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Reply to the 'Comment on "Relation between metastable zone width and induction time of butyl paraben in ethanol"' by L.-D. Shiau, CrystEngComm, 2015, 17, DOI: 10.1039/C5CE00101C

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Abstract

In my original article[1], an interpretation equation showing the relation between metastable zone width and induction time was derived from the Classical Nucleation Theory. In the Comment by Shiau[2], another interpretation was put forth and the equation and results are all in good consistence with those in my original article. The parameter "critical nucleation potential" in the interpretation in my original article, derived directly from the equations of the Classical Nucleation Theory, is only dependent on the interfacial energy. The parameter "critical crystal density" in the Comment by Shiau is assumed to be constant at nucleation. The accumulated "nucleation potential" and "crystal density" in both the isothermal and the polythermal experiments raises to the critical value at nucleation, respectively. The difference between these two interpretations and the deviation between the experimental metastable zone widths with extrapolated values from induction time may result from the fact that the induction time is composed of relaxation time, nucleation time and growth time.

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I would like to acknowledge Prof. Shiau for taking sufficient interest in my original article[1] so as to correctly introduce another interpretation in the Comment by Shiau[2] based on the equations in my original article, and with this interpretation metastable zone width estimated from experimental induction time results are highly consistent with metastable zone widths extrapolated with the method in my original article.

Based on the Classical Nucleation Theory, induction time, t_{ind}, in isothermal experiments is inversely proportional to the nucleation rate[3], J, in a solution with volume of V,

$$ln t_{ind} = -ln JV = -ln AV + \frac{16\pi\sigma^3 v_m^2}{3k^3 T^3 (ln S)^2} \quad (1)$$

where σ is solid-liquid interfacial energy and v_m is molecular volume. T and S is the temperature and the supersaturation of the solution, respectively. We can rewrite Equ. (1) to

$$3k^3 \cdot T^3 (ln S)^2 \cdot ln(AV t_{ind}) = 16\pi\sigma^3 v_m^2 = N \quad (2)$$

where N is a constant nucleation parameter and then is denominated as critical nucleation potential[1] in my original article.

In a polythermal experiment, during each short time period Δt, the accumulated nucleation potential till time t_m (equal to $m\Delta t$), becomes:

$$\int_0^{m\Delta t} \Delta N \, dt \approx \sum_{n=1}^m \Delta N = \sum_{n=1}^m \frac{\Delta t}{t_n} = \sum_{n=1}^m AV\Delta t \cdot exp(-\frac{N}{3k^3 T^3 (ln S)^2})N \quad (3)$$

Nucleation happens at the minimum time of $m\Delta t$ when $\sum_{n=1}^m \Delta N$ is equal to or bigger than the value of the critical nucleation potential, N.

As the solution is cooled at a constant rate $z_c = -dT/dt$ in a polythermal experiment and $T = T_0 - z_c t$, where T_0 is the saturated temperature and N is constant for a system, accordingly

$$N = \int_0^{m\Delta t} \Delta N \, dt = -\frac{1}{z_c} \int_{T_m}^{T_0} AVN \exp\left(-\frac{N}{3k^3 T^3 (ln S)^2}\right) dT \quad (4)$$

2

In the Comment by Shiau[2], the interpretation equation is given as

$$1 = \int_0^{t_m} \frac{A}{f_N} \exp\left(-\frac{16\pi\sigma^3 v_m^2}{3k^3 T^3 (lnS)^2}\right) dt = -\frac{1}{z_c} \int_{T_m}^{T_0} \frac{A}{f_N} \exp\left(-\frac{N}{3k^3 T^3 (lnS)^2}\right) dT \qquad (5)$$

Since f_N, critical crystal density, assumed to be constant in the Comment by Shiau[2], therefore Equ. 5 (Equ. 9 in the Comment by Shiau) is consistent with Equ. 4, as well as Equ. 3 (Equ. 12 in my original article[1]), where $AV = \frac{A}{f_N} = 1.376 \times 10^{-2}$ s^{-1}, and it is easier to understand if Equ. 5 is reformed as,

$$\sum_{n=1}^{m} \Delta f_N \approx \int_0^{t_m} \Delta f_N \, dt = \int_0^{t_m} A \exp\left(-\frac{N}{3k^3 T^3 (lnS)^2}\right) dT \qquad (6)$$

which indicates during the period of t_m after the solution becomes saturated in the cooling crystallization, the accumulative "nucleus crystal" density continuously increases, approaching the constant parameter, f_N, above whose value the nucleation happens. The complex equations combined with Figure 1 in my original article clearly show the relation between polythermal and isothermal experiments and the accumulated nucleation potential increases more and more quickly with the increase of the supersaturation, which are also applicable for the interpretation in the Comment by Shiau (and Equ. 6) that with the increase of the supersaturation in the polythermal experiment, the increase rate of accumulated density of "nucleus crystals" becomes higher and higher. Figure 1 in my original article and Equ. 3-6 also indicate that the accumulated density of "nucleus crystals" and the accumulated nucleation potential increases at equal rate in the isothermal experiment, respectively.

Equ. 5 (Equ. 9 in the Comment by Shiau), as well as Equ. 4, offers a simple interpretation and is applied to obtain the accurate results if an IMSL routine[2] with Fortran is essentially used. In the Comment by Shiau, the f_N, which is the critical density of "nucleus crystals", is assumed to be constant in different nucleation experiments, whereas the value of f_N may not be constant but dependent on the experimental conditions[4]. The parameter N in my original

article, which is deviated from Equ. 1, is a parameter only determined by the solid-liquid interfacial energy. As long as the linear correlation between the supersaturation and the induction time in Equ. 1 is established, the parameter N is constant, in despite of the deviation between the linear correlation with the experimental data.

The induction time, t_{ind}, is the time period from the establishment of the supersaturated state to the first observation of crystals in the solution and is assumed to contain three parts [3]: a relaxation time or transient period t_R, the nucleation time t_N required for formation of a stable nucleus, and the time t_G for a nucleus to grow to detectable size. Usually as well as in nucleation experiments of butyl paraben [5, 6] it is assumed that the relaxation time and the growth time are negligible and that the nucleation time is inversely proportional to the nucleation rate in homogeneous nucleation i.e. $t_{ind} \approx t_N$. Some researchers suggest, the induction time is the period that the density of "crystals" in the solution reaches a certain visible value [4, 7] i.e. $t_{ind} \approx t_G$, and some researchers could estimate both t_N and t_G, by fitting the distribution [5, 8] of the induction time at equal experimental conditions, i.e. $t_{ind} \approx t_N + t_G$. It is incontestable that the nucleation time from the "first nucleus" to being visible is more or less delayed. However, if there is certain density of "crystals" already existing in the solution long time before nucleation after the temperature of solution reaches constant and the supersaturation of the solution maintains, it can hardly explain that the density of crystals reach the critical value of f_N quite sooner after adding crystals seeds than without seeding when the existing "crystals" in the solution need minutes or hours to raise to the critical value of f_N. It is very difficult to capture the boundary among t_R, t_N and t_G. Usually the time for cluster redistribution is assumed to be negligible, but the actual situation for organic molecules in organic solvents hasn't really been clarified. The history of solution effects [9] indicates a relatively long redistribution time.

Besides several factors affecting the accuracy of the estimation of metastable zone width, a) a short time period required to reach constant temperature in isothermal experiment as I mentioned in my original article, b) the fluctuation of the linear cooling temperature profile in the polythermal experiment, c) deviation among the relaxation time, the nucleation time and the growth time under isothermal and polythermal method respectively, it is worth nothing that non-steady state nucleation induced by polythermal method could have stronger influence on the estimation than anticipated. The cluster distribution could not immediately adjust to the steady state distribution in each short time period with the continuously decreasing temperature and total delayed time of redistribution time in every short time period may accumulate to be not neglectable.

Notations

A	Pre-exponential factor	$[\text{m}^{-3} \bullet \text{s}^{-1}]$
B	Slope in determination of interfacial energy	$[\text{K}^3]$
f_N	Crystal density at nucleation	$[\text{m}^{-3}]$
J	Nucleation rate	$[\text{m}^{-3} \bullet \text{s}^{-1}]$
k	Boltzmann constant, 1.38×10^{-23}	$[\text{J} \bullet \text{K}^{-1}]$
m, n	Integer number parameter	
N	Critical nucleation potential	$[\text{kJ}^3]$
S	Supersaturation	
t_{ind}	Induction time of nucleation	$[\text{s}]$
t_G	Growth time for nucleus growing to be detectable	$[\text{s}]$
t_n	Estimated induction time	$[\text{s}]$
t_N	Nucleation time required for formation a stable nucleus	$[\text{s}]$
t_R	Relaxation time or transient period	$[\text{s}]$
T	Temperature	$[\text{K}]$
T_0	Saturated temperature	$[\text{K}]$
T_m	Nucleation temperature	$[\text{K}]$
v_m	Molecular volume of solute	$[\text{m}^3]$
V	Solution volume	$[\text{m}^3]$
z_c	Linear cooling rate	$[\text{K} \bullet \text{s}^{-1}]$
σ	Solid-liquid interfacial energy in homogenous nucleation	$[\text{mJ} \bullet \text{m}^{-2}]$
Δf_N	Crystal density accumulated during Δt	$[\text{m}^{-3}]$
ΔN	Nucleation potential accumulated during Δt	$[\text{kJ}^3]$
Δt	Time step, short time period	$[\text{s}]$

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