Determination of Seeded Metastable Zone Width of L-Arabinose by an Automated Temperature Logging Device

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Abstract: Determination of the metastable zone width (MSZW) is of great importance in L-arabinose crystallization, yet it has not been reported before. In this study, the use of an automated temperature logging device (ATLD) to monitor the nucleation temperature (T_m) of L-arabinose in an aqueous solution was demonstrated. Direct comparison with focused beam reflectance measurements (FBRM) confirmed that the T_m determined by the ATLD was reliable. A multiple linear regression model of the T_m and a set of exploratory factors indicated that the T_m was affected by the solution concentration and stirring rate but not the cooling rate. The MSZW of L-arabinose in an aqueous solution was not constant, but ranged from 27.36 to 31.55 ℃.The addition of 2% and 4% impurities (sodium chloride, galactose, glucose, and xylose) decreased the MSZW of L-arabinose. This study offers new opportunity for the use of ATLD as simple, inexpensive, and convenient alternative tool in crystallization monitoring.

Key words: L-arabinose;impurities; nucleation; crystallization;metastable zone width; focused beam reflectance measurement
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自动温度仪法测定晶核诱导下L-阿拉伯糖介稳区的研究

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摘要：介稳区测定对 L-阿拉伯糖的工业化生产有很强的指导作用，但还没有文献报道过 L-阿拉伯糖介稳区。本文采用自动温度记录仪法测定了 L-阿拉伯糖的介稳区宽度。通过对比聚焦光束反射仪法数据，发现自动温度记录仪法所得到的数据真实可靠。对 L-阿拉伯糖成核温度及其影响因素进行多重线性回归分析，发现成核温度与溶液浓度和搅拌速度呈正相关，浓度越高成核温度越高，成核温度也随着搅拌速度的增大而增高，冷却速度对成核温度没有显著性影响。研究发现在水溶液中 L-阿拉伯糖的介稳区并非一个常数而是一个介于 27.36 到 31.55 ℃的区间。相比于纯水系统，添加 2%和 4%的杂质（氯化钠、半乳糖、葡萄糖和木糖）均能降低 L-阿拉伯糖的介稳区宽度。通过研究发现自动温度记录仪法是一种结构简单、价格低廉、检测结果可靠的实用方法，它可替代其它昂贵的结晶检测仪器应用于生产实践过程中。

关键词：L-阿拉伯糖；杂质；成核；结晶；介稳区宽度；聚焦光束反射仪法

Metastable zone width (MSZW) is defined as the extent of supersaturation or supercooling. In the past decade, several techniques have been used for MSZW determination, such as direct visual observation, turbidity monitoring [1, 2], focused beam reflectance measurement (FBRM)[3, 4], and electric conductivity method[5].

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Among these, the turbidity monitoring technique is widely used because in this case, the signal increases markedly with the appearance of “first crystals.”However, this technique is unfit for seeded MSZW detection since the addition of seeds would seriously interfere with laser transmission, which might make the light intensity too low to be detected[3].On the other hand, FBRM is suitable for both seeded and unseeded experiments. However, measurement noise and fouling of the FBRM probe will lead to inaccuracy in the absolute particle counts [2, 3].

Crystallization refers to the phase transition of a substance from a super cooled or supersaturated mother medium to a crystalline state with lower energy. The excess energy radiates in the form of latent heat during nucleation and crystallization [6, 7]. The evolution of the latent heat of crystallization increases the temperature of the solution [8, 9], which is immediately recorded by an automated temperature logging device (ATLD). Studies conducted by other research groups have shown that the calorimetric method can be used for super saturation detection[10] and optimization of batch crystallization[11-13].

Here, we demonstrate the use of an ATLD for the detection of the MSZW in L-arabinose. To validate the proposed detection technique, we performed a direct comparison study using FBRM.

1 Experimental Details

1.1 Materials

L-arabinose (purity: 99.7%, Shandong Futaste Co., Ltd.), D-galactose, glucose, xylose (purity: > 98%, Shanghai Yuanju Bio-Tech Co., Ltd.) and sodium chloride (AR, Sinopharm chemical Reagent Co., Ltd.) were used without further purification. Deionized water was used in all the experiments.

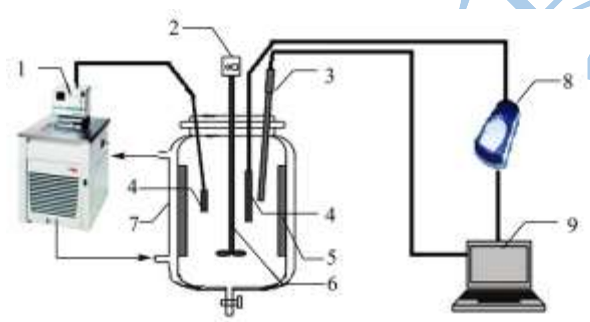

Fig.1 Schematic of experimental setup

Note: (1) Water circulator; (2) Overhead motor; (3) FBRM probe; (4) Thermocouple; (5) Baffle; (6) Impeller (7) One-Liter Crystallizer; (8) Data logging module; (9) Computer.

1.2.2 FBRMComparison

To validate the reliability of the T_m detected by the ATLD, a Lasentec-D600L FBRM system (Lasentec Inc., USA) was used to monitor the nucleation of L-arabinose simultaneously. Data were obtained every 10 s and compared to analyze the difference between the T_m-values obtained by both the methods. A schematic of the FBRM and ATLD profiles from a typical run is depicted in Fig. 2.

1.2.3 SPSS Analysis

To analyze the effect of operation factors on the T_m, the significant difference of the results between the operations were investigated. For each effect study, multiple linear regression was used with a step-wise technique based on correlation values and model significant levels. Analysis of variance was performed for each regression model. The actual calculations were carried out utilizing the Statistical package (SPSS 16.0, IBM Co., USA).

1.2.4 Seeded MSZW Determination of L-Arabinose

To prepare L-arabinose solutions (57%~73%), 50.0 g of L-arabinose and a certain amount of water were added to the crystallizer (50 mL round bottom flask with a rubber stopper). After complete dissolution, a well-formed crystal seed (about 2 mm×2 mm×10 mm) bundled with nylon was suspended vertically in the solution at saturation temperature. To avoid collisions and breakage of the seed crystal or any contact with the crystallizer wall, the use of a thermocouple wire and magnetic stirrer was avoided. The stirring rate was 50 r/min.

To evaluate the effect of impurity on the MSZW of L-arabinose, 2% and 4% of impurity was added to the solution before complete dissolution of L-arabinose, and then, similar experiments were carried out (Figures 3a–3d).

2 Results and Discussion

2.1 A Typical Experiment

The FBRM and ATLD profiles of a typical run are shown in Fig. 2. The whole process can be divided into four stages.

Stage one (Dissolution): L-arabinose solutions of different concentrations are prepared. This stage is not recorded by FBRM or any online thermometer.

Stage two (Cooling): The solution remains homogeneous. The L-arabinose concentration and the total particle count, determined by FBRM, are constant.

Stage three (Nucleation): After the onset of nucleation, simultaneous secondary nucleation takes place, leading to a rapid increase in the total particle count. In this stage, phase transition of L-arabinose from the supercooled mother medium to the crystalline state takes place, and the excess energy is radiated in the form of latent heat. The radiated heat would increase the temperature of the solution, which changes the course of the cooling profile. The net outcome of temperature increase shows that the energy radiation effect is dominant.

Stage four (Crystallization): In this stage, nucleation rate decreases significantly due to the de-supersaturation of the solution. The net outcome of temperature decrease shows that the cooling effect is dominant. A slight increase in the total particle count, followed by a plateau, implies that the nucleation is complete, as determined by FBRM.

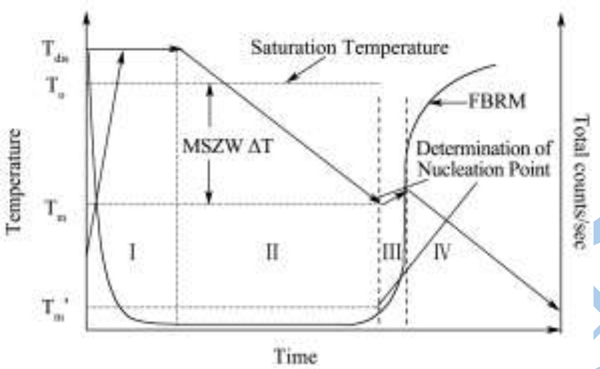

Fig.2 Schematic of a typical run of FBRM and ATLD profile

Phase transition points T_m, corresponding to the onset of nucleation during the cooling stage, could be observed by both FBRM and the ATLD. Theoretically, T_m should indicate the appearance of the first crystal. However, in the present experiment, it is only observed through a drastic change in the temperature profile of the solution, which results from the release of latent heat due to nucleation. The first crystal is expected to appear before this drastic change in the solution temperature. Therefore, T_m should be regarded as an approximation of the nucleation onset. The T_m values observed under various experimental conditions are shown in Table 1.

2.2 FBRM Comparison

In order to examine the accuracy of the T_m value determined by the ATLD, direct comparison with FBRM was performed. In the comparison study, the phase transition point monitored by FBRM was recorded and marked as $T_{m'}$. The transition point was set at the point when the total particle count reached 2% of the maximum total count[4].

Table 1 The nucleation temperature of L-arabinose in aqueous solution

Concentration /%	Cooling rate Degree C/h	Stirring rate r/min	T_m	$T_{m'}$	ΔT_m (T_m-$T_{m'}$)
68	-18	50	40.17	40.42	-0.25
68	-15	50	43.16	43.36	-0.2
68	-12	50	40.15	40.1	0.05
68	-18	100	55.32	55.41	-0.09
68	-15	100	55.85	55.88	-0.03
68	-12	100	50.34	50.37	-0.03
68	-18	200	69.52	69.81	-0.29
68	-15	200	61.27	61.2	0.07
68	-12	200	54.18	54.21	-0.03
70	-18	50	51.18	51.3	-0.12
70	-15	50	61.56	61.47	0.09
70	-12	50	52.96	52.92	0.04
70	-15	100	58.37	58.35	0.02
70	-12	100	60.59	60.58	0.01
70	-18	200	78.02	77.91	0.11
70	-15	200	75.54	75.43	0.11
70	-12	200	77.55	77.31	0.24
73	-18	50	73.74	73.82	-0.08
73	-15	50	74.14	74.31	-0.17
73	-12	50	74.06	74.14	-0.08
73	-18	100	89.41	89.68	-0.27
73	-15	100	84.5	84.6	-0.1
73	-12	100	81.73	81.31	0.42
73	-18	200	91.14	91.34	-0.2
73	-15	200	87.33	87.42	-0.09
73	-12	200	86.75	87.07	-0.32

Note: T_m is detected by ATLD, and $T_{m'}$ by FBRM.

Table 1shows a direct comparison of T_m with $T_{m'}$. Statistical package (SPSS 16.0) was used to analyze the difference between T_m and $T_{m'}$. Results showed that the differences between the two transition points came from the normal population (Shapiro-Wilk test: P=0.410); hence, the paired-samples t-test was adopted. The test showed that there was no significant difference between the average transition points detected by the two methods (t=-1.387, df=25, P=0.178). Detailed statistic analysis is shown in Table 2. This comparison study confirms that the ATLD is a reliable tool to monitor the nucleation of L-arabinose solution.

Table 2 The nucleation temperature detected by two methods

groups	n	Average ($\overline{X} + s$)	P_{25}~P_{75}
ATLD method	25	66.4819±3.0884	53.8750~78.9475
FBRM method	25	66.5277±3.08909	53.8875~78.7600

2.3 SPSS Analysis and Regression Model

MSZW is an intrinsic property of a substance, which is also influenced by a variety of parameters, including but not limited to, sample volume, cooling rate, seeding, additives, and detector sensitivity. In this study, we try to describe the linear association between the phase transition point T_m *(Y)* and a set of exploratory factors, including concentration (X_1), stirring rate (X_2), and cooling rate (X_3). For this purpose, we developed amultiple linear regression model by the stepwise method (Table 3).

The results indicated that the T_m was affected by the solution concentration and stirring rate but not by the cooling rate. Among the exploratory variables, solution concentration has the most significant effect on T_m considering the standardized coefficients. Considering the correlation coefficient (R^2), we observed that the three independent variables showed 92.3% variation in the T_m, indicating that the final model fitted the data very well.

Table 3 Parameter estimation of regression model

Variables	Unstandardized Coefficients B	Unstandardized Coefficients Std.Error	Standardized Coefficients	t	P
Constant	-374.468	30.153		-12.419	<0.001
Concentration (X_1)	6.066	0.428	0.822	14.181	<0.001
Stirring rate (X_2)	0.121	0.014	0.498	8.592	<0.001

Note: F=137.257, P <0.001, R^2=0.923, Dependent Variable: T_m.

2.4 Seeded MSZW of L-Arabinose

2.4.1 Pure Water System

In a previous study, we found that the T_m is affected by the concentration and stirrer rate but not by the cooling rate. In this part, we demonstrate the relationship between super saturation and temperature, which can be described by the following empirical exponential equation (Eq. 1).

$$Ws = 93.434 + 0.4105T + 0.0337T^2 (R^2 = 0.9938) \text{........Eq.1}$$

Table 3 The seeded Metastable Zone Width of L-arabinose at 50 r/min

Concentration /%	Solubility (10^{-2}g/g water)	To^*	T_m^{**}	ΔT_m
57	132.56	55.68	28.32	27.36
59	143.9	60.84	33.48	27.36
61	156.41	66.00	38.09	27.91
63	170.27	71.16	41.60	29.56
65	185.71	76.32	46.94	29.38
67	203.03	81.48	50.00	31.48
69	222.58	86.64	56.65	29.99
71	244.83	91.80	62.84	28.96
73	270.37	96.96	65.41	31.55

Note: T_0: Saturation temperature in Celsius; T_m: Average T_m of three experiments.

We observed that the MSZW (ΔT_m) was not constant but spread from 27.36 to 31.55 ℃ (mean±std. error = 29.28 ℃±0.526) (Table 3), which might be explained by following reasons. First, MSZW is a function of the induction period of nucleation (t_{ind}) and cooling rate [1, 14~17]. It is seen that log (ΔT_m) increases linearly with an increase in log *R*(cooling rate), such that the cooling rate is not constant but a spread, which may result in the deflection of the MSZW. Second, the size and number of seed crystals influence the MSZW of secondary nucleation [14]. The size of the seed crystal varies with time, which might lead to deflection of the MSZW. Third, the volume of the crystallizer and stirrer, too, influence the MSZW to a great extent. It has been observed that the MSZW is not reproducible at small volumes but spreads out. The spread increases further with a decrease in the volume [18]. In addition, the MSZW is influenced by the detection method and sensitivity. To reach the detectable transition point, the latent heat dissipated from L-arabinose nucleation must overcome the heat emission from the solution to the environment, which means that there exists a time lag between the nucleation point and the detection point.

2.4.2 Seeded MSZW of L-Arabinose with Impurities

In many instances, small amounts of additives have a dramatic effect on crystal growth, morphology, and nucleation. Here, the influence of impurities (sodium chloride, glucose, xylose, and galactose) on the seeded MSZW of L-arabinose solution has been investigated using an ATLD.

MSZW measurements were conducted after adding 2% and 4% impurities to L-arabinose solutions (57%~73%). The results are shown in (Figures 3a~3d). It is found that the addition of sodium chloride elevates the T_m of L-arabinose in aqueous solution and thus decreases the MSZW (Figure 3a). The salting-out effect and nucleation modification effect can be used to explain this behavior. First, as per the salting-out effect, sodium chloride competes with L-arabinose to combine with water molecules, and consequently, L-arabinose crystallizes from the aqueous solution. Gonzalez et al.[19]showed that sodium chloride exerted a salting-out effect with anthracene and that the salting-out coefficients did not vary significantly. This is because the average size of the sodium chloride-water clusters remained almost constant over the temperature range 20~70 ℃[20]. Second, impurities present in the solution can change the nucleation rate by affecting both the kinetic and the solute–solvent interfacial energy [21]. Sodium chloride acts as a nucleation accelerant, which decreases the MSZW of L-arabinose.

The addition of monosaccharides also decreases the MSZW of L-arabinose(Figures 3b~3d). The ability to decrease the MSZW is in the order of glucose > galactose > xylose (Table 4). The addition of galactose elevates the T_m of L-arabinose in aqueous solution (Figure 3b) and thus decreases the MSZW. The T_m value at 4% is almost identical to that at 2% when the concentration is below 65%, while the T_m at 4% is lower than that at 2% when the concentration is above 65%. This is because galactose would compete with L-arabinose to combine with water molecules, and as a result, L-arabinose crystallizes from the aqueous solution. The total solid content at 4% impurity is higher than that at 2%, implying higher viscosity at 4% impurity. Viscosity and nucleation rate are inversely related; hence, the T_m at 4% impurity is slightly lower than that at 2% impurity.

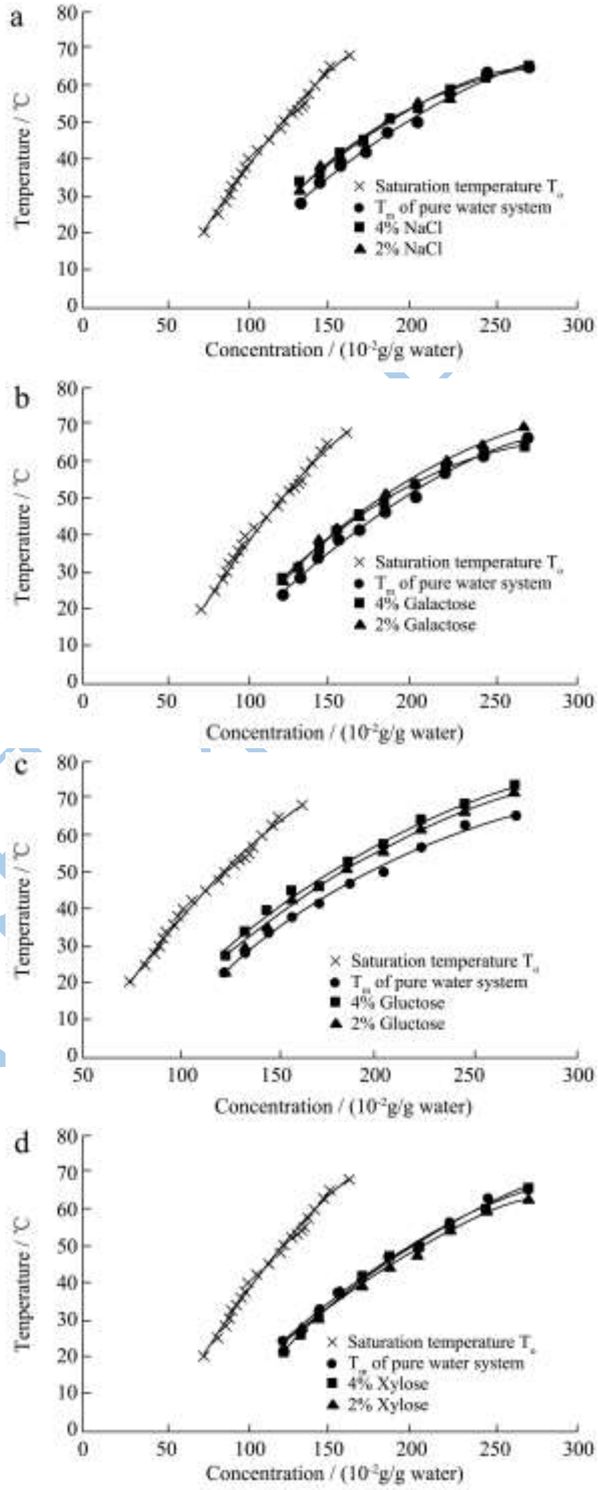

Fig.3 Effect of impurities on the MSZW of L-arabinose

We observed that the T_m value for the 4% glucose-water system is higher than that for the 2% glucose-water system (Figure 3c), which is slightly higher than that of the pure water system. In other words, the MSZW decreased in the glucose-water system, which means the higher the glucose concentration, the smaller the MSZW is. A possible reason for this effect is that the solubility of L-arabinose is decreased by the addition of glucose, which increases the effect of super saturation.

The effect of xylose on the MSZW of L-arabinose is not as obvious as that of galactose or glucose (Figure3d). This may be because glucose and galactose are hexoses, while xylose is a pentose whose structure is similar to that of L-arabinose.

The presence of an impurity can alter the solution thermo dynamics (primarily, the solubility) and therefore, influence effective supersaturation. The monosaccharides used in this study may have the ability to decrease the solubility of L-arabinose and thus might increase the effective super saturation and decrease the MSZW. In addition, impurities can alter the solution kinetics and interfacial energy[14, 21], which have a great influence on the MSZW. Impurities can also alter the crystallization kinetics. It is known that the crystal nuclei are very small and undetectable at the formation stage; hence, changes in the crystallization kinetics would influence the induction period of nucleation, which in turn affects MSZW detection. Ouiazzane et al.[22] have shown that the addition of glucose or fructose decreases the overall growth kinetics of sucrose, indicating a decrease in the MSZW of sucrose. Our finding is similar to that of a previous study where the addition of an impurity was proposed to decrease the MSZW [23, 24]. Though it is known that the MSZW is affected by impurities, the specific principles have not been pointed out, to the best of our knowledge. Models that can be used to predict the effects of impurities on the MSZW have not been established, and hence, further research in this direction is necessary.

3 Conclusion

The ATLD has been successfully applied for monitoring the nucleation of L-arabinose solution. The T_m values detected by the ATLD and FBRM are not significantly different (t=-1.387, *df*=25, *P*=0.178), indicating that the ATLD can be used to detect the phase transition point and obtain reliable results.

A multiple linear regression analysis of the relationship between the T_m and a set of exploratory factors showed that the T_m is significantly affected by the concentration and stirring rate but not by the cooling rate. The MSZW of L-arabinose in aqueous solution is not constant but spreads from 27.36 to 31.55 ℃. The addition of 2% and 4% sodium chloride would decrease the MSZW of L-arabinose. Galactose, glucose, and xylose at 2% and 4% levels can alsodecrease the MSZW of L-arabinosein the orderof glucose > galactose > xylose.This study opens a new opportunityfor the use of an ATLD as a simple, inexpensive, and convenient alternative tool in the crystallization monitoring.

Table 4 Phase transition temperature at 59%, 65% and 71%

Group	Pure water	2% xylose	4% xylose	2% galactose	4% galactose	2% glucose	4% glucose	2% NaCl	4% NaCl
59%	33.48	34.32	35.04	38.99	36.16	35.50	39.30	38.18	36.0
65%	46.94	47.8	50.28	52.20	48.11	51.06	52.42	51.38	51.02
71%	62.84	63.01	63.36	64.60	62.43	66.80	68.25	62.03	61.61

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