Comment on "Relation between metastable zone width and

induction time of butyl paraben in ethanol" by H. Yang,

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Abstract

In a recent paper, Yang[1] proposed a complicated summation equation to relate the induction time and the metastable zone width (MSZW) in cooling crystallization based on the classical nucleation theory. In the Yang's model, the nucleation is assumed to occur when the accumulated nucleation potential approaches the critical nucleation potential in both the induction time and MSZW experiments. However, the definition of the accumulated nucleation potential and critical nucleation potential is ambiguous. In this comment, the MSZW limit is defined the same as in the induction time as the time needed for the number density of accumulated crystals to reach a fixed (but unknown) value, f_N. An integral equation is developed to predict MSZW from the induction time results based on the classical nucleation theory.

Keywords: crystallization; nucleation; induction time; metastable zone width

In a recent paper, Yang[1] proposed a model to relate the induction time and the metastable zone width (MSZW) in cooling crystallization based on the classical nucleation theory. It is assumed in both the induction time and MSZW experiments that the accumulation of the nucleation potential continuously approaches critical nucleation potential before the nucleation occurs. A complicated summation equation is subsequently developed to extrapolate MSZW from the interfacial energy and the pre-exponential factor obtained from the induction time data in homogeneous primary nucleation. It is found that the experimental MSZWs of butyl paraben in ethanol are fairly close to those extrapolated from the induction time results. I would like to bring to attention that the concept of the nucleation potential in this model is ambiguous although the model is satisfactory to predict MSZW from the induction time results. A new approach is developed in this work to relate the induction time and the MSZW based on the classical nucleation theory.

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Based on the classical nucleation theory,[2,3] the nucleation rate is expressed as

$$J = A_J \exp[-\frac{16\pi \, v_m{}^2\gamma^3}{3k_B{}^3T^3(\ln S)^2}]$$ (1)

As the induction time, t_i, is inversely proportional to the nucleation rate in a solution with volume of V, one obtains[1,4,5]

$$\ln(\frac{1}{t_i}) = \ln(JV) = \ln(A_JV) - \frac{16\pi \, v_m{}^2\gamma^3}{3k_B{}^3T^3(\ln S)^2}$$ (2)

Experimental induction time results can be evaluated by plotting $\ln(\frac{1}{t_i})$ versus $\frac{1}{(\ln S)^2}$ for determination of γ from the slope and A_JV from the intercept, respectively.

In the model proposed by Yang, the accumulated nucleation potential at temperature T and under supersaturation S in a polythermal experiment, during each short time period (a step of time), Δt, is estimated as

$$\Delta N = \frac{\Delta t}{t_m} N = \frac{A_J V \Delta t}{\exp[\frac{N}{3k_B{}^3 T^3 (\ln S)^2}]} N \qquad (3)$$

where the critical nucleation potential is defined as

$N = 16\pi\, v_m{}^2 r^3$. For a solubility equation with the form of

$\ln x = A_s T^{-1} + B_s + C_s T$, [6] the supersaturation at T during the

cooling process can be calculated as

$$\ln S = \ln x - \ln x^* = A_s (T_0^{-1} - T^{-1}) + C_s (T_0 - T) \qquad (4)$$

where T_0 is the initial saturation temperature at $t = 0$.

Yang derived the accumulated nucleation potential from

time $t = \Delta t$, to $t = m\Delta t$, as

$$\sum_{n=1}^{m} \Delta N = \sum_{n=1}^{m} \frac{N A_J V \Delta t}{\exp[\frac{N}{3k_B{}^3 T^3 (\ln S)^2}]} \qquad (5)$$

where n and m are positive integers. Note that $T = T_0 - z_c n \Delta t$

for the linear cooling rate of z_c. The accumulated

nucleation potential increases with time, and at the

minimum value of m allowing $\sum_{n=1}^{m} \Delta N$ to be equal to or

greater than N, nucleation occurs at $t = m\Delta t$. Based on $A_J V$

and N obtained from the induction time results, Eq.(5) is

satisfactory to predict MSZW for butyl paraben in ethanol.

Yang's model is derived based on the assumption that

the accumulated nucleation potential increases with time in

both the induction time and MSZW experiments. The

nucleation is assumed to occur when the accumulated

nucleation potential approaches the critical nucleation

potential in Eq.(5). However, the definition of the

accumulated nucleation potential and critical nucleation

potential is ambiguous. A new approach is developed in the

following to predict MSZW from the induction time results

based on the classical nucleation theory.

In some induction time studies, the nucleation event is

assumed to correspond to a point at which the total number

density of accumulated crystals has reached a fixed (but

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unknown) value, f_N.[7-9] Thus, at the induction time t_i, one

obtains

$$f_N = J\ t_i \qquad\qquad\qquad (6)$$

where f_N depends on the measurement device and on the

substance. Note that Eq.(6) is consistent with $t_i \propto J^{-1}$

reported in the literature.[2,3] Substituting Eq.(1) into

Eq.(6) yields

$$\ln(\frac{1}{t_i}) = \ln(\frac{A_J}{f_N}) - \frac{16\pi\ v_m{}^2\gamma^3}{3k_B{}^3 T^3 (\ln S)^2} \qquad\qquad (7)$$

Experimental induction time results can be evaluated by

plotting $\ln(\frac{1}{t_i})$ versus $\frac{1}{(\ln S)^2}$ 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 in the induction time as the time needed for

the number density of accumulated crystals to reach f_N.[7-10]

Thus, at the MSZW limit t_m, one obtains[8,9]

$$f_N = \int_0^{t_m} J \ dt \tag{8}$$

As the solution is cooled at a constant rate $z_c = -dT/dt$,

$dt = -dT/z_c$. Substituting Eq.(1) into Eq.(8) leads to

$$1 = \frac{-1}{z_c} \int_{T_0}^{T_m} \frac{A_J}{f_N} \exp[-\frac{16\pi \ v_m^2 \gamma^3}{3k_B^3 T^3 (\ln S)^2}] \ dT \tag{9}$$

where T_m is the maximum supercooling temperature at t_m and

$\ln S$ is given in Eq.(4). Thus, MSZW is defined as $\Delta T_m = T_0 - T_m$.

As $\frac{A_J}{f_N}$ and γ are obtained from the induction time results,

Eq.(9) provides a simple method to predict MSZW from the

induction time results based on the classical nucleation

theory.

Table 1 lists results of the experimental and predicted

MSZW for butyl paraben in ethanol. Eq.(9) is integrated to

determine T_m at $T_0 = 313.14K$ for each z_c by Fortran using an

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IMSL routine, DQDAGS (double precision). The obtained ΔT_m

in this work agrees very well with that obtained from Eq.(5)

by Yang. In calculation of Eq.(9), $\dfrac{A_J}{f_N} = 1.376*10^{-2}\ s^{-1}$ and

$\gamma = 1.15\ mJ/m^2$ are taken from the induction time results

based on Eq.(7), as compared to $A_J V = 1.376*10^{-2}\ s^{-1}$ and

$\gamma = 1.15\ mJ/m^2$ adopted in calculation of Eq.(5).[5] The unique

feature of the present model is that the MSZW limit is

defined the same as in the induction time as the time

needed for the number density of accumulated crystals to

reach a fixed (but unknown) value, f_N. Although f_N remains

unknown, an integral equation is developed based on the

classical nucleation theory to predict MSZW using the

obtained values of $\dfrac{A_J}{f_N}$ and γ from the induction time study.

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Notation

A_J = kinetic parameter in the nucleation rate $(m^{-3}s^{-1})$

A_s, B_s, C_s = constant in solubility equation (-)

f_N = minimum detectable number density of accumulated

crystals for a certain detector (m^{-3})

J = nucleation rate $(m^{-3}s^{-1})$

k_B = Boltzmann constant $(=1.38*10^{-23}J\ K^{-1})$

M_w = molar mass $(kg\ mol^{-1})$

m = integer number parameter in accumulation equation (-)

N = Critical nucleation potential (kJ^3)

N_A = Avogadro number $(=6.02*10^{23}\ mol^{-1})$

n = integer number variable (-)

S = supersaturation ratio $(-)$

T = temperature (K)

T_0 = saturated temperature (K)

t = time (s)

t_i = induction time (s)

t_m = nucleation time in MSZW experiment (s)

V = solution volume (m^3)

x = actual solute molar fraction solubility (–)

x^* = equilibrium solute molar fraction solubility (–)

z_c = linear cooling rate ($K\ s^{-1}$)

ΔN = nucleation potential accumulated during Δt (kJ^3)

Δt = time step, short time period (s)

Greek letters

γ = interfacial energy ($J\ m^{-2}$)

ρ_C = crystal density ($kg\ m^{-3}$)

v_m = volume of the solute molecule, $\quad v_m = \dfrac{M_w}{\rho_C N_A}$ (m^3)

References

1 H. Yang, *CrystEngComm,* 2015, **17,** 577-586.

2 J. W. Mullin, Crystallization, Butterworth-Heinemann,

   Oxford, 1993.

3 D. Kashchiev , Nucleation: Basic theory with applications,

   Butterworth-Heinemann, Oxford, 2000.

4 H. Yang, A. C. Rasmuson, *Cryst. Growth Des.*, 2013, **13,**

   4226-4238.

5 H. Yang, M. Svard, J. Zeglinski, A. C. Rasmuson, *Cryst.*

   Growth Des., 2014, **14,** 3890-3902.

6 H. Yang, A. C. Rasmuson, *J. Chem. Eng. Data.,* 2010, **55,**

   5091-5093.

7 N. Kubota, J. *Cryst. Growth*, 2008, **310,** 629–634.

8 L. D. Shiau, T. S. Lu, *J. Cryst. Growth*, 2014, **402,**

   267-272.

9 L. D. Shiau, T. S. Lu, *CrystEngComm,* 2014, **16,** 9743-9752.

10 N. A. Mitchell, P. J. Frawley, *J. Cryst. Growth*, 2010,

   312, 2740-2746.

Table 1. Results of the experimental and predicted MSZW

for butyl paraben in ethanol at $T_0 = 313.14K$.

(the solubility equation: $\ln x = -1430.23T^{-1} + 1.3469 + 0.00826T$,

$T \ in \ K$; $v_m = 2.57*10^{-28}m^3$)[6]

z_c (K/hr)	z_c (K/s)	experimental $\Delta T_m(K)$	$\Delta T_m(K)$ by Eq.(5)[1]	$\Delta T_m(K)$ by Eq.(9)
4.0	0.00111	3.44	4.39	4.39
6.0	0.00167	3.52	4.68	4.69
12.0	0.00333	3.97	5.30	5.31
15.0	0.00417	4.07	5.55	5.56
20.0	0.00556	4.40	5.90	5.91