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The effect of ultrasound on the homogeneous nucleation of $BaSO_4$ during reactive crystallization

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Abstract

The effect of ultrasound on reactive crystallization is studied by measuring the induction time when nucleation is predominantly homogeneous. Barium sulphate is used as the working substance precipitated by mixing aqueous $BaCl_2$ and Na_2SO_4 solutions. The experiments were carried with various energy inputs. It is observed that at a given supersaturation level, the induction time significantly decreases with increasing ultrasonic energy.

The mechanism of the ultrasonic effect on homogeneous nucleation is analyzed. The main effect of ultrasound is to increase the diffusion coefficient (D_{AB}). The surface tension (γ_{CL}) changes only slightly or remains constant in the ultrasonic field. This suggests that diffusion acceleration is the main reason for the reduction of the induction time. The relationship between D_{AB} and energy input is also investigated and it is found that D_{AB}– D_{AB0} has an exponential relationship with energy input.

Keywords: Ultrasound; Induction time; Homogenous nucleation; Crystallization; Diffusion coefficient

1. Introduction

Sonocrystallization is the use of power ultrasound to control the course of a crystallization process (AEA Technology, 2001). The effect of ultrasound on crystallization was first observed in 1927 (Patrick et al., 2004). In the last decade, sonocrystallization has received much attention. The ultrasonic effect on crystallization has been reported to accelerate crystal precipitation (Nishida, 2004; Ichitsubo et al., 2004), retard precipitation (Dalas, 2001), change the crystal size distribution and crystal habit (Lee et al., 2001; Amara et al., 2001; Li et al., 2003; Guo et al., 2005), change crystal character (Enomoto et al., 1996), increase nucleation rate (Teipel et al., 2002; Lyczko et al., 2002; Chow et al., 2003, 2004), depress agglomeration (Kim et al., 2002; Guo et al., 2005) and agglomerate particles (Kusters et al., 1993; Enomoto et al., 1997).

In industrial crystallization, primary nucleation is difficult to control because it occurs in a thermodynamically unstable region. Primary nucleation commonly requires very high levels of supersaturation, which brings difficulties in controlling the crystallization process. When operating crystallization in a controlled way, crystal products with a large mean size and narrow size distribution can be obtained. In industrial crystallization processes, this is frequently done by seeding (Teipel et al., 2002). Grinding processes are often employed to produce crystal seeds, but the mean size and size distribution of seeds are commonly unsatisfactory, while grinding processes may introduce impurities into seeds and may pollute the environment. When added into solution, seed particles often agglomerate and are difficult to disperse. These undesirable phenomena do not appear in the seeds that are formed by insonated nucleation (AEA Technology, 2001; Guo et al., 2005).

In this paper, barium sulphate is used as the working substance precipitated by mixing aqueous solutions of $BaCl_2$ and Na_2SO_4. Induction time, which has an inversely proportional relationship with nucleation rate, is studied to determine the ultrasonic effect on primary nucleation in a reactive

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crystallization process. From this, the mechanism of the ultrasonic effect on nucleation is also investigated.

2. Theory

When ultrasound propagates through a liquid medium, its power not only is a driving force for mass transfer, but also initiates an important phenomenon known as cavitation. Cavitational bubbles forms during the negative-pressure period of the sound wave. When a cavitational bubble implodes, a localized hot spot is formed with a high temperature and high pressure with the release of a powerful shock wave. The reason for the above phenomena is that the collapse process is very rapid. The collapse time of a cavitational bubble is normally very short compared to its birth time. The power of ultrasound and cavitation phenomena influence primary nucleation during crystallization processes (Repacholi and Grandolifo, 1987; Li and Lin, 1995; Cains et al., 1998).

From classical primary nucleation theory, the rate of homogeneous nucleation can be obtained from the number of critical clusters that cross the nucleation barrier. So the nucleation rate (B_{hom}) can be expressed as (Mersmann, 2001; Mersmann et al., 2002):

$$B_{\mathrm{hom}} = k' n_c Z, \tag{1}$$

where B_{hom} is homogeneous nucleation rate, k' is the rate which clusters cross the barrier, n_c is the number concentration of critical clusters, and Z is the imbalance factor, which relates the number of critical nuclei in the equilibrium distribution to the number in the steady-state distribution.

For the critical cluster (n_c) can be described by a Boltzmann distribution.

$$n_c = n_0 \exp\left(-\frac{\Delta G_c}{kT}\right), \tag{2}$$

where n_0 is the number concentration of molecules in the supersaturated solution, ΔG_c is the free energy of critical cluster, k is Boltzmann constant, and T is absolute temperature.

The free energy ΔG_c can be expressed by the following equation (Mersmann, 2001).

$$\Delta G_c = \frac{16\pi\gamma_{CL}^3 V_m^2}{3(kT \ln S)^2}, \tag{3}$$

where γ_{CL} is the surface tension, V_m is the molecular volume, and S is supersaturation ratio.

The molecular volume (V_m) is given by

$$V_m = \frac{1}{C_c N_A}, \tag{4}$$

where N_A is Avogadro's number, and C_c is molecular density of solid. So

$$n_c = n_0 \exp\left[-\frac{16}{3}\pi\left(\frac{\gamma_{CL}}{kT}\right)^3\left(\frac{1}{C_c N_A}\right)^2\frac{1}{(v \ln S)^2}\right], \tag{5}$$

where v is the number of moles of ions formed from one mole of electrolyte. The coefficient k' can be derived from (Mersmann, 2001):

$$k' = \frac{3}{4} n_0^{4/3} D_{AB} A_c, \tag{6}$$

where D_{AB} is the diffusion coefficient, and A_c is the surface area of cluster.

The imbalance factor (Z) is given by (Mersmann, 2001):

$$Z = \sqrt{\frac{Q}{2\pi kT}} = \sqrt{\frac{\Delta G_c}{3\pi kT i_c^2}} = \frac{2}{\pi C_c N_A L_c^2}\sqrt{\frac{\gamma_{CL}}{kT}}, \tag{7}$$

where Q is quantity of heat, i_c is the critical cluster number, and L_c is the cluster diameter.

Inserting Eqs. (5)–(7) into Eq. (1), the homogeneous nucleation rate can be obtained from the following equation:

$$\begin{aligned} B_{\mathrm{hom}} = {} & 1.5 D_{AB}(C N_A)^{7/3}\sqrt{\frac{\gamma_{CL}}{kT}}\,\frac{1}{C_c N_A}\exp \\ & \times\left[-\frac{16}{3}\pi\left(\frac{\gamma_{CL}}{kT}\right)^3\left(\frac{1}{C_c N_A}\right)^2\frac{1}{(v \ln S)^2}\right]. \end{aligned} \tag{8}$$

The induction time is normally found to have an inverse ratio relationship with nucleation rate. It can be expressed by (Mullin, 2000; Myerson, 2002):

$$t_{\mathrm{ind}}^{-1} = K B, \tag{9}$$

where K is a coefficient of proportionality. Combining Eqs. (8) and (9), the following equation is obtained:

$$\begin{aligned} t_{\mathrm{ind}}^{-1} = {} & 1.5 K D_{AB}(C N_A)^{7/3}\sqrt{\frac{\gamma_{CL}}{kT}}\,\frac{1}{C_c N_A} \\ & \times \exp\left[-\frac{16}{3}\pi\left(\frac{\gamma_{CL}}{kT}\right)^3\left(\frac{1}{C_c N_A}\right)^2\frac{1}{(v \ln S)^2}\right]. \end{aligned} \tag{10}$$

Taking the natural logarithm on each side of Eq. (10):

$$\ln t_{\mathrm{ind}} = A_1 + B_1 \ln^{-2} S, \tag{11}$$

where

$$A_1 = -\ln 1.5 K D_{AB}(C N_A)^{7/3}\sqrt{\frac{\gamma_{CL}}{kT}}\,\frac{1}{C_c N_A}, \tag{12}$$

$$B_1 = \frac{16}{3}\pi\left(\frac{\gamma_{CL}}{kT}\right)^3\left(\frac{1}{C_c N_A v}\right)^2. \tag{13}$$

The interfacial tension (γ_{CL}) can also be determined from the following equation (Mersmann, 1990):

$$\frac{\gamma_{CL}}{kT} = K_1 (C_c N_A)^{2/3} \ln\left(\frac{C_c}{C^*}\right). \tag{14}$$

The diffusion coefficient (D_{AB}) increases with ultrasonic power applied to the crystallization system (Sivakumar and Rao, 2003; Mitragotri, 2001; Moholkar and Warmoeskerken, 2004). Assuming the molecule of solute is spherical, when it moves