Journal of Crystal Growth 475 (2017) 220–231

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/crys

Interpretation of the microwave effect on induction time during $CaSO_4$ primary nucleation by a cluster coagulation model

Zhichao Guo [a,*], Liye Li [a], Wenxiang Han [a], Jiawei Li [a], Baodong Wang [b], Yongfeng Xiao [b]

[a] *College of Chemical Engineering and Materials Science, Tianjin University of Science & Technology, Tianjin 300475, China*
[b] *National Institute of Clean-and-Low-Carbon Energy, Future Science & Technology City, Changping District, Beijing 102211, China*

ARTICLE INFO

Article history:
Received 24 February 2017
Received in revised form 29 May 2017
Accepted 30 May 2017
Available online 1 June 2017

Keywords:
Microwave
Induction time
Homogeneous nucleation
Heterogeneous nucleation
Coagulation
Cluster

ABSTRACT

The effects of microwave on the induction time of $CaSO_4$ are studied experimentally and theoretically. In the experiments, calcium sulfate is precipitated by mixing aqueous $CaCl_2$ solution and Na_2SO_4 solution. The induction time is measured by recording the change of turbidity in solution. Various energy inputs are used to investigate the effect of energy input on nucleation. The results show that the induction time decreases with increasing supersaturation and increasing energy input. Employing the classical nucleation theory, the interfacial tension is estimated. In addition, the microwave effects on nucleation order (n) and nucleation coefficient (k_N) are also investigated, and the corresponding values of homogeneous nucleation are compared with the values of heterogeneous nucleation in the microwave field.

A cluster coagulation model, which brings together the classic nucleation models and the theories describing the behavior of colloidal suspension, was applied to estimate the induction time under various energy inputs. It is found that when nucleation is prominently homogeneous, the microwave energy input does not change the number of monomers in dominating clusters. And when nucleation is prominently heterogeneous, although the dominating cluster size increases with supersaturation increasing, at the same supersaturation level, the dominating cluster size remains constant in the microwave field.

1. Introduction

During the last two decades it was claimed by a large number of scientific publications that microwave technology is an efficient and suitable tool in the chemical synthesis and processing of materials [1–4]. Microwaves exhibit potential for various applications, thereby, saving energy and shortening synthesis time [5,6]. Ji and Wang [7,8] found that the mass transfer is improved significantly under microwave irradiation, which is one of the main reasons why microwave irradiation can bring significant effect on crystallization process control. Rizzuti [9] and Serrano [10] used microwave radiation on the crystallization process which can give a high yield of product. Wu [11] and Hart [12] found that microwave field can promote the phase transform of crystal. Tian [13], Mahmoud [14] and Aquino [15] concluded that microwave can be used to attain the rapid growth of crystal during crystallization process. Asakuma and Miura [16] found that microwave can accelerate the crystal precipitation and control the crystal size. Thus, microwave has attracted considerable attention as a new way to control crystallization process.

The induction time (t_{ind}) is defined as the time interval between the establishment of supersaturation (S) and the formation of critical nuclei. Conventionally, two ways are used to interpret the experimental t_{ind}-S data. One of them is prediction of a linear relationship between the logarithm of induction time [$\ln(t_{ind})$] and the logarithm of relative supersolubility ($\ln\sigma$) [17]. According to this method, the empirical nucleation rate constant and nucleation order can be estimated from the intercept and slope of a straight line, respectively. The second one is the prediction of a linear relationship between $\ln(t_{ind})$ and $\ln^{-2}S$. Qian [18] and Tai [19] applied a cluster coagulation model to calculate the induction time at different levels of supersaturation. From this model, the microwave effect on the clusters in the solution can be investigated.

In this paper, calcium sulfate is used as the working substance precipitated by mixing aqueous $CaCl_2$ and Na_2SO_4 solutions [20]. Induction time, which has an inverse proportional relationship with nucleation rate, is studied to determine the microwave effect on primary nucleation in a reactive crystallization process. The microwave effect on nucleation is investigated by both the model of t_{ind}-σ and the cluster coagulation model. And the cluster coagulation model was used to investigate the effect of energy input on dominating cluster size in microwave field.

---

* Corresponding author.
E-mail address: zhichao.guo@tust.edu.cn (Z. Guo).

http://dx.doi.org/10.1016/j.jcrysgro.2017.05.031
0022-0248/

Nomenclature

a	the slope of the straight line
A', A''	a frequency factor
B	the nucleation rate
C	the concentration
C_C	the molecular density of solid
C^*	the equilibrium saturation
D_{AB}	the diffusion coefficient
E	the microwave energy input
E_N	the activation energy for nucleation
f	the geometric correction factor
g	number of monomers in a cluster
g_c	the number of monomers in a critical cluster
$\bar{g}$	the number of monomers in dominating clusters
ΔG_g	overall excess free energy of formation of a g-mer
ΔG_v	the volume excess free energy
k	the Boltzmann constant
k_N	the nucleation coefficient
K_{sp}	the solubility product
K, K_1	a proportion constant
n	the apparent nucleation order
n_g	the number concentration of g-mers
$n_{\bar{g}}$	the number concentration of dominating clusters
n_1	the number concentration of monomers
N_A	the Avogadro's constant
P	the displayed energy value of microwave synthesizer
r	the radius of curvature of the nucleus
r_g	the radius of a spherical g-mer
$r_{\bar{g}}$	the radius of $\bar{g}$-mer
R	the gas constant
S	the supersaturation ratio of the solution
t_c	a constant (1 s) to normalize t_{ind} to a dimensionless number
t_{ind}	the induction time
T	the temperature
V_m	the monomer volume
γ_{CL}	the interfacial energy of the crystal
σ	the relative supersolubility
θ	the contact angel

2. Theory

When microwave propagates through a liquid medium, its power will not only cause temperature increase, but also initiate an important phenomenon known as electromagnetic effect, which can enhance the rate of mass transfer [7,8,16]. Janney [21] and Wilson [22] found that the diffusion coefficient of system is enhanced by the microwave electromagnetic effect as well.

The classical nucleation theory indicates that when the solution is supersaturated, the monomers in solution start to coagulate and form clusters. If the size of a cluster exceeds a critical size, a nucleus forms and the subsequent growth of nucleus leads to a crystal. According to this theory, a stable nucleus is unlikely to result from the simultaneous collision of the required number of monomers since this would constitute an extremely rare event. More likely, it could arise from sequence of bimolecular additions according to the scheme [20]:

$$\begin{aligned} &A + A \Longleftrightarrow A_2 \\ &A_2 + A \Longleftrightarrow A_3 \\ &A_{g_c-1} + A \Longleftrightarrow A_{g_c} \quad \text{(critical cluster)} \end{aligned} \tag{1}$$

The nucleation rate (B) can be expressed by [18]:

$$B = A' \exp\left(-\frac{1}{2} g_c \ln S\right) \tag{2}$$

where g_c is the number of monomers in a critical cluster, and A' is a frequency factor of homogeneous nucleation, which is of the order 10^{25} no/cm^{3}s for the case of crystallization from solution [18], and has a direct proportional relationship with diffusion coefficient (D_{AB}) [23]. After a cluster reaches the critical size, it will grow spontaneously. Clusters whose sizes are below the critical size are termed as embryos whereas those above are called nuclei. This model can be incorporated into the classical primary nucleation model, which can be expressed by [23]:

$$B = A' \exp\left[-\frac{16}{3}\pi\left(\frac{\gamma_{CL}}{kT}\right)^3\left(\frac{V_m}{\ln S}\right)^2\right] \tag{3}$$

where V_m is the monomer volume, γ_{CL} is the surface tension, k is the Boltzmann constant, T is the absolute temperature.

And the supersaturation ratio (S) can be expressed as [20]:

$$S = \frac{C}{C^*} \tag{4}$$

where C is the concentration of calcium sulfate, C^* is the equilibrium saturation at the given temperature (25 °C) and the solubility product of calcium sulfate $K_{sp} = 9.10 \times 10^{-6}$ [24], so $C^* = (K_{sp})^{1/2} = 3.017 \times 10^{-3}$ [20].

The induction time is believed to have an inverse ratio relationship with nucleation rate. It can be expressed by [20,23]:

$$B = K t_{ind}^{-1} \tag{5}$$

where t_{ind} is the induction time and K is a constant of proportionality. So Eq. (3) can be transformed to:

$$\ln t_{ind} = -\ln\frac{A'}{K} + \frac{16}{3}\pi\left(\frac{\gamma_{CL}}{kT}\right)^3 V_m^2 \ln^{-2} S \tag{6}$$

The logarithmic plot of induction time (t_{ind}) against relative supersolubility (σ) forms three straight lines [17,25]. These correspond to different nucleation mechanisms: heterogeneous nucleation, homogeneous nucleation and mixed mechanisms respectively [26]. Because the straight lines are not parallel and the intercepts are different, the apparent nucleation orders (n) and the nucleation coefficients (k_N) are not similar in different regions:

$$\ln\left(\frac{t_{ind}}{t_c}\right) = \ln\left(\frac{K_1}{k_N C^{*n}}\right) - n\ln(\sigma) \tag{7}$$

where K_1 is a constant of proportionality, k_N is the nucleation coefficient, C^* is the equilibrium saturation at the given temperature, σ is the relative supersolubility and n is the apparent nucleation order. t_c, which is 1 s, is a constant to normalize the induction time (t_{ind}) to a dimensionless number.

The nucleation coefficient (k_N) is usually described by an Arrhenius-type equation [27]:

$$k_N = k_{N,\infty} \exp\left(\frac{-E_N}{RT}\right) \tag{8}$$

where E_N is the activation energy for nucleation, R is the gas constant.

The relative supersolubility (σ) can be expressed by [20]:

$$\sigma = S - 1 \tag{9}$$