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Analysis of the effect of volume on induction time and metastable zone width using a stochastic model

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ABSTRACT

The effect of sample volume on induction time and metastable zone width (MSZW) is discussed theoretically by using a stochastic model. The effect of sample volume on induction time and MSZW is different depending on the detection criterion of nucleation used. The induction time and MSZW both decrease with an increase in sample volume when these values are determined on the basis of total number of crystals per sample N (an extensive variable). However, when the number density of crystals N/V (an intensive variable) is used, both of them remain unchanged even when the volume is changed. Although nucleation is stochastic by nature, the induction time and the MSZW, which are both nucleation-related, are not always observed as stochastic. In case of small samples, the stochastic aspects are usually observed, because a single crystal or a small number of crystals are used as a detection criterion of nucleation. Even for large samples, the stochastic aspect could be observed in theory. However, it is not usually the case in actual experiments because a small number of crystals are rather difficult to detect when the sample is large. The stochastic induction time and MSZW are mathematically related to the deterministic induction time and MSZW, respectively.

1. Introduction

The induction time is usually defined for a solution as the time elapsed from the moment of achievement of supersaturation to the detection of a first crystallization event at a specified constant supercooling, and the metastable zone width (MSZW) is similarly defined as the supercooling at which a first crystallization event is detected when the solution is cooled at a constant rate [1]. The induction time and MSZW are both nucleation-related quantities.

In a previous paper [2], the author discussed the effect of sample volume on induction time and MSZW using both stochastic and deterministic models. When a single crystal is detected as a first crystallization event, both the induction time and MSZW distribute widely and the mean values decrease with an increase of sample volume. The induction time and MSZW are stochastic and volume-dependent; however, in the case where a predetermined number density of crystals or the detection criterion of nucleation $(N/V)_{det}$ is used as a detection criterion of nucleation, the induction time and MSZW are both deterministic and volume-independent. Kubota [2] considered that such difference in the volume dependence of induction time and MSZW is caused by the difference in the detection criterion of nucleation (not caused by the difference in nucleation mechanism). Harano et al. [3] proposed an interesting view on the effect of sample volume on induction time, which could be also applied to MSZW, that the induction time should be volume-independent if it is determined on the basis of the number density of crystals N/V; however, if it is determined on the basis of the total number of crystals N, it should be volume-dependent. N is an extensive variable; however N/V is an intensive variable, since N increases in proportion to sample volume (nucleation can be assumed to occur in a spatially uniform manner) and hence N/V does not depend on volume. The view of Harano et al. [3] is basically the same as that of Kubota [2] in that the volume dependence is related to the detection criterion. Kashchiev et al. [4] also studied, but in a different way, the effect of sample volume on induction time (they did not treat MSZW). They considered that the difference in the volume dependence is due to the difference in nucleation mode. In small samples where $V \ll \alpha^{-1/4}(G/J)^{3/4}$ (α: volume fraction of crystalline phase to the whole sample, G: growth rate and J: nucleation rate), the formation of a single nucleus was assumed to occur as a first nucleation event (they called this mononuclear mechanism), however, in large samples where $V \gg \alpha^{-1/4}(G/J)^{3/4}$, multiple nuclei were assumed to be formed as a first nucleation event (polynuclear mechanism). In the former case, a single crystal was used as a detection criterion, whereas, in the latter case, a predetermined volume α was used as a detection criterion.

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Nomenclature

$b1$	order of primary nucleation rate
$B(t)$	time-dependent nucleation rate per unit volume, $s^{-1}\ m^{-3}$
B_1	primary nucleation rate per unit solvent mass, s^{-1} kg-solvent^{-1}
CV	coefficient of variation of induction time or MSZW
k_{b1}	primary nucleation constant, s^{-1} kg-solvent^{-1} $°C^{-b1}$
$f(t)$	probability distribution function of induction time, s^{-1}
$f(\Delta T)$	probability distribution function of metastable zone width, $°C^{-1}$
$F_N(t)$	$P(T_N \le t)$, cumulative distribution function for the time T_N when at least N crystals have nucleated
M	size of sample (mass of solvent), kg-solvent
N	number of crystals
N_{det}	detection criterion of nucleation
N/M	number density of crystals, kg-solvent^{-1}
$(N/M)_{det}$	detection criterion of nucleation in number density basis, kg-solvent^{-1}
$r_{N\ \Delta T}$	ratio of mean stochastic MSZW ΔT_{Nmean} to deterministic MSZW ΔT_{Nm}
$r_{NM\ \Delta T}$	ratio of mean stochastic MSZW ΔT_{NMmean} to deterministic MSZW ΔT_{NMm}
P_N	probability that N crystals appear in a sample
R	cooling rate, $°C\ s^{-1}$
t	time or stochastic induction time, s
t_N	time when at least N crystals have nucleated, s
t_{Nind}	deterministic induction time in number basis, s
t_{NMind}	deterministic induction time in number density basis, s
t_{Nmean}	mean stochastic induction time in number basis, s
t_{NMmean}	mean stochastic induction time in number density basis, s
T	temperature, °C
T_0	initial saturation temperature of solution, °C
ΔT	$T_0 - T$, supercooling or stochastic MSZW, °C
ΔT_{Nmean}	mean stochastic MSZW in number basis, °C
ΔT_{NMmean}	mean stochastic MSZW in number density basis, °C
ΔT_{med}	median value of MSZWs, °C
ΔT_{sp}	specified supercooling at which the induction time is defined or measured, °C
V	volume of sample, m^3
$\Gamma(x)$	complete Gamma function of x
κ	nucleation probability per unit time per sample, s^{-1}
σ	standard deviation of induction time or MSZW, s or °C

The results they obtained are the same as those obtained by Kubota [2] in that the mean (stochastic) induction time decreases with an increase of sample volume where the mononuclear mechanism was applied, and, for large samples where the polynuclear mechanism was used, the (deterministic) induction time is volume-independent. Kashchiev et al. [4] considered that the problem of volume dependence is caused by the range of volume itself. Kadam et al. [6] took a view on the volume effect similar to that of Kashchiev et al. [4]; they proposed the concept of the transition volume, above which the MSZW is deterministic and volume-independent; however, below this it is stochastic and volume-dependent. Experimental studies on the effect of sample volume on induction time and MSZW will be briefly summarized in the next section, where it is shown that the induction time and MSZW decrease with an increase of sample volume in some cases but do not change in other cases.

The aim of this study is dual; one is to answer the question why the effect of sample volume is observed in some cases but not in some other cases, and the other aim is to make clear the relation between the stochastic model and deterministic model. This paper is a continuation and extension of the previous study [2] so that the volume effects on the induction time and MSZW are treated in a more general way. There is no intention of discussing the nucleation mechanism itself.

2. Some reported experimental data

The MSZWs reported by Liang et al. [5] are shown in Fig. 1 as a function of crystallizer volume. Liang et al. detected nucleation points using a turbidometric optical probe for agitated L-glutamic acid aqueous solutions at a cooling rate of 2 °C min^{-1}. The obtained MSZWs are rather reproducible and deterministic. The MSZWs do not depend on the volume of crystallizer. Kadam et al. [6,7] also studied the effect of sample volume on MSZW for paracetamol aqueous solution [7] and paracetamol aqueous solution and isonicotinamide ethanol solution [6]. For small samples of 1 mL, MSZWs were determined by detecting the decrease in transmission of light through the agitated sample cell. The MSZW was irreproducible and it distributed widely, reflecting the stochastic nature of nucleation. The decrease in light transmission was caused by the burst of secondary nuclei generated from a grown first single nucleus [7]. The burst could be treated as an indication of the appearance of a first crystal, because it occurred immediately (about 5 s) after the appearance of a first single crystal. Kadam et al. [6,7] also measured MSZWs using an *in situ* camera under agitated condition for large vessels ranging in volume from 0.5 to 1 L. The MSZW was determined differently by detecting the presence of crystals (not a single crystal). The MSZW obtained was irreproducible to some extent as seen in Fig. 2, where the range of distribution is shown by vertical bars and the central value is indicated by open circles. The central value

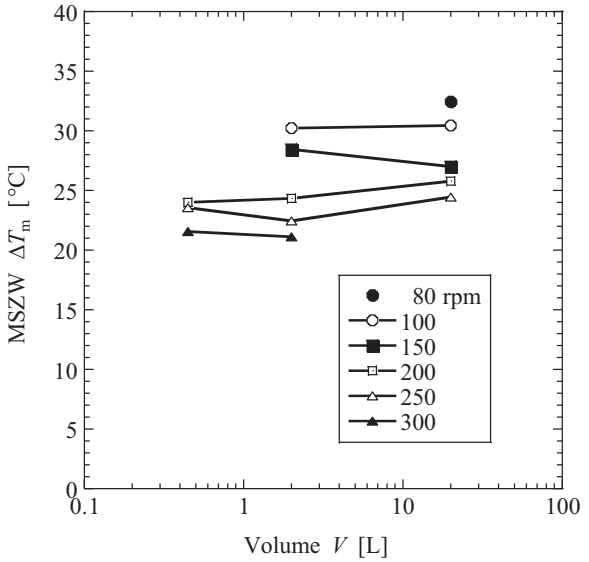

Fig. 1. Effect of crystallizer volume on MSZW. The graph was reproduced from the original data reported by Liang et al. [5] for agitated aqueous solution of L-glutamic acid.