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Comparison of the interfacial energy and pre-exponential factor calculated from the induction time and metastable zone width data based on classical nucleation theory

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ABSTRACT

The pre-exponential factor and interfacial energy obtained from the metastable zone width (MSZW) data using the integral method proposed by Shiau and Lu [1] are compared in this study with those obtained from the induction time data using the conventional method ($t_i \propto J^{-1}$) for three crystallization systems, including potassium sulfate in water in a 200 mL vessel, borax decahydrate in water in a 100 mL vessel and butyl paraben in ethanol in a 5 mL tube. The results indicate that the pre-exponential factor and interfacial energy calculated from the induction time data based on classical nucleation theory are consistent with those calculated from the MSZW data using the same detection technique for the studied systems.

1. Introduction

The induction time is defined as the time interval between the creation of the supersaturation and the formation of detectable nuclei [2–4]. As the induction time can be experimentally determined by the isothermal method at a constant supersaturation level, the induction time data are frequently used as a measure of the nucleation event to calculate the interfacial energy of the crystallized substance in the literature [5–13].

The metastable zone width (MSZW) is also an important characteristic property of nucleation for a system. The MSZW is defined as the temperature interval between the creation of the supersaturation and the formation of detectable nuclei during the cooling process, which is usually determined by the polythermal method at a constant cooling rate [2–4]. Although the induction period and the MSZW of a crystallization system are closely related, only a limited number of studies have been reported to calculate the interfacial energy directly from the MSZW data [1,14,15].

As both the induction period and the MSZW of a crystallization system are directly related to the nucleation rate of the supersaturated solution, the same nucleation kinetics should be obtained based on either the induction time data or the MSZW data for the same system. To validate this point, the pre-exponential factor and interfacial energy obtained from the MSZW data using the integral method proposed by Shiau and Lu [1] are compared in this study with those obtained from the induction time data using the conventional method ($t_i \propto J^{-1}$) for three crystallization systems.

2. Theory

Based on classical nucleation theory (CNT), the nucleation rate is often expressed by two alternative equations as [2]

$$J = A_J \exp\left[-\frac{16\pi\, v^2\gamma^3}{3{k_B}^3T^3 \ln^2 S}\right] \tag{1a}$$

or [3,4]

$$J = A_J S \exp\left[-\frac{16\pi\, v^2\gamma^3}{3{k_B}^3T^3 \ln^2 S}\right] \tag{1b}$$

In the induction time study, the nucleation event is usually assumed to correspond to a point at which the total number density of accumulated crystals in a vessel has reached a fixed (but unknown) value, f_N [1,16,17]. As J remains unchanged for the chosen S at a constant T during the induction time study, one obtains at the nucleation point

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Notation

A_J	the pre-exponential factor in nucleation rate ($m^{-3}\,s^{-1}$)
C_0	initial saturated concentration of solutes at T_0 (kg/m^3)
C_{eq}	saturated concentration of solutes (kg/m^3)
CV	coefficient of variation among all $\left(\frac{A_J}{f_N}\right)_j$ (dimensionless)
f_N	the minimum detectable number density of accumulated crystals (m^{-3})
f_V	the minimum detectable volume fraction of accumulated crystals (dimentionless)
J	nucleation rate ($m^{-3}\,s^{-1}$)
k_B	the Boltzmann constant ($= 1.38{*}10^{-23}$ J/K)
k_V	the volume shape factor (dimentionless)
M_w	the molar mass (kg/mol)
N_A	Avogadro number ($= 6.02{*}10^{23}$ mol^{-1})
R	cooling rate (K/s)
S	supersaturation ratio (dimentionless)
T	temperature (K)
T_0	initial saturated temperature (K)
T_m	temperature at the MSZW limit at t_m (K)
t	time (s)
t_i	induction time (s)
t_m	time at the MSZW limit (s)
V	solution volume (m^3)

Greek letters

γ	interfacial energy (J/m^2)
ρ_C	crystal density (kg/m^3)
v	volume of the solute molecule, $v = \frac{M_w}{\rho_C N_A}$ (m^3)
ΔT_m	MSZW (K)

$$f_N = J\,t_i \quad (2)$$

where f_N depends on the measurement device and on the substance. Note that Eq. (2) is consistent with $t_i \propto J^{-1}$ [2–4]. Substituting Eq. (1a) or Eq. (1b) into Eq. (2) yields

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

or

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

Experimental induction time results can be evaluated by plotting $\ln\left(\frac{1}{t_i}\right)$ or $\ln\left(\frac{1}{t_i S}\right)$ versus $\frac{1}{T^3\ln^2 S}$ for determination of γ from the slope and $\frac{A_J}{f_N}$ from the intercept, respectively. If f_N is known, A_J can be determined.

As the MSZW and the induction time are both the reflection of nucleation, the MSZW limit is also defined, the same as the induction time, as the time needed for the number density of accumulated crystals in a vessel to reach f_N during the cooling process [1,16,17]. Thus, one obtains at the MSZW limit

$$f_N = \int_0^{t_m} J\,dt \quad (4)$$

To compare the MSZW and the induction time data using the same detection technique, it is assumed that f_N is independent of t_i as well as of t_m and that f_N is equal for both approaches.

If the solution is cooled at a constant rate defined as

$$R = -dT/dt \quad (R > 0) \quad (5)$$

One obtains $T(t) = T_0 - R\,t$ during the cooling process. By substituting Eq. (1a) or Eq. (1b) into Eq. (4), Shiau and Lu [1] derived

$$\frac{A_J}{f_N} = \frac{1}{\frac{-1}{R}\int_{T_0}^{T_m}\exp\left[-\frac{16\pi\, v^2\gamma^3}{3k_B^3T^3\ln^2 S(T)}\right]dT} \quad (6a)$$

or

$$\frac{A_J}{f_N} = \frac{1}{\frac{-1}{R}\int_{T_0}^{T_m}S(T)\exp\left[-\frac{16\pi\, v^2\gamma^3}{3k_B^3T^3\ln^2 S(T)}\right]dT} \quad (6b)$$

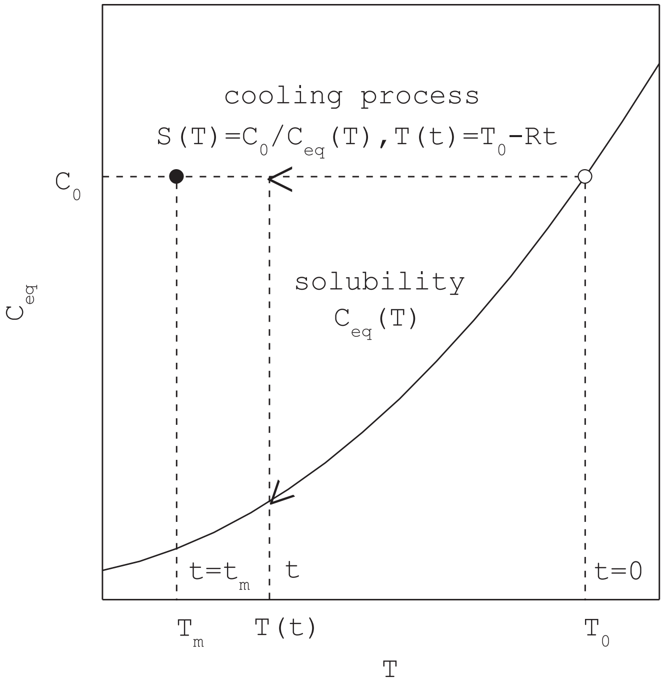

Fig. 1. A schematic diagram showing the increase of supersaturation during the cooling process for the saturated concentration C_0 (○ represents the starting point and ● represents the nucleation point at a given R).

where, as shown in Fig. 1, T_0 is the initial saturated temperature at $t = 0$, T_m is the maximum supercooling temperature at t_m, $\Delta T_m = T_0 - T_m$ is the MSZW, C_0 is the saturated concentration at T_0, and $S(T) = \frac{C_0}{C_{eq}(T)}$ is the temperature-dependent supersaturation during the cooling process. Note that C_0 remains unchanged before the onset of nucleation while $C_{eq}(T)$ usually decreases with decreasing temperature. Thus, if $C_{eq}(T)$ is a known temperature-dependent function, the integral from T_0 to T_m can be numerically integrated for a given γ.

The following nonlinear regression procedure is adopted to determine two parameters, γ and $\frac{A_J}{f_N}$, in Eq. (6a) or Eq. (6b) for the studied system from the experimental data of T_m versus R at a given C_0 with a known $C_{eq}(T)$: (a) Guess γ; (b) Determine $\left(\frac{A_J}{f_N}\right)_j$ for each pair of T_m versus R data from Eq. (6a) or Eq. (6b) by numerical integration; (c) Calculate $\left(\frac{A_J}{f_N}\right)_{av}$; (d) Calculate the coefficient of