleation rate and decrease in crystal size than its absence in the solution. With an increase in the frequency of ultrasound, a further decrease in induction period, increase in nucleation rate and decrease in the size of the crystal is noticed even at the same relative supersaturation levels. The increase in the nucleation rate explains the combined dominating effects of both the ultrasound frequency and the supersaturation in the solution. Analytically, the nucleation parameters of the nucleated polymorph have been deduced at different ultrasonic frequencies based on the classical nucleation theory and correlations with the experimental results have been obtained. Structural affirmation of the nucleated polymorph has been ascertained by powder X-ray diffraction.

1. Introduction

Crystallization, a phase change occurring in solution is the main key technique employed in the separation, purification and production of a wide range of materials. Over the past decades crystallization has been augmented by a lot of methods, techniques and recently ultrasound have evolved as a powerful tool in inducing and investigating this crystallization mechanism in various systems. Though ultrasound has been reported to influence every aspect of the crystallization process its effect on the phenomenon of nucleation is highly significant. In addition to the initiation of nucleation in the system, irradiation of ultrasound was also found to influence several other factors of crystallization such as polymorphism, agglomeration, crystal size etc. [1–15]. Ultrasound has proven as an efficient tool to establish control over the number of primary nuclei and their crystal size. Li et al. [5] has studied the relation between the insonation periods and the size of the resulted crystals. Nanev and Penkova stated that narrow size distribution could be achieved in the presence of ultrasound, but still the end results are characteristic of the target material used [16]. Lyczko et al. studied the cooling-based primary nucleation in the presence of ultrasound and revealed the effect of ultrasound on the reduction of the metastable zone width and induction time and thereby the solid formation rate [17]. Guo et al. studied the anti-solvent crystallization process in the presence of ultrasound and obtained the same reduced effect on the metastable zone width and induction time as obtained by Lyczko et al. [18]. Miyasaka et al. revealed that there was an energy threshold above which ultrasonic irradiation increased the crystal number and promoted nucleation, at the region where a low level of ultrasonic energy was applied [19]. Moreover, sonocrystallization studies on amino acids by Kurotani et al., again pointed out that the induction time increased with increasing ultrasonic irradiation energy up to a certain degree and then decreased, indicating the earlier energy threshold theory [20]. In most applications, ultrasonic frequency in the range of kilohertz is utilized while, the use of megahertz range ultrasound is rarely reported [21,22]. The use of higher frequency ultrasound avoids the problem of cavitation erosion and in the megahertz frequency range, a different environment for crystallization will be created due to higher acceleration of medium as well as formation of smaller bubbles than 20 kHz

* Corresponding author. Tel.: +91 422 2428442; fax: +91 422 2422387.
E-mail address: nivas_5@yahoo.com (K. Srinivasan).

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[22]. Although cavitation effects become comparatively gentler than 20 kHz, a high frequency ultrasound increases the number density of bubbles and potentially enhances bubble-related phenomena such as interfacial adsorption, bubble interaction, bubble oscillation, microstreaming etc. [23,24]. Glycine the simplest amino acid and a very interesting molecule exhibiting the phenomenon of polymorphism with three polymorphs α, β and γ under ambient conditions is the target material in the present work [25–31]. From the existing literature it is clear that, so far the effects of ultrasonic frequencies only up to 1.6 MHz have been experimented on glycine crystallization while the effects of frequencies beyond this is unrevealed. Hence this form the novel objective of this work that is to reveal for the first time the effects of ultrasound in the diagnostic frequency range of 1–10 MHz on the nucleation and growth characteristics of glycine polymorphs. The experiments were also carried out at a constant insonation time over a wide range of relative supersaturation from $\sigma = -0.09$ to 0.76 in the solution in order to study the dominating and overlapping effects of ultrasound and supersaturation in assisting the nucleation in the solution.

2. Materials and methods

Glycine (G.R. Grade, Merck) and laboratory double distilled water were used for solution preparation. Solutions of glycine each of about 100 mL capacity were saturated at different temperatures in the range from 30 to 70 °C in steps of 5 °C in a 250 mL round bottom flask fitted with ground sleeve attachment for effective stirring. The solution was saturated for about 12 h at a stirring speed of 150 rpm. The entire set up was placed inside a CTB having the temperature controlling accuracy of about ±0.01 °C. After saturation, the solution was filtered using Whatman No. 41 filter sheets into another similar RBF and maintained at the saturation temperature for 1 h. The entire solution was split up into capacities of 5 mL each into 20 test tubes. The temperature of the CTB was then reduced to 32 °C and maintained in it for 1 h. The solutions were then transferred into ultrasonic irradiation chambers and set for irradiation. One set of solution was kept apart to study the effects in the absence of ultrasound. A multi-frequency ultrasonic interferometer shown in Fig. 1 was used for the experiments. A constant insonation time of 5 min was employed in all the cases. After insonation, about 500 µL of the insonated solution was pipetted out onto a microscope slide for investigation under the optical microscope and the nucleation events were recorded. The type of polymorph nucleated was ascertained based on their morphology and confirmed further by powder X-ray diffraction through BRUKER D8 Advance powder X-ray diffractometer.

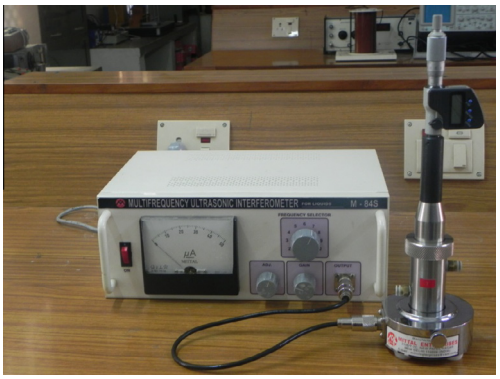

Fig. 1. Experimental setup.

3. Results and discussion

3.1. Effect of ultrasound on the induction period of nucleation

When the solutions saturated in the temperature range from 30 to 70 °C were cooled down to 32 °C a relative supersaturation is generated in the range from $\sigma = -0.09$ to 0.76 in the solution. In our experiment, the induction periods of nucleation were measured both in the presence (insonated) and absence (uninsonated) of ultrasound and compared quantitatively under various supersaturations. The measured induction period of nucleation both in the absence and presence of ultrasound over the entire supersaturation range is shown in Fig. 2a and b, respectively.

No nucleation was observed in the lower supersaturation range from $\sigma = -0.09$ to 0.07 in the solution in the absence of ultrasound as shown in Fig. 2a. While only above the supersaturation of $\sigma = 0.15$ nucleation was observed in the solution. At the supersaturation of $\sigma = 0.15$, the induction period of nucleation was higher of about 28 min and with further increase in supersaturation from $\sigma = 0.15$ to 0.76, the induction period of nucleation decreases from 28 to 2 min in the solution.

In the presence of ultrasound even at the lower frequency of 1 MHz, nucleation has been induced in the lower supersaturation range from $\sigma = -0.09$ to 0.07 in the solution as evident from Fig. 2b. Ultrasound with its inherent phenomenon of mixing and cavitation due to its propagation in the solution medium promotes the mass transfer and thereby the nucleation in the solution [5]. In

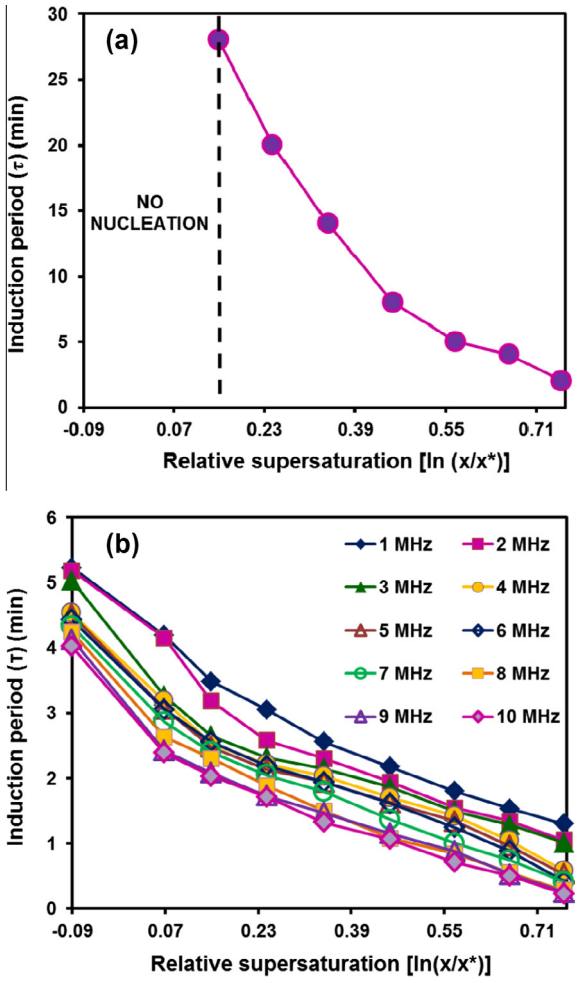

Fig. 2. Variations in the induction period of nucleation in (a) absence and (b) presence of ultrasound in the solution.