



Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Quantitative evaluation on the heterogeneous nucleation of amino acid by a thermodynamic analysis

Yohei Kamano^a, Kazunori Kadota^{a,b,*}, Atsuko Shimosaka^a, Yoshiyuki Shirakawa^{a,*}, Jusuke Hidaka^a

^a Department of Chemical Engineering and Materials Science, Doshisha University, 1-3 Miyakodani, Tatara, Kyotanabe, Kyoto 610-0321, Japan

^b Osaka University of Pharmaceutical Sciences, 4-20-1 Nasahara, Takatsuki, Osaka 569-1094, Japan

ARTICLE INFO

Article history:

Received 21 June 2014

Received in revised form 21 October 2014

Accepted 14 November 2014

Available online xxxx

Keywords:

Heterogeneous nucleation

Homogeneous nucleation

Thermodynamic analysis

Differential scanning calorimeter

ABSTRACT

Quantitative evaluation of heterogeneous nucleation is important in order to control crystal form or particle morphology. In the present work, heterogeneous nucleation was quantitatively estimated from induction time, which was defined as the period required for nucleation. The induction time of heterogeneous nucleation was thermodynamically measured with a differential scanning calorimeter. As a result, the free energy change of glycine nucleation in the supersaturated solution was calculated from the heterogeneous nucleation rate. The free energy change decreased with an increase in the occurrence frequency of heterogeneous nucleation. This method suggested that there was a possibility of making the distinction between homogeneous nucleation and heterogeneous nucleation from quiet supersaturated solution. Characteristic parameters of critical nucleus of homogeneous nucleation gave a good agreement with the experimental results. We could quantitatively predict the characteristic properties of heterogeneous nucleation introducing substance-specific parameters.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Improvement in functionality of materials grows increasingly important to enhance human quality of life. Composite technology is remarkable as an attractive method for developing the functional materials. Creation of composite particles is indispensable for developing chemical industry, because this technique enables materials to possess various characteristics. The composite technology has a potential of creating unprecedented and innovative materials with high functions [1]. The control of particle properties is an essential requirement to obtain the composite particles with high performance as the physical and chemical properties of particle have much influence on product performance [2].

Crystallization is a prospective isolated process for manufacturing composite particles because this process combines both particle generation and purification to control physical and chemical properties [3,4]. Crystallization and polymerization in oil-in-water or water-in-oil emulsions have been applied to particle production techniques [5]. Kawashima et al. developed the novel and economical crystallization techniques, which could obtain drugs and biocompatible polymers with a spherical shape during crystallization process [6,7]. The spherical crystallization is expected as a production technique of hybrid particles in one step process. However, crystallization is a complicated

phenomenon, which proceeds in two stages, nucleation and growth. Nucleation, which is classified into the primary and the secondary nucleation, is the first step in the crystallization process. The primary nucleation takes places in the absence of crystalline surfaces, namely nuclei are generated directly from solution. The primary nucleation has two types of homogeneous nucleation and heterogeneous nucleation [8]. Nucleation without preferential nucleation sites is homogeneous nucleation, which occurs spontaneously, although it requires much higher supersaturation. The secondary nucleation results in the presence of crystals in the supersaturated solution. These parent crystals have a catalyzing effect on the nucleation phenomena. The second step in the crystallization is crystal growth, indicating that the nuclei grow to mature crystals. The various conditions of crystal growth have a significant impact on the particle size, morphology and structure [9]. An understanding of crystal growth theory is important in the development of controlling the particle properties. There have been various investigations of crystal growth models [10–17]. Volmer suggested that the growth of a face on a crystal must be a periodic process which is accomplished by a successive formation and spreading of crystal layers [10]. The theory of the surface energy assumes that the shape of crystal growth has the minimum surface energy. This approach has largely fallen into disuse. Gibbs showed that the growth of a crystal could be considered as a special case of this principle [18]. The total free energy of a crystal under equilibrium conditions would be a minimum volume. Moreover, the diffusion mechanism is based on a theory that matter is deposited continuously on a crystal face proportionally to the difference in concentration between the point of deposition and the bulk of solution.

* Corresponding authors at: Osaka University of Pharmaceutical Sciences, 4-20-1 Nasahara, Takatsuki, Osaka 569-1094, Japan.

E-mail addresses: kadota@gly.oups.ac.jp (K. Kadota), yshiraka@mail.doshisha.ac.jp (Y. Shirakawa).

A better understanding of the nucleation mechanism may make it easier to control the particle properties. Nucleation plays a decisive role in determining the crystal structure and size distribution [19]. Classical nucleation theory was proposed by many researchers such as Gibbs, Volmer and Weber. Classical nucleation theory is based on a condensation process from a vapor to a liquid [18,20–22]. Nucleation from solution has been established based on this theoretical treatment. The most important factor in this theory is a concept of the free energy barrier corresponding to energy required for the generation of a critical nucleus. Classical nucleation theory is founded on a hypothesis that the size of the clusters increases by attachment of single molecule and neglects collision between two clusters. This hypothesis causes discrepancy between theoretical predictions and experimental results [19]. The development of the two-step nucleation theory has been raised [23–26]. The two-step nucleation theory is composed of two steps as its name suggested. The first step is the formation of a liquid-like cluster of solute molecules. The second step is the reorganization of a cluster into an ordered crystalline structure. Wolde and Frenkel proved the two-step nucleation theory by computer simulations [23]. They simulated the homogeneous nucleation in a Lennard-Jones system by Monte Carlo algorithms. These results revealed that the homogeneous nucleation was formed by highly disordered liquid-like droplets. The re-structure of molecules inside the droplet is necessary to form crystalline nucleus beyond a certain critical size. The frequency of critical nuclei formation is estimated from induction time, which is defined as the period required for a nuclei generation on the seed particles or in the bulk solution [27]. There are many methods for detecting the induction time such as light scattering, electric conductivity and calorimetric measurement [28–37]. Harano et al. monitored the heat of crystallization from an aqueous solution using a differential scanning calorimeter (DSC) and theoretically proposed the equation of homogeneous nucleation rate [32,33]. In our previous paper, the properties of clusters with changing habit modifiers were determined by DSC measurements [37]. However, this result is subject to the law of only homogeneous nucleation theory, indicating that the heterogeneous nucleation at the wall and bottom of the vessel was neglected. The effect of the surface on the nucleation should be discussed on heterogeneous nucleation theory.

In the present study, a new approach was attempted for evaluating heterogeneous nucleation quantitatively. The induction time for nucleation with DSC was measured to calculate the free energy change for nucleation on the basis of the heterogeneous nucleation rate. The impact of the surface area of solution on the free energy change was examined. The method separated homogeneous and heterogeneous nucleation from quiet supersaturated solution that was constructed by the surface area dependence of the free energy change. The properties of heterogeneous nucleation were calculated.

2. Theory

2.1. Homogeneous nucleation and heterogeneous nucleation

There have been many researches about nucleation and crystal growth [18–27]. Homogeneous nucleation occurs in the bulk of supersaturated solutions. The free energy change expresses the sum of the free energy change caused by the formation of the surface when the birth of nucleus occurs. The critical size of nucleation can be found by minimizing a function of free energy with respect to radius. The relation between the critical size of nucleation and supersaturation ratio is given by the Gibbs–Thomson equation associated with a non-electrolyte [8]. Smaller clusters dissolve whereas larger clusters grow until they reach a critical size, and as a result, a new phase is created according to thermodynamic fluctuations. The thermodynamic part of the classical nucleation theory was developed by Gibbs [38,39]. He assumed that the condensation and vapor could be modeled as if they were homogeneous bulk phases with extensive internal energies and entropies, proportional to the numbers of molecules. According to the Gibbs–Thomson effect,

smaller crystals have higher solubility while larger crystals grow faster as described above. Assuming that the rate of nucleation can be expressed as the form of the Arrhenius reaction velocity equation [8], Kanagasekaran et al. calculated the nucleation parameters such as the radius of critical nucleus and critical free energy change for benzimidazole [40]. The interfacial energy obtained from their experiments was in good agreement with the theoretically calculated values [41].

A foreign substance existing in a supersaturated solution is known as the reduction in the energy for nucleation [8]. The relation between free energy change and radius of particles is shown in Fig. 1(a) to explain the nucleation phenomenon in a container. Fig. 1(a) also shows a conceptual diagram and just represents the difference between homogeneous nucleation and heterogeneous nucleation. Mullin [8] reported that the activation energy was caused by the competition of surface energy and inside energy of aggregates of particles. The nucleus corresponding to the top of the activation energy is the critical nucleus. Owing to this energy gap, the occurrence ratio of homogeneous nucleation and heterogeneous nucleation varies with the supersaturation ratio. Nucleation in a container consists of homogeneous nucleation from solution and heterogeneous nucleation from boundary interface of the wall. Heterogeneous nucleation occurs at a lower supersaturation relative to homogeneous nucleation. A schematic representation of heterogeneous nucleation is illustrated in Fig. 1(b). This illustration depicts an interfacial energy diagram for three stages of interphase. The interfacial tension is denoted by γ_{CL} (between the solid crystalline phase and the liquid), γ_{SL} (between another solid surface and the liquid) and γ_{CS} (between the solid crystalline phase and the foreign solid surface), respectively. The overall free energy change is expressed by replacing the nucleus surface with the sum of solid–liquid interface area and substrate–crystalline interface area and the nucleus volume with the crystal volume of heterogeneous nucleus [8],

$$\Delta G = \left(2\pi r^2(1 - \cos\varphi) + \pi r^2 \sin^2\varphi \right) \sigma + \frac{\pi r^3(2 + \cos\varphi)(1 - \cos\varphi)^2}{3} \Delta G_v \quad (1)$$

where ΔG is the free energy change for the formation of new phase, σ is the surface energy, r is the radius of the critical nucleus and φ is the contact angle between the crystalline deposit and the foreign solid surface. The free energy change associated with the formation of a critical nucleus under heterogeneous conditions must be less than the corresponding

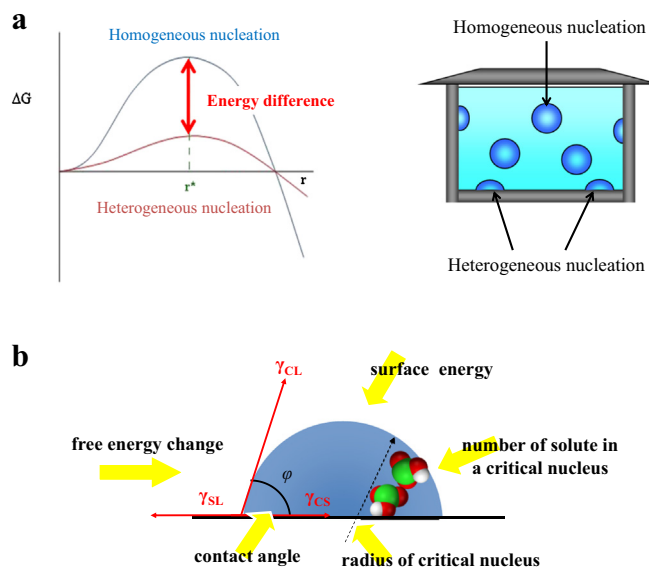


Fig. 1. (a) Relation between free energy change and radius of nucleation. (b) Schematic illustration of heterogeneous nucleation.

Download English Version:

<https://daneshyari.com/en/article/5411148>

Download Persian Version:

<https://daneshyari.com/article/5411148>

[Daneshyari.com](https://daneshyari.com)