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Simultaneous determination of interfacial energy and growth activation energy from induction time measurements

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ABSTRACT

A model is developed in this work to calculate the interfacial energy and growth activation energy of a crystallized substance from induction time data without the knowledge of the actual growth rate. Induction time data for α L-glutamic acid measured with a turbidity probe for various supersaturations at temperatures from 293 to 313 K are employed to verify the developed model. In the model a simple empirical growth rate with growth order 2 is assumed because experiments are conducted at low supersaturation. The results indicate for α L-glutamic acid that the growth activation energy is 39 kJ/mol, which suggests that the growth rate of small nuclei in the agitated induction time experiments is integration controlled. The interfacial energy obtained from the current model is in the range of 5.2–7.4 mJ/m^2, which is slightly greater than that obtained from the traditional method ($t_i^{-1} \propto J$) for which the value is in the range 4.1–5.7 mJ/m^2.

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1. Introduction

The induction time in a crystallization system is defined as the time between the creation of the supersaturation and the appearance of detectable nuclei [1,2]. Thus, induction time strongly depends on the detection method. Various techniques have been developed for detecting the onset of nucleation, including visual observation of crystal appearance [3–6], the detection of a change of solution conductivity [7–10] or the detection of a change in the intensity of transmitted or scattered light [11–15] in solution.

According to classical nucleation theory (CNT), only nuclei greater than a critical nucleus size are thermodynamically stable and can continue to grow to a detectable size [1,2]. The formation of critical nuclei is closely related to the interfacial energy of the crystallized substance. Generally, the higher the value of the interfacial energy, the more difficult it is for the solute to crystallize. Thus, the interfacial energy is an important characteristic property of the crystallized substance in the nucleation process. The interfacial energy is usually calculated from induction time data in the literature by assuming that $t_i^{-1} \propto J$ regardless of the detection technique [1].

To incorporate the combined effect of nucleation and growth, Kashchiev et al. [16] derived a general formula to relate the induction time to the solid phase formation in terms of the mononuclear or polynuclear mechanism. Recently, Shiau and Lu [17] have developed a model to calculate the interfacial energy of the crystallized substance from induction time data based on various techniques for the detection of the nucleation point. Knowledge of the crystal growth rate is required in these models to account for the crystal size distribution of the resulting nuclei at the point of detection [17–19]. As it is difficult to experimentally measure the growth rate of very small nuclei, the applicability of these models is restricted. In the present work, a novel approach is developed to calculate the interfacial energy and growth activation energy from induction time data without knowledge of the real growth rate of small nuclei.

2. Theory

According to CNT [1,2], the nucleation rate is expressed as

$$J = A_J \exp\left(-\frac{16\pi v^2\gamma^3}{3k_B^3T^3\ln^2 S}\right) \quad (1)$$

where $v = \frac{M_w}{\rho_c N_A}$ and $S = \frac{C}{C_{eq}}$.

To account for the combined effect of nucleation and growth detected at the nucleation point, the growth rate of the nuclei is required in the induction time study. From a thermodynamic point of view, Mohan and Myerson [20] developed a simple empirical power-law growth rate expression as

$$G = k_G\left(\frac{\Delta\mu}{RT}\right)^g = k_G\left[\ln\left(\frac{a}{a^*}\right)\right]^g \quad (2)$$

where $\Delta\mu$ is the difference in the chemical potential of a given

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Nomenclature

A_J	kinetic parameter in Eq. (1) ($m^{-3}s^{-1}$)
A_G	kinetic parameter in Eq. (4) (ms^{-1})
a	activity (dimensionless)
a_{eq}	activity at the equilibrium condition (dimensionless)
C	concentration of solutes (kg solute/kg solution)
C_{eq}	saturated concentration of solutes (kg solute/kg solution)
E_G	growth activation energy (kJ/mol)
f_A	minimum detectable projected area density of accumulated crystals in the detector direction for a certain detector (m^2m^{-3} or m^{-1})
f_N	minimum detectable number density of accumulated crystals for a certain detector (m^{-3})
f_V	minimum detectable volume density of accumulated crystals for a certain detector (dimensionless)
G	growth rate (ms^{-1})
g	growth rate order (dimensionless)
J	nucleation rate ($m^{-3}s^{-1}$)
k_A	area shape factor (dimensionless)
k_B	Boltzmann constant ($=1.38*10^{-23}$ JK^{-1})
k_G	growth rate constant ($m\,s^{-1}$)
k_V	volume shape factor (dimensionless)
M_w	molar mass ($kg\,mol^{-1}$)
N_A	Avogadro number ($=6.02*10^{23}$ mol^{-1})
R	ideal gas constant ($=8.314*10^{-3}$ kJ/mol−K)
S	supersaturation ratio (dimensionless)
T	temperature (K)
t	time (s)
t_i	induction time (s)

Greek letters

γ	interfacial energy ($J\,m^{-2}$)
ρ_C	crystal density ($kg\ m^{-3}$)
v	volume of the solute molecule (m^3)

substance in the supersaturated solution and saturated solution. If the supersaturation is low, the power g according to the BCF model should equal 2 [21], and Eq. (2) reduces to

$$G = k_G\left[\ln\left(\frac{a}{a_{eq}}\right)\right]^2 \cong k_G\left[\ln\left(\frac{C}{C_{eq}}\right)\right]^2 = k_G \ln^2 S \tag{3}$$

Mohan and Myerson [20] reported that Eq. (3) could be successfully applied to describe the dependence of growth rate on the supersaturation for a number of system, including L-glutamic acid in water. The temperature dependence of k_G can be expressed in terms of the Arrhenius equation as

$$k_G = A_G \exp\left(-\frac{E_G}{RT}\right) \tag{4}$$

2.1. Determination of γ based on f_N

For simplicity, the nucleation event is assumed to correspond to a point at which the total number density of accumulated crystals has reached a fixed (but unknown) value, f_N [22–24]. Thus, one obtains at the induction time t_i

$$f_N = J\,t_i \tag{5}$$

Substituting Eq. (1) into Eq. (5) yields

$$\ln\left(\frac{1}{t_i}\right) = \ln\left(\frac{A_J}{f_N}\right) - \frac{16\pi v^2\gamma^3}{3k_B^3T^3\ln^2 S} \tag{6}$$

This is consistent with the common method adopted in the literature to calculate γ from induction time data [1]. Thus, a plot of $\ln\left(\frac{1}{t_i}\right)$ versus $\frac{1}{\ln^2 S}$ at a given temperature should give a straight line, the slope and intercept of which permit determination of γ and $\frac{A_J}{f_N}$, respectively. If f_N is known, A_J can be determined.

2.2. Determination of γ based on f_A with a known G

When induction time data are measured using a turbidity meter, the measurements are based on the change in intensity transmitted or scattered light along the detector direction, which is related to the total projected area density of accumulated crystals in the detector direction [17,25–26]. Because the nuclei are generated continuously during the induction time, nuclei born at time t can grow from t to t_i and their surface area at time t_i is given by

$$A(t) = k_A G^2 (t_i - t)^2 \tag{7}$$

As described by Shiau and Lu [17], the total projected area density of these crystals in the detector direction at t_i should correspond to f_A. Thus, one obtains at the induction time t_i

$$f_A = \int_0^{t_i} J\,\frac{1}{4}A(t)dt = \frac{Jk_A G^2 {t_i}^3}{12} \tag{8}$$

where the factor $\frac{1}{4}$ is incorporated to account for the projected portion of the surface.

If G is a known function of S and T, substituting Eq. (1) into Eq. (8) yields

$$\ln\left(\frac{12}{k_A G^2 t_i^3}\right) = \ln\left(\frac{A_J}{f_A}\right) - \frac{16\pi\, v^2\gamma^3}{3k_B^3T^3\ln^2 S} \tag{9}$$

Thus, a plot of $\ln\left(\frac{12}{k_A G^2 t_i^3}\right)$ versus $\frac{1}{(\ln S)^2}$ at a given temperature should give a straight line, the slope and intercept of which permit determination of γ and $\frac{A_J}{f_A}$, respectively. If f_A is known, A_J can be determined.

2.3. Determination of γ based on f_A with an unknown G

It is usually difficult to experimentally determine the actual growth kinetics of small nuclei. To apply Eq. (8) without the knowledge of actual growth kinetics, substituting Eqs. (1) and (3) into Eq. (8) yields

$$\ln\left(\frac{12}{k_A t_i^3 \ln^4 S}\right) = \ln\left(\frac{A_J k_G^2}{f_A}\right) - \frac{16\pi\ v^2\gamma^3}{3k_B^3T^3\ln^2 S} \tag{10}$$

A plot of $\ln\left(\frac{12}{k_A t_i^3 \ln^4 S}\right)$ versus $\frac{1}{\ln^2 S}$ at a given temperature should give a straight line, the slope and intercept of which permit determination of γ and $\frac{A_J k_G^2}{f_A}$, respectively. If $\frac{A_J k_G^2}{f_A}$ is determined at different temperatures, substitution of Eq. (4) yields

$$\ln\left(\frac{A_J k_G^2}{f_A}\right) = \ln\left(\frac{A_J A_G^2}{f_A}\right) - \frac{2E_G}{RT} \tag{11}$$

Thus, a plot of $\ln\left(\frac{A_J k_G^2}{f_A}\right)$ versus $\frac{1}{T}$ should give a straight line, the slope and intercept of which permit determination of E_G and $\frac{A_J A_G^2}{f_A}$, respectively. It should be noted that only $A_J A_G^2$ can be determined

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