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A model for determination of the interfacial energy from the measured metastable zone width by the polythermal method



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ABSTRACT

A model is proposed in this work for progressive nucleation to interpret the measured metastable zone width (MSZW) by the polythermal method using the classical nucleation theory. As similar to Kubota's model [1], the MSZW limit is assumed to correspond to a point at which the number density of accumulated crystals has reached a fixed (but unknown) value during the cooling process. The model yields an integral formula to directly determine the interfacial energy of the crystallized substance from the measured MSZW data at various cooling rates. It is found that the model fits well with the experimental data in the literature.

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1. Introduction

Metastable zone width (MSZW) in supersaturated solutions is an important characteristic property of crystallization for each system. MSZW is usually determined by the polythermal method when the solution is continuously cooled at a constant cooling rate. The MSZW can vary significantly among different solute–solvent systems and is also affected by the hydrodynamic and operating conditions of the studied system [2]. The measurements of MSZW depend on the sensitivity of the detection techniques for the change of electrical conductivity [3], ultrasound velocity [4–7], turbidity [4,8,9], or video imaging [10] of the solution at the MSZW limit during the cooling process.

The Nyvlt's approach [11,12] has been traditionally adopted to interpret the MSZW at constant cooling rates by the polythermal method. Basically, it is assumed that the nucleation only occurs at the MSZW limit; then, the nucleation rate is related to the supersaturation consumption rate at the MSZW limit in mass basis. Recently, Sangwal [13] proposed the self-consistent Nyvlt-like equation using the theory of regular solutions for the temperature dependence of solubility. The power-law form of the nucleation rate is assumed in these models, both of which lead to a linear relationship of $\log(\Delta T_m/T_0)$ versus $\log R$ for the experimental data on the maximum supercooling ΔT_m , a measure of MSZW, for solutions saturated at a temperature T_0 as a function

of cooling rate R . Based on Nyvlt's approach and the classical nucleation theory [14,15], Sangwal [16] also developed a new approach to analyze the MSZW determined by the polythermal method. The resulting equation yields a linear relationship of $(T_0/\Delta T_m)^2$ versus $\log R$.

To elucidate the dependence of MSZW on cooling rate based on the classical theory of nucleation, Kashchiev et al. [17] assumed progressive nucleation, in which new crystallites are continuously nucleated among the already growing ones during the cooling process. The MSZW limit is assumed to correspond to a point at which the detectable crystallite volume fraction has reached a fixed value. The resulting model verifies that the often used semi-empirical Nyvlt equation is an approximation which contains only the linear terms in the relationship between $\log(\Delta T_m/T_0)$ and $\log R$. Kashchiev et al. [18] also considered the case of instantaneous nucleation, in which all crystallites appear at a particular time and grow in the absence of crystallites born subsequently during the cooling process. Compared to progressive nucleation, a more simplified model is obtained for instantaneous nucleation, which also yields a linear relationship between $\log(\Delta T_m/T_0)$ and $\log R$.

As MSZW of a system depends on the detection method of the first nucleation event, Kubota [1,19] proposed a model based on progressive nucleation to account for the MSZW limit corresponding to a point at which the number density of accumulated crystals has reached a fixed (but unknown) value during the cooling process. The simple power-law form of the nucleation rate is adopted in Kubota's model [1], leading to a linear relationship of $\log \Delta T_m$ versus $\log R$. In the present work, a new model is

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developed based on the classical nucleation theory to interpret MSZW measured for unseeded solutions by the polythermal method.

2. Model

In the MSZW experiments by the polythermal method, the MSZW limit is assumed to correspond to a point at which the number density of accumulated crystals has reached a fixed (but unknown) value. Thus, at the MSZW limit, the number density of accumulated crystals in a stirred vessel by the time t_m can be integrated as

$$N_m = \int_0^{t_m} J dt \quad (1)$$

where J is the primary nucleation rate in number basis and the minimum detectable number density of the newly formed solid phase, N_m , depends on the measurement device and on the substance. If the solution is cooled at a constant rate $R = -dT/dt$ during the time $t = 0 \sim t_m$, Eq. (1) reduces to

$$N_m = -\frac{1}{R} \int_{T_0}^{T_0 - \Delta T_m} J dT \quad (2)$$

where T_0 is the initial saturation temperature at $t = 0$, T_m is the maximum supercooling temperature at t_m , and $\Delta T_m = T_0 - T_m$ is the MSZW.

Based on the classical nucleation theory [14,15], J is often expressed by two alternative equations as

$$J = A \exp \left[\frac{16\pi V^2 \gamma^3}{3k_B^3 T^3 (\ln S)^2} \right] \quad (3a)$$

or

$$J = AS \exp \left[\frac{16\pi V^2 \gamma^3}{3k_B^3 T^3 (\ln S)^2} \right] \quad (3b)$$

where A is a kinetic parameter, γ is the interfacial energy of the crystal, k_B (1.38×10^{-23} J/K) is the Boltzmann constant, and the molecular volume of the solute is defined as

$$V = \frac{M_w}{\rho_c N_A} \quad (4)$$

where M_w is the molar mass, ρ_c is the crystal density, and N_A (6.02×10^{23}) is the Avogadro number. The fundamental dimensionless supersaturation ratio is defined by

$$S = \frac{a}{a_{eq}} \quad (5a)$$

where a is the activity of a solution and a_{eq} is the activity of a saturated solution. For sparingly soluble salts, it is more appropriate to define

$$S = \left(\frac{IP}{K_a} \right)^{1/\nu} \quad (5b)$$

where IP is the ion activity product of the lattice ions in solution and K_a is the activity solubility product of the salt, and ν is the number of ions in a formula unit of the salt. For simplicity, the most common expression of supersaturation ratio is

$$S = \frac{C}{C_{eq}} \quad (5c)$$

where C is the solute concentration and C_{eq} is the saturated solute concentration.

Substituting Eq. (3a) or Eq. (3b) into Eq. (2) yields

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

or

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

where $S = C_0/C_{eq}(T)$ is the temperature-dependent supersaturation ratio and C_0 is the initial saturation concentration at T_0 . Thus, the dependence of ΔT_m on R is related in Eq. (6a) or Eq. (6b) if the temperature dependence of solubility $C_{eq}(T)$ is known. Using the theory of regular solutions, Sangwal [13] described the temperature dependence of solubility as

$$\ln S = \frac{\Delta H_S}{R_C} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (7)$$

where ΔH_S is the enthalpy of dissolution and R_C (8.314 J/mol $-$ K) is the ideal gas constant. Substituting Eq. (7) into Eq. (6) yields the dependence of ΔT_m on R through the enthalpy of dissolution for a solute-solvent system.

The following procedure is adopted to determine γ and N_m/A for a given T_0 in Eq. (6a) or Eq. (6b) by nonlinear regression from the MSZW data of ΔT_m versus R if the temperature-dependent $S(T)$ is known: (a) Guess γ ; (b) determine N_m/A for each MSZW data by solving Eq. (6a) or Eq. (6b); (c) calculate the average value $(N_m/A)_{av}$ for all MSZW data by Eq. (8); and (d) calculate ε by Eq. (9). For the guessed γ , the average value $(N_m/A)_{av}$ is obtained by

$$\left(\frac{N_m}{A} \right)_{av} = \frac{1}{H} \sum_{j=1}^H \left(\frac{N_m}{A} \right)_j \quad (8)$$

where H is the number of data points ($H \geq 2$) and j is a dummy variable ($j = 1 \sim H$). The average relative deviation between $(N_m/A)_j$ and $(N_m/A)_{av}$ is defined as

$$\varepsilon = \frac{1}{H} \sum_{j=1}^H \frac{|(N_m/A)_j - (N_m/A)_{av}|}{(N_m/A)_{av}} \quad (9)$$

For comparison, coefficient of variation for $(N_m/A)_j$ is also determined by

$$CV = \frac{\sigma}{(N_m/A)_{av}} \quad (10)$$

where the standard deviation is defined as

$$\sigma = \sqrt{\frac{1}{H-1} \sum_{j=1}^H [(N_m/A)_j - (N_m/A)_{av}]^2} \quad (11)$$

The same procedure from (a) to (d) is repeated to find the optimal γ with the smallest ε or CV. Then, the corresponding $(N_m/A)_{av}$ is taken as the optimal N_m/A . Nevertheless, the kinetic parameter A cannot be determined as the actual value of N_m is unknown in the MSZW measurements. Further investigations are needed to determine A and N_m . However, as N_m/A is determined, the ratio of A between two systems can be obtained if the same detection technique is applied.

3. Results and discussion

Some experimental MSZW data measured by the polythermal method in the literature are illustrated here to verify the developed model. Tables 1–4 list the optimal values of γ and N_m/A with the smallest ε or CV obtained by the present model based on Eq. (6a) and Eq. (6b), respectively. Note that the obtained values of γ , N_m/A , ε and CV only vary slightly between Eq. (6a) and Eq. (6b) for the studied systems.

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