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Contributed Paper

Investigation of Metastable Zone Width and Nucleation Kinetics of 2-cyanoguanidine by Cooling Crystallization

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ABSTRACT

Metastable zone widths (MSZW) of 2-cyanoguanidine in water, methanol, and ethanol are determined at different cooling rates ((6-30) K·h^{-1}) using polythermal method, respectively. The metastable zone widths of solute in the three solvents increase linearly with the cooling rate increasing. Three nucleation theories are employed to estimate nucleation kinetic parameters based on measured MSZW data. The apparent nucleation order *m* is computed by Self-consistent N□ vlt-like approach and Kubota's model, which suggests that the nuclei are formed by instantaneous nucleation in methanol and ethanol, while the 2-cyanoguanidine nucleate in water shows the occurrence of progressive nucleation mechanism. The activation energy E_{sat} for nucleation of crystals in solution also is estimated by Arrhenius-type equation.

Keywords: 2-cyanoguanidine, metastable zone width, nucleation kinetics, model

1. INTRODUCTION

High-purity 2-cyanoguanidine (DCD) is one of the fundamental chemical compounds, and is widely used in the printing, dyeing and electronic industries [1]. Several methods can be used for the purification of industrial 2-cyanoguanidine, and thereby removing impurities (Ca^{2+}, Fe^{2+}, Mg^{2+}, Al^{3+}). Among those technologies, crystallization presents several advantages such as having higher efficiency, being more economic to operate, and being environmentally friendly [2]. Industrial crystallizers have to be operated at the optimum supersaturation which is less than the metastable zone width to obtain desired products, with respect to median particle size, crystal size distribution (CSD), shape and purity [3, 4]. The final CSD in a batch crystallizer is determined by various kinetic processes, which includes primary and secondary nucleation, crystal growth, aggregation, and breakage [5].

In order to obtain a product of high purity, it is necessary to understand a lot of thermodynamic properties. Supersaturation in solution alone is not enough for nucleation to occur. A certain extent of supersaturation, also known as the supersolubility, is required for the creation of new solid interfaces [6]. The region between the supersolubility and the solubility turn is taken as the metastable width zone (MSZW) [7], the region is deemed to be ideal for crystal growth [8, 9]. The crystal growth process takes place within a region called the metastable zone. This region lies between the saturation and nucleation limits. In this region the solution is supersaturated and no nucleation occurs while the crystals are growing. It is generally advocated that solution should avoid nucleating spontaneously in industrial crystallization. The goal of final products obtained with uniform particle size distribution can be accomplished by controlling MSZW in industrial crystallization. Meanwhile, metastable zone width of solution is one of fundamental research in the process of industrial crystallization. Even it is required for design of crystallizer.

In previous work, we have investigated the solubility of 2-cyanoguanidine and calculated the corresponding dissolution enthalpy, dissolution entropy and the molar Gibbs energy. In this experiment, the difference between the saturation temperature and the temperature of appearance of "first crystals" is the metastable zone width. Identification of the MSZW [10] is pivotal for product quality control in industrial crystallization. Traditionally, the MSZW in batch cooling crystallization has been defined as a kind of static property of a solution that mainly depends on cooling rate [11]. In industry, methanol was used as a solvent to purify the industrial 2-cyanoguanidine again and again. But it is unfavorable to use methanol for a long time because of its high toxicity. So the new solvents is urgently need to explore for the purification of 2-cyanoguanidine.

2-cyanoguanidine can dissolve in ethanol and water, which is verified by literature [12]. In addition, the two solvents were not poisonous. Thus, water and ethanol were planned to select for purifying the low-purity 2-cyanoguanidine. At the same time, in order to evaluate the further cost of production in cooling crystallization, the MSZW data is necessary to know. However, the MSZW data of 2-cyanoguanidine in various solvents (water, methanol, and ethanol) have not been reported in the literature. At present, there are many theories to estimate nucleation kinetics from metastable zone width data. Previously, the nucleation parameters were deduced from metastable zone width data by Nyvlt for a variety of systems, and the influence of secondary nucleation on MSZW was investigated by *Kadam et al* [13]. Generally, the MSZW mainly depends on temperature, solution, cooling rate, impurity, stirring intensity, the presence of the seed, cooling rate etc. The N□vlt's model [14,15] has been commonly used to analyze the MSZW at constant cooling rates by the polythermal method. The final equation gets a linear relationship of $\Delta T_{max}/T_0$ versus log *b*. Recently, Sangwal also put forwarded a new model to estimate the MSZW determined by the polythermal method. The resulting equation yields a linear relationship of $(T_0/\Delta T_{max})^2$ versus log *b*. So the primary nucleation kinetics can be estimated from measuring the metastable zone width for different cooling rates [16].

The aim of this paper is to determine metastable zone width (MSZW) [17] of 2-cyanoguanidine by the polythermal (increasing supercooling) method as a point at which first nucleation events are detected when the solution is continuously cooled at a constant rate [18, 19]. Further, the experiment data is used to evaluate some nucleation parameters including nucleation order (*m*) and the activation energy (E_{sat}) by three theories.

2. THE ORETICAL BACKGROUNDS

The polythermal method of metastable

zone width of a solute-solvent system is based on the determination of the maximum supercooling $\%T_{max}$ by cooling the solution at a constant cooling rate *b*. the determination of the nucleation kinetics from MSZW data is employed to analyze the experimental data presented in this work, which will be summarized in the following sections.

2.1 Self-consistent Nývlt-like Approach

Nývlt's equation [16] has been used for deducing the nucleation kinetic, which can be described as [20]:

$$\lg\Delta T_{max} = \frac{1-m}{m}\lg\left(\frac{dc}{dT}\right) - \frac{\lg k}{m} + \frac{1}{m}\ln b \quad (1)$$

Here, ΔT_{max} is the metastable zone width. *c* and *T* refer to the initial composition and absolute temperature, and *m*, *k* and *b* stand for the apparent nucleation order, nucleation constant and cooling rate, respectively.

Self-consistent N□ vlt-like approach [20] predicts relationship between maximum supercooling ratio ($\Delta T_{max/}$T) and cooling rate:

$$\frac{\Delta T_{max}}{T} = \left(\frac{f}{KT}\right)^{1/m}\left(\frac{\Delta Hd}{RT_n}\right)^{(1-m)/m} b^{1/m} \quad (2)$$

Where f is a constant computed by solute concentration, $\%H_d$ is the heat of dissolution. And can be deduced by van't Hoff equation:

$$\ln c = \frac{\Delta H_d}{RT} + \frac{\Delta S_d}{R} \quad (3)$$

The linear dependence of ln($\Delta T_{max/}$T) and lnb can be got by taking logarithms on both sides of Eq.(3):

$$\ln u = \varphi + \beta \ln b \quad (4)$$

Where

$$\beta = \frac{1}{m} \quad (5)$$

$$\varphi = \varphi' - \beta \ln T \quad (6)$$

$$\varphi' = \frac{1-m}{m}\ln\left(\frac{\Delta H_d}{RT_n}\right) + \frac{1}{m}\ln\left(\frac{f}{K}\right), \quad (7)$$

2.2 Approach Based on Three-dimensional Nucleation Theory

In the classical 3D nucleation theory approach, the nucleation rate *J* is refined as [21]

$$J = A\exp\left[-B/(\ln S)^2\right] \quad (8)$$

Where A is a pre-exponential factor, B is a thermodynamic parameter relate to the formation of stable nuclei, which presents

$$B = \frac{16\pi}{3}\left(\frac{\gamma\Omega^{2/3}}{k_B T_{lim}}\right)^3 = \frac{16\pi}{3}\left(\frac{\omega}{1-u}\right)^3 \quad (9)$$

$$\omega = \frac{\gamma\Omega^{2/3}}{k_B T} \quad (10)$$

Where γ and Ω represent the solid-liquid interfacial energy and the molecular volume of solute. k_B is the Boltzmann constant equal to R/N_A (N_A is the Avogadro number). Combining Eqs. (8), (9), and (10) the following equation can be obtained.

$$\frac{1}{(1-u)u^2} \approx u^2 = \frac{X}{\psi} - \frac{1}{\psi}\ln b = F(1 - Z\ln b) \quad (11)$$

$$\text{where } F = \frac{X}{\psi} = \frac{1}{Z\psi},\ Z = \frac{1}{X} \quad (12)$$

$$\psi = \frac{16\pi}{3} \times \frac{\omega^3}{\lambda^2}; \quad (13)$$

$$Z = \frac{1}{X} = \ln\left[\frac{f}{AT_0} \times \frac{1}{(1-u)}\right] \quad (14)$$

According to above equations, u=D$T_{max/}$T, the slope *Z* and intercept *F* can be obtained with u^2 and ln*b* plotted. In the latter estimation, the intercept and slope are used to calculate the required activation energy for 2-cyanoguanidine nucleation occurred in different solvents. It should be mentioned that the constant Z is not a dimensionless quantity, instead, its value depends the units of cooling rate b, but the term Z lnb is a constant quantity for a crystallization system.

2.3 Kubota's Interpretation

The lack of success of the classical nucleation theories in explaining the behavior of real system has led a number of authors to suggestion that most primary nucleation in industrial crystallizers is heterogeneous rather than homogeneous and that empirical relationship such as

$$J = k(\Delta T_{max})^m \quad (15)$$

only ones that can be justified [23]. Where k, ΔT_{max}, and m are the nucleation rate constant, supercooling, and the apparent nucleation order. The number density, N_m/V of grown primary nuclei by time, t_m, can be evaluated through integration of the nucleation rate ((N/V)) [23]:

$$\frac{N_m}{V} = \int_0^{N_m} d\left(\frac{N}{V}\right) = \int_0^{t_m} J dt \quad (16)$$

For a given cooling rate, Eq. (16) can be rewritten as:

$$\frac{N_m}{V} = \int_0^{\Delta T_{max}} \frac{J}{b}\, d(\Delta T_{max}) \quad (17)$$

After substituting Eq. (16), integrating Eq. (17) and rearranging leads to

$$\Delta T_{max} = [(\frac{N_m}{kV})(m+1)]^{1/(m+1)} b^{1(m+1)} \quad (18)$$

Taking the logarithm of both sides of Eq. (18) gives

$$\log(\Delta T_{max}) = \frac{1}{m+1}\log[(\frac{N_m}{V}\frac{1}{k})(m+1)] + \frac{1}{m+1}\log b \quad (19)$$

Based on foregoing equation, from the slope of the linear relationship between log (dT_{max}) and log b, with a slope equal to 1/(m+1), then the apparent nucleation order m can be computed. The nucleation rate constant, k, can also be estimated from the intercept provide that the detectable number density, N_m/V, is known.

3. EXPERIMENT SECTION

3.1 Materials

The information of reagents used concerning 2-cyanoguanidine, methanol, ethanol and water in the experiment is listed in Table 1.

Table1. Details of chemical source, purification method, final purity and analysis method.

Chemical name	CAS No.	Formula	Mass purity	Purification method	Analysis method	Source
2-cyanoguanidine	461-58-5	$C_2H_4N_4$	>99%	re-crystallization	HPLC	NingXia Jiafeng
methanol	67-56-1	CH_3OH	>99.99%	-	HPLC	Tianjin Damao
ethanol	64-17-5	C_2H_6O	>99.7%	-	-	Tianjin Beilian
water	7732-18-5	H_2O	>99%	distillation	-	Ningxia university

3.2 Measurements for the Metastable Zone

The metastable zone width experiments are conducted following the well known polythermal method. [24] Where a saturated solution is cooled with a constant cooling rate until the "first crystal" appears. For a particular experiment, a saturated solution of 2-cyanoguanidine is prepared in the double jacketed crystallizer according to solubility data. Take the upper clear and saturated solution of 80 mL into double jacketed crystallizer with a measuring cylinder. The saturated solution is preheated to 5 K above the saturation temperature under stirring for 1.5 h to keep the solute dissolve absolutely. Then the solution is cooled at constant rate of 6 K·h^{-1}, 12 K·h^{-1}, 18 K·h^{-1}, 24 K·h^{-1}, and 30 K·h^{-1} with a thermostatic until the first crystal appeared. Saturation temperature is the point where the system reached solid-liquid phase equilibrium; nucleation temperature is the temperature when the first crystal appears from the solution. The difference between the saturation temperature and the nucleation temperature is taken as metastable zone width. A thermostatic bath (PHDC4015, Shanghai, China), with an uncertainty of ± 0.01 K, is used to maintain constant temperature. In order to prevent evaporation of solvents, the vessel is sealed during entire measurement process. The experimental method is verified workable in literature [25]. All the determinations are repeated three times to check reproducibility, and then an average value is given. In this work, MSZW data of 2-cyanoguanidine in water and ethanol from T = 283.15 K to 323.15 K., and the values in methanol were determined from 293.15 K to 323.15K.

4. RESULTS AND DISCUSSION

Many factors can affect the metastable width zone of 2-cyanoguanidine, such as saturated temperature, stirring intensity, impurity, solvent composition, and cooling rate. In this work, the influence of cooling rate, saturated temperature, and solvent composition on MSZW are investigated in the cooling crystallization.

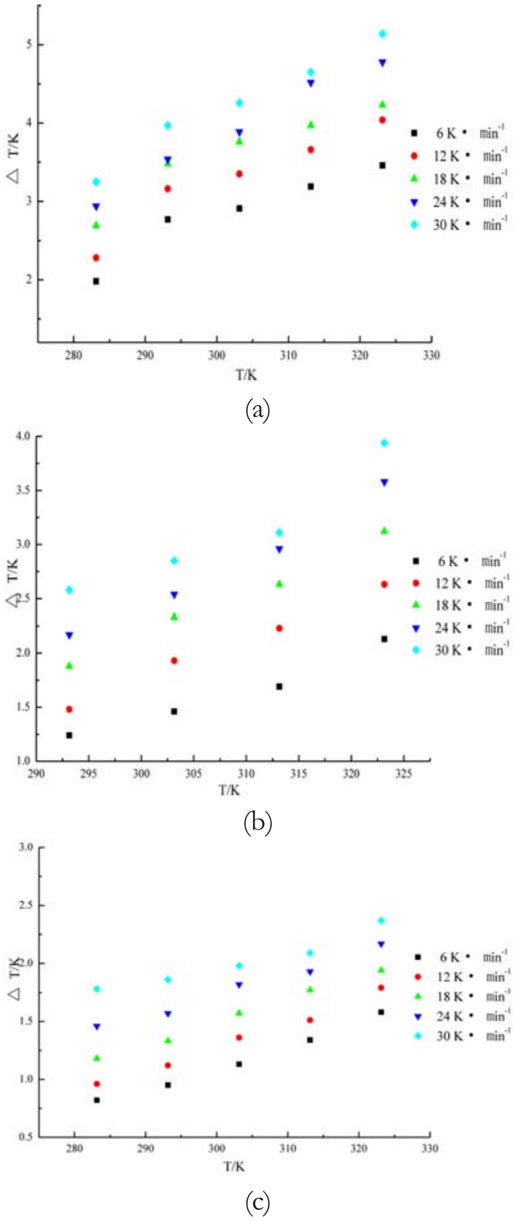


Figure 1. Measured metastable zone width's as a function of temperature for 2-cyanoguanidine. (a) in water; (b) in methanol (c) in ethanol.

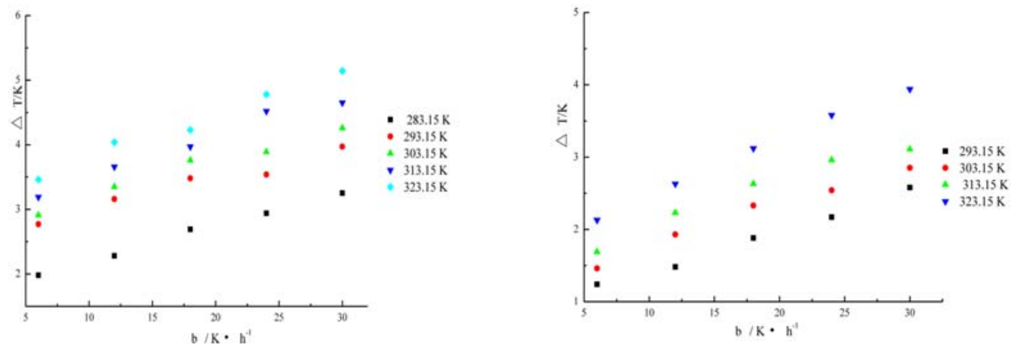
4.1 Effect of Cooling Rate on Metastable Zone

In the current work, the experimental MSZW values of 2-cyanoguanidine in methanol and ethanol obtained by the polythermal method as a function of cooling rate at T_0 = (283.15, 293.15, 303.15, 313.15, 323.15) K and the values in methanol were determined from 293.15 K to 323.15K are presented in Table 2 and Figure 2. It shows the dependence of MSZW with cooling rate for 2-cyanoguanidine in the three solvents (methanol, ethanol, and water) at different saturation temperature. It is probably because that the increase of saturated temperature accelerates the diffusion of solute and reduces the collision chances of solute, which lead to a lower nucleation rate and later observation of crystal. On the other hand, it needs a period of time to form the visible nucleus in solution. That is to say, nucleus don't have enough time to generate tiny crystal at a rapid cooling rate, thereby, the MSZW widens.

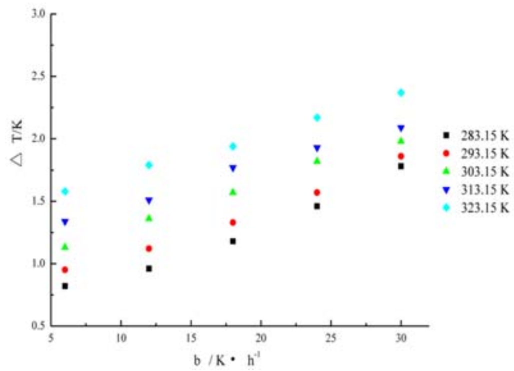
Table 2. Experimental MSZW data of 2-cyanoguanidine in different solvents at temperature T_0.

solvent	T_0/K	ΔT_{max}/K				
		b = 6 K·h^{-1}	b =12 K·h^{-1}	b =18 K·h^{-1}	b =24 K·h^{-1}	b = 30 K·h^{-1}
H_2O	283.15	1.98	2.28	2.69	2.94	3.25
	293.15	2.77	3.16	3.48	3.54	3.97
	303.15	2.91	3.35	3.76	3.89	4.26
	313.15	3.19	3.66	3.97	4.52	4.65
	323.15	3.46	4.04	4.23	4.78	5.14
methanol	293.15	1.24	1.48	1.88	2.17	2.58
	303.15	1.46	1.93	2.33	2.54	2.85
	313.15	1.69	2.23	2.63	2.96	3.11
	323.15	1.91	2.63	3.12	3.58	3.94
ethanol	283.15	0.82	0.95	1.13	1.34	1.58
	293.15	0.96	1.12	1.36	1.51	1.79
	303.15	1.18	1.33	1.57	1.77	1.94
	313.15	1.46	1.57	1.82	1.93	2.17
	323.15	1.78	1.86	1.98	2.09	2.37

[a]Standard uncertainties *u* are *u(T)* =0.01 *K*, *u(p)* = 0.5 kPa, and *u(%T_{max})* = 0.02 *K*. *b* is the cooling rate.



(a) (b)



(c)

Figure 2. Measured metastable zone width's as a function of cooling rate for 2-cyanoguanidine. (a) in water; (b) in methanol (c) in ethanol.

4.2 Effect of Saturated Temperature on Metastable Zone

Usually, MSZW decreases with increase in saturation temperature for a particular cooling rate, but there are some compounds' MSZW data increases with the increase of saturation temperature increase. Such as the metastable zone width of lovastatin in different solvents reported by *X. Y. Zhang et al.* [1] It is worth noting that the metastable zone width increases linearly with the increasing cooling rate *b*. For all cases, despite the difference is in the slope and intercept, which mainly depends on the saturation temperature. Moreover, Figure 1 shows that the MSZW of 2-cyanoguanidine increases with the rise of the saturation temperature at a fixed cooling rate. With the temperature increasing, the viscosity of solution decreased; so the diffusion coefficient of solute also decreased and the solute molecular thermal motion increased. Basing on these reasons, linear relationship between ΔT_{max} and b is presented and 2-cyanoguanidine molecular is more easily dissolved in a certain solvent. For the same reason, metastable zone width increases linearly with the increasing cooling rate. In order to get final product with uniform CSD and high purity, behavior of crystallization should be taken place in that region named MSZW.

4.2 Effect of Solvent Composition on Metastable Zone

It can be seen from Figures 1 and 2, MSZWS data of 2-cyanoguanidine in water is larger than that in methanol and ethanol. Maybe the reason that intermolecular interaction between solvents and solute, the inherent polarity of solvents selected, and the solubility of 2-cyanoguanidine in three solvents can account for this tendency.

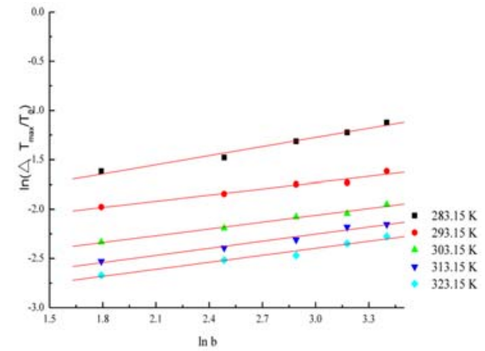
4.4 Estimated Nucleation Kinetics

Based on three nucleation theories mentioned in theory background section, the nucleation kinetics parameters are computed to estimate the nucleation mechanism. Slopes and intercepts from Self-consistent N□ vlt-like approach, Classical 3D nucleation theory, and Kubota's theory are summarized in Table 3.

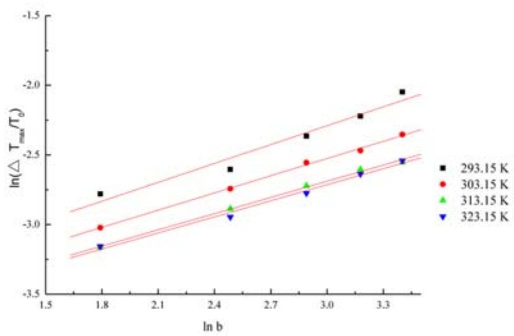
Figure 3 presents the plots of ln ($\Delta T_{max}/T_0$) against lnb for 2-cyanoguanidine in the three solvents at different saturation temperature respectively.

Table 3. Values of kinetics parameter estimation using different nucleation theories for 2-cyanoguanidine at different temperature.

solvents	Self-consistent N□vlt-like			3D		Kubota	
	T_0/K	-Φ	β	F(10^2)	Z	n	N_m/k_nV
H_2O	283.15	2.200	0.308	0.438	0.232	2.241	0.126
	293.15	2.357	0.209	0.801	0.198	3.792	4.438
	303.15	2.587	0.179	1.367	0.185	4.558	16.567
	313.15	2.981	0.252	2.533	0.218	2.972	4.197
	323.15	3.063	0.222	3.227	0.206	3.508	10.188
methanol	293.15	4.068	0.449	7.481	0.258	1.214	0.107
	303.15	3.853	0.388	9.775	0.255	1.427	0.172
	313.15	3.762	0.410	12.285	0.265	1.576	0.254
	323.15	3.868	0.385	9.828	0.251	1.598	0.344
ethanol	283.15	3.424	0.472	2.862	0.260	1.119	0.044
	293.15	3.831	0.407	8.178	0.251	1.457	0.052
	303.15	3.934	0.351	12.383	0.243	1.847	0.077
	313.15	3.927	0.281	15.051	0.223	2.559	0.120
	323.15	3.919	0.245	16.264	0.211	3.076	0.239



(a)



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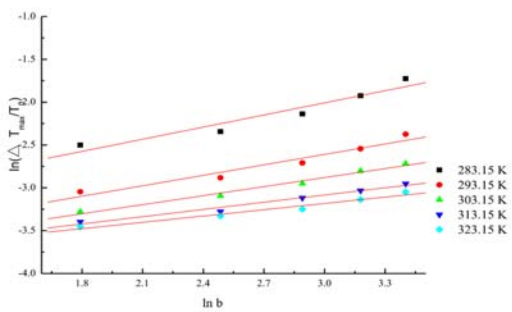


(c)

Figure 3. Plot of ln ($\Delta T_{max}/T_0$) against lnb for different solvents at various saturation temperatures using self-consistent N□vlt-like approach. (a) in water; (b) in methanol; (c) in ethanol.

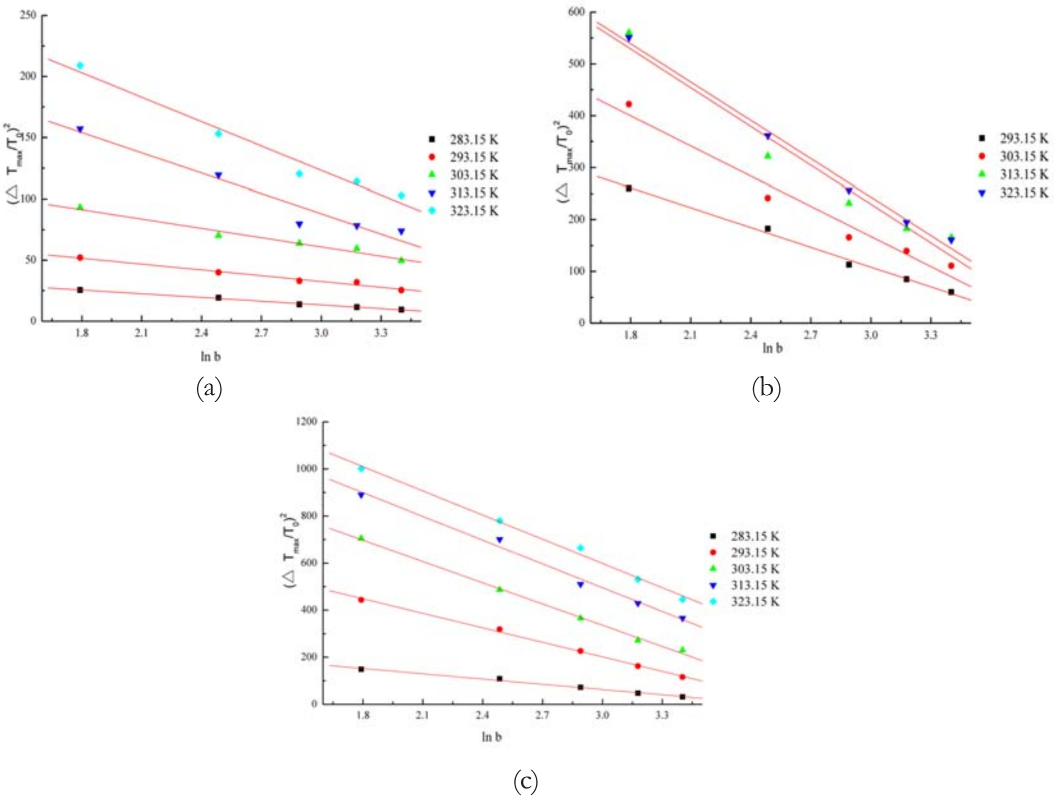
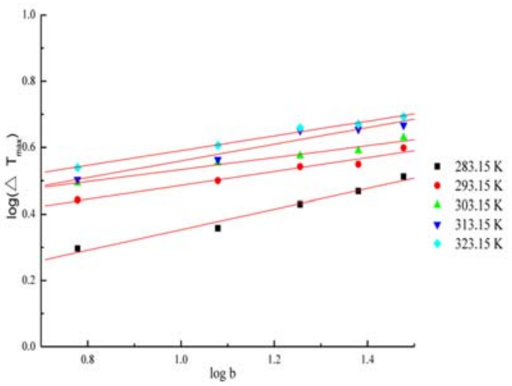
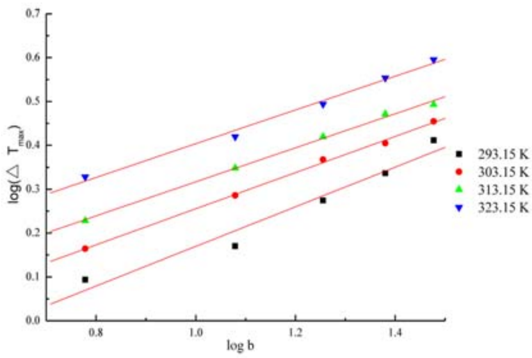


Figure 4. Plot of $(T_0/\Delta T_{max})^2$ against ln b for different solvents at various saturation temperatures using classical 3D nucleation theory; (a) in water; (b) in methanol; (c) in ethanol.

Figure 4 presents the plots of $(T_0/\Delta T_{max})^2$ against ln b for 2-cyanoguanidine in the three solvents at different saturation temperature respectively. The average values of nucleation apparent order *m* computed for water and methanol is about 4.42, 2.46; and 60% *m* estimated from ethanol not exceed 3.00. Analysis of the reported data on *m* obtained from experimental measurement of ΔT_{max} as a function of cooling rate at different saturation temperatures for various systems suggests that the values of *m* usually exceeding about 3 suggests that crystallization in aqueous solutions occurs by progressive nucleation [1] during metastable zone width measurements. Thus, the relatively low result of apparent nucleation order in methanol and ethanol suggests that the nuclei in the solution are formed by instantaneous nucleation mechanism. [2] For 2-cyanoguanidine nucleation in water, the relatively high apparent nucleation order of 4.42 suggests the occurrence of progressive nucleation.



(a)



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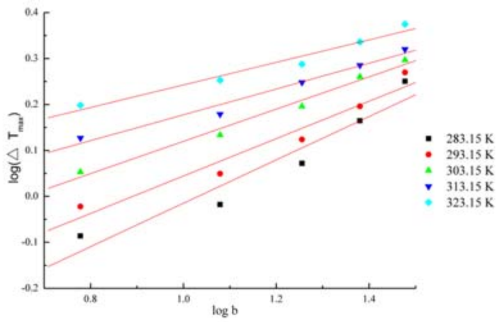

(c)

Figure 5. Plot of log (ΔT_{max}) against log b for different solvents at various saturation temperatures using Kubota's interpretation; (a) in water; (b) in methanol; (c) in ethanol.

Figure 5 presents the plots of log (ΔT_{max}) against ln$b$ for 2-cyanoguanidine in the three solvents at different saturation temperature respectively. Furthermore, the nucleation rate constant m for 2-cyanoguanidine in water, methanol, and ethanol is computed by Kubota's interpretation, which are 3.41, 1.45, 2.01. The result is also consistent with previous conclusion drawn by self-consistent N□ vlt-like approach. The 2-cyanoguanidine nucleate in water suggested the occurrence of progressive nucleation, Crystals in methanol, and ethanol formed by instantaneous nucleation mechanism.

As suggested by Sangwal, -Φ and ln($F^{1/2}$) as a function of saturation temperature T_0 may be expressed by an Arrhenius-type equation.

$$y = y_0 e^{-E_{sat}/RT_0} \quad (20)$$

Taking logarithms on both sides of Eq.(20):

$$\ln y = \ln y_0 - \frac{E_{sat}}{RT_0} \quad (21)$$

Where R is the gas contant, ln$y$ refers to -Φ or ln($F^{1/2}$), ln y_0 can be extrapolated by the intercept of the straight line, and E_{sat} is the activation energy for nucleation of crystals in solution.

Table 4. Intercepts $-\Phi_{0,}$ $[\ln(F^{1/2})]_0$ and activation energy E_{sat}.

solvent	plot	intercept	E_{sat} (kJ/mol)
water	$-\Phi(1/T_0)$	7.445	1.431
	$[\ln(F^{1/2})](1/T_0)$	3.983	1.955
methanol	$-\Phi(1/T_0)$	0.372	1.293
	$[\ln(F^{1/2})](1/T_0)$	9.918	1.954
ethanol	$-\Phi(1/T_0)$	7.184	1.021
	$[\ln(F^{1/2})](1/T_0)$	9.702	1.900

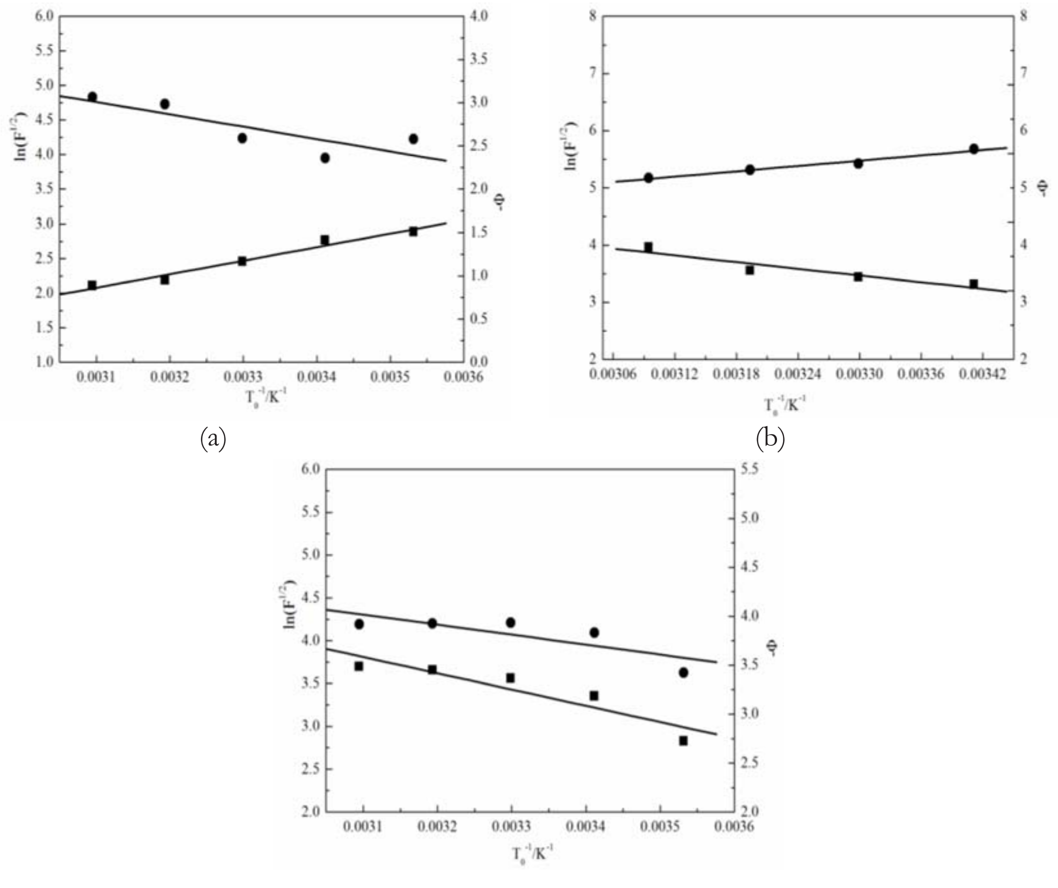

Figure 6. Plots of $\ln(F^{1/2})$ and $-\Phi$ against $1/T_0$ for 2-cyanoguanidine indifferent solvents. Plot: ●; $-\Phi$, ■, $\ln(F^{1/2})$. (a) in water; (b) in methanol; (c) in ethanol.

The relationship of ln $(F^{1/2})$ and $-\Phi$ against $1/T_0$ and the calculated values for 2-cyanoguanidine according to Eq. (21) have been presented in Table 4 and Figure 6, the E_{sat} values of ethanol calculated by both plot of ln $(F^{1/2})$ and $-\Phi$ against $1/T_0$ is much lower than the activation energy of water and methanol. The higher E_{sat} value of 2-cyanoguanidine suggests stronger solvent-solute interaction. At the same time, the relatively low activation energy can lead to a result that solute is prone to dissolve into the solvent compared with other mentioned solvents.

5. Conclusions

Metastable zone width (MSZW) is determined by the polythermal (increasing supercooling) method as a point at which first nucleation events are detected when the solution is continuously cooled at a constant rate. The conclusions have been drawn as follows:

(1) The MSZW for 2-cyanoguanidine in water, methanol, and ethanol increased linearly with the increasing of saturated temperature and cooling rate. And the MSZW narrows according to the order of water, methanol, and ethanol.

(2) Nucleation kinetic parameters are estimated from MSZW data of 2-cyanoguanidine using self-consistent N□vlt-like theory, classical 3D nucleation theory, and Kubota's model. Apparent nucleation orders of 2-cyanoguanidine in three solvents are computed. The results obtained from self-consistent N□vlt-like theory and Kubota's model are consistent. It suggested nuclei in water formed by progressive nucleation and crystals in methanol and ethanol formed by instantaneous nucleation mechanism.

(3) Activation energy E_{sat} for nucleation of crystals in solution also was estimated by Arrhenius-type equation, and higher E_{sat} value of 2-cyanoguanidine suggested stronger solvent-solute interaction. The relatively low activation energy can lead to a result that solute is prone to dissolve into the solvent compared with other mentioned solvents.

Crystallization behavior of 2-cyanoguanidine in different solvents as a function of composition and temperature is mainly evaluated for the purposes of material raw purification and understanding of the mechanisms involved in the physical and chemical stability of material dissolutions.

Acknowledgments

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Reference

[1] Ren Y.S., Duan X.X. and Yang J., *J. Mol. Liq.,* 2014. DOI 10.1016/j.molliq. 2013.11.029.

[2] Beierling T., Micovic J., Lutze P. and Sadowski G., *Chem. Eng. Prog.*, 2014. DOI 10.1016/j.cep.2014.07.011.

[3] Mersmann A. and Bartosch K., *J. Cryst. Growth*, 1998. DOI 0022-0248/98.

[4] Liang K.P., White G., Wilkinson D., Ford L.J., Roberts K.J. and Wood W.M.L., *Ind. Eng. Chem. Res.,* 2004. DOI 10.1021/ie0305014.

[5] Nagy Z.K., Fujiwara M., Woo X.Y. and Braatz R.D., *Ind. Eng. Chem. Res.,* 2008. DOI 10.1021/ie060637c.

[6] Mitchell A.N. and Frawley P.J., *J. Cryst. Growth,* 2010. DOI 10.1016/j.jcrysgro. 2010.05.043.

[7] Ulrich J. and Strege C., *J. Cryst. Growth*, 2002. DOI 10.1016/S0022-0248(01) 02284-9.

[8] Parsons A.R., Black S.N. and Colling R., *Trans. IchemE.*, 2003. DOI 10.1205/ 026387603322150552.

[9] Mullin J.W. and Jancic S.J., *Trans. Inst. Chem. Eng.,* 1979. DOI 0046-9858/79/ 030188-06.

[10] Lorenz H., Perlberg A. and Sapoundjiev D., *Chem. Eng. Prog.,* 2006. DOI 10.16/ jcep.2005.11.013.

[11] Yang D.R., Lee K.S., Lee J.S., Kim S.G., Kim D.H. and Bang Y.K., *Ind. Eng. Chem. Res.,* 2007. DOI 10.1021/ie070209m.

[12] Zhang N., Chen J., Zhao H.P., Shen W., Zhang X.R. and Ren Y.S., *J. Chem. Thermodyn.,* 2015. DOI 10.1016/j.jct.2015.05.025.

[13] Kadam S.S., Kramer H.J.M. and Horst J.H., *Cryst. Growth Des.,* 2011. DOI 10.1021/cg101504c.

[14] Nyvlt J., Sohnel O., Matuchova M. and Broul M., *Academia Prague*, 1986. DOI 0009-286X/86/0808-0665.

[15] Shiau L.D. and Lu T.S., *J. Cryst. Growth,* 2014. DOI 10.1016/j.jcrysgro.2014.06.024.

[16] Nyvlt J., *J. Cryst. Growth,* 1968. DOI 10.1016/0022-0248(68)90179-6.

[17] Bonnin-Paris J., Bostyn S., Havet J.L. and Fauduet H., *Chem. Eng. Commun.*, 2011. DOI 10.1080/00986445.2001.545301.

[18] Mullin J.W., Crystallization, 4th Edn., Butterworth-Heinemann, Oxford, 2001.

[19] Ó'Ciardhá C.T., Frawley P.J. and Mitchell N.A., *J. Cryst. Growth,* 2011. DOI 10.1016/j.jcrysgro.2011.06.017.

[20] Sangwal K., *Cryst. Res. Technol.,* 2009. DOI 10.1002/crat.200800501.

[21] Mersmann A.and Bartosch K., *J. Cryst. Growth*, 1998. DOI 0022-0248/98.

[22] Mullion J.W., *Crystallization*, 3rd Edn., Emeritus professor of chemical engineering, university of London, 1997.

[23] Kubota N., *J. Cryst. Growth*, 2008. DOI 10.1016/j.jcrysgro.2007.11.123.

[24] Dang L.P., Wang Z.Z. and Liu P.B., *J. Chem. Eng. Data.,* 2007. DOI 10.1021/je600544k.

[25] Kulkarni S.A., Kadam S.S. and Meekes H., *Cryst. Growth Des.,* 2013. DOI 10.1021/cg400139t.

[26] Zhang X.Y., Yang Z.Q., Chai J., Xu J.Y., Liang L. and Qian G., *Chem. Eng. Sci.*, 2015. DOI 10.1016/j.ces.2015.01.042.

[27] Sangwal K., *J. Cryst. Growth,* 2011. DOI 10.1016/j.jcrysgro.2010.11.078.

[28] Sangwal K., *Cryst. Growth Des.,* 2009. DOI 10.1021/cg800704y.