

CRYSTALLIZATION KINETICS OF AMMONIUM PERCHLORATE IN AN AGITATED VESSEL

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ABSTRACT

Overall crystal growth kinetics for ammonium perchlorate in laboratory scale batch agitated vessel crystallizer have been determined from batch experiments performed in an integral mode. The effects of temperature between 30-60°C, seed size 0.07, 0.120 and 0.275 mm and stirrer speed 160, 340, and 480 rpm, on the kinetics of crystal growth were investigated. Two different methods, viz. polynomial fitting and initial derivative were used to predict the kinetics expression. In general both methods gave comparable results for growth kinetics estimation. The order of growth process is not more than two. The activation energy for crystal growth of ammonium perchlorate was determined and found to be equal to 5.8 kJ/ mole.

Finally, the influence of the affecting parameters on the crystal growth rate gives general expression that had an obvious dependence of the

growth rate on each variables of concern (temperature, seed size, and stirrer speed) .

$$R_G = 22.438 \times 10^{-4} \exp\left(\frac{5.80}{8.314T}\right) . N^{0.19} . L^{0.79} . \Delta C^{1.38}$$

The general overall growth rate expression had shown that super saturation is the most significant variable. While the positive dependence of the stirrer speed demonstrates the importance of the diffusional step in the growth rate model. Moreover, the positive dependence of the seed size demonstrate the importance of the surface integration step in the growth rate model. All the studied variables tend to suggest that the growth rate characteristics of ammonium perchlorate from aqueous solution commenced in a batch crystallizer are diffusion kinetic controlled process.

KEYWORDS: Crystallization, Ammonium perchlorate , crystal growth kinetics, seeded solutions

NOMENCLATURES

b Rate of cooling ,C/min

C Concentration ,kg/kg

C* Saturation concentration,kg/kg

kn Rate constant of nucleation,kg/s

L Seed size,m

N Stirrer speed,rpm

q Mass deposit per unit mass of
free solvent ,kg/kg

RG Overall growth rate,kg/m².s

T Temperature ,°C

ΔT_{\max} Maximum allowable
undercooling temperature,°C

INTRODUCTION

Crystallization is one of the basic processes in the final treatment of the products in the chemical industry. Kinetic data on crystallization process are of basic importance for the design of industrial crystallization equipment. These data determine the size of the crystallizer and the crystal size of the product, and consequently even-increasing attention is being rapid in the literature to the kinetics of crystallization (Nyvlt, 1989) .

The crystallization process consists of two stages. The first called (nucleation) which is the formation of the solid phase, whereas the second, entitled growth, is the build-up of layer of solute on nucleus (Ullman, 1988). Super saturation is the driving force for both stages of the process. The degree of the supersaturation or deviation from equilibrium of saturated condition is the main factor controlling the deposition process. The

super saturation of a system may be achieved by cooling, evaporation, or as a result of chemical reaction. In other words, the crystallization and nucleation phenomena occur where solute concentration exceeds solute solubility (William, 1994). Formation of crystalline masses implies conjection between nucleation and crystal growth. Nevertheless, due to the complexity of each one of these different stages, and in order to perform studies which establish clear conclusions about crystal growth, it is of great importance to control the system at maximum and avoid nonexpected phenomena, i.e. primary or secondary nucleation during crystal growth experiments (Grases, 1993).

The present study is mainly directed to study the kinetics of crystal growth and nucleation for ammonium perchlorate and state the expression rates for nucleation and for crystal growth in accordance with the previous mentioned

forms. Although, the process has a great complexity and distinction between the two mechanism that conducted through crystal formation would take a great deal of attention. The crystal growth kinetic will be studied at temperature range, agitation speed and range of seed size at constant degree of super saturation .

EXPERIMENTAL SECTION

The determination of super saturation curves and consequently the metastable limits was commenced in a 100 ml Erlenmeyer flask fitted with a magnetic stirrer, and a digital temperature reader which incorporated with a calibrated thermocouple. A schematic diagram of the apparatus had been illustrated in Fig. (1). The flask was immersed in a water bath. The temperature of the cooling medium (water) was carefully controlled via two needle valves suited at the inlet and exit ports to alter the flow rate of the inlet and outlet streams from the bath. 100 W lamp was used for good observation to illuminate the sample under test. 100 ml of saturated solution of prescribed concentration had been prepared of pure Ammonium perchlorate (99.95% pure) .

The solution had been introduced in a flask supplied with an enclosure to minimize evaporation of water. The enclosure was supplied with a calibrated thermocouple. Later on, the solution was heated to (10°C) higher than the prescribe temperature to ensure complete solvating of the stock. Afterwards, the solution was cooled incrementally at constant rate till the desired temperature was reached. This was accomplished by adjusting the flow rate of the coolant medium (water). At first sight of nucleus formation, the temperature of the solution was recorded. The difference between the saturation and nucleus formation temperature represents the maximum allowable undercooling difference (ΔT_{max}) that corresponds to the particular cooling rate. This maximum allowable undercooling difference may be interpreted latter to determine the maximum super saturation allowance before nucleation occurs (i.e, the metastable zone width) and subsequently, to estimate the nucleation rate expression.

The widths of the metastable zone between temperature range (30-60°C) and various cooling rates range between (0.5-2°C/min) was determined. Similarly in a same manner the nucleation in the

presence of the crystalline material (i.e. seeds) was determined. The solution was seeded with (0.8 gm) of crystal (0.275 mm). Afterwards the solution was cooled down to its working saturation temperature.

Growth kinetics determination was evaluated from isothermal desupersaturation curve. The process take place in a batch crystallizer shown in Fig. (2). The crystallizer is constructed from glass vessel of 16 cm internal diameter and of 2 Liter capacity. To prevent evaporation from the aqueous solution, which might cause an appreciable error, the vessel was supplied with an enclosure made from Perspex. A digital thermometer with a thermocouple, a regulatory stirrer and cooling coil had been incooperated with the vessel to commence the determination of the super saturation curves. A stainless steel propeller mixer 6 cm diameter is incorporated with a motor to provide agitation.

To maintain the solution at the desired temperature, the vessel had placed inside a water bath incorporated with inlet and outlet port streams in addition the water bath was manufactured with a thermostat. The crystallizer was

operated in a batch wise sequence over a range of variables; temperature range (30-60°C), stirring speed (160, 340, and 480 rpm) and seed size (275 μm , 118 μm , 70 μm).

MATHEMATICAL TREATMENT

It has been frequently suggested by Nyvlt (1971) and Mullin (1984) that nucleation rate in bulk system is most conveniently correlated by an expression of the form :-

$$R_n = K_n \Delta C^n \dots\dots\dots (1)$$

Where (K_n) is the mass nucleation rate coefficient and (n) is the order of the process with respect to super saturation (ΔC). The nucleation rate may also be expressed in term of the rate at which super saturation is created by cooling:

$$R_n = qb \dots\dots\dots (2)$$

Where $b = -\frac{dT}{dt}$, and (q) is the mass deposited per unit mass of free solvent present in a solution, which is cooled by (1°C). However, (q) is a function of concentration and of crystallizing species. Mathematically, this can be expressed in this way:

$$q = -\frac{dC}{dt} \dots\dots\dots (3)$$

Where C is the solution concentration expressed as mass of anhydrous salt per unit mass of solvent. Maximum allowable super saturation (ΔC_{\max}), may be expressed in term of maximum allowable undercooling (ΔT_{\max}):

$$\Delta C_{\max} = \left(\frac{d^*C}{dT} \right) \Delta T_{\max} \dots\dots\dots (4)$$

Hence Eq. (1) can be rewritten to give:

$$\left(\frac{d^*C}{dT} \right) b = kn \left[\left(\frac{d^*C}{dT} \right) \Delta T_{\max} \right]^n \dots\dots\dots (5)$$

Or

$$\log b = (n-1) \log \left(\frac{d^*C}{dT} \right) + \log K_n + n \log \Delta T_{\max} \dots\dots\dots (6)$$

Which indicate that the dependence of ($\log b$) on ($\log \Delta T_{\max}$) is linear and the slope of the line gives the order of the nucleation process (n). The experimental data for the ammonium perchlorate solution over the temperature range between 30 and 60 °C are analyzed using least squares method in accordance with Eq. (6).

RESULTS AND DISCUSSION

1) Metastable Zones : from Figs 3 & 4, it was noted that the width of the

metastable limits become more narrowed when the solution was super saturated (seeded) (i.e. between 1.2 and 2.65°C) than the unseeded solution that ranged between (2.0 and 3.80°C). This was contributed to the existence of the seeds that work as an initiators (as a catalyst) for nucleus formation.

2) Nucleation kinetics of ammonium perchlorate :-

Typical relationships between the maximum allowable undercooling temperature and the rate of cooling increased, the degree of super saturation for nucleation was increased that in return increased the rate of nucleation.

Eventually, the lesser degree of rate of cooling affected the rate of nucleation in a way that leads to greater median size of crystals.

3) Crystal growth kinetics :- in this events it was intended to investigate the growth kinetic of ammonium perchlorate crystals from aqueous solution in a laboratory batch cooling crystallizer.

Isothermal desupersaturation curves are constructed from the experimental data taking into consideration the

influence of temperature, stirrer speed and seed size.

The experimentally determined desupersaturation curves were subsequently manipulated mathematically (i.e., the polynomial fitting and the initial derivative) to determine expressions of crystal growth rate and also to formulate general expression of the crystalline growth rate, which takes into account, the effects of the three variables (i.e., temperature, stirrer speed, and seed size). A fourth – order polynomial fitting by the least squares technique and initial derivative techniques which gave superior evaluation in comparison to the second order polynomial technique (Initial derivative method). A typical desupersaturation curves and its polynomial fittings are shown in Figs. 7, 8, 9. It was found that the fourth polynomial and the second-order polynomials give good fit for experimental.

All results of growth rate data as a function of super saturation are depicted in Figs. 10, 11, 12.

General expression of crystal growth rate:

To formulate the most general rate model to account the effect of the variables (temperature, stirrer speed and seed size), equation suggested by Nyvlt (1971) and Mullihn (1984):-

$$R_n = K_n \Delta C^n$$

Can be modified to :

$$R_G = aL^c \exp\left(-\frac{E}{RT}\right) N^d \Delta C^g \dots\dots\dots (7)$$

The values of the growth rate model in Eq. (7) were estimated by implementing Rosenbrock and Quasi-Newton optimization method to the data of eight experiments. The graphical presentation of the growth rate correlation between the observed and predicted growth rates is shown in Fig. 13. The last Fig. of constants are shown in the following Eq.

$$R_G = 0.00224 \exp\left(\frac{5.80}{8.314T}\right) N^{0.19} L^{0.79} \Delta C^{1.38} \dots\dots\dots (8)$$

CONCLUSIONS

1) In determining the metastable limits, it was observed that the metastable limits for ammonium perchlorate have relatively narrow limits, e.g. between 2.0 to 3.6 °C for the unseeded solution and between 1.2 to 2.65 °C for the seeded solution.

2) Increasing the rate of cooling, the metastable limits become more broadening for both seeded and unseeded solution. Accordingly, higher rate of cooling gave higher rate of nucleation and consequently smallest median size of the produced crystals.

3) the temperature dependence of the nucleation expression, (K_n) was found more sensitive to the temperature variations in unseeded solution than in seeded solution.

4) The values of nucleation parameters show lower numeric value in seeded solution than in unseeded solution, which means faster and lower rate for the seeded solution than the unseeded solution.

5) The affecting parameters on the crystal growth rate of ammonium perchlorate from aqueous solution (e.g. temperature, seed size, and stirrer speed), fourth order polynomial fitting gave superior evaluations in comparison to the second order polynomial technique (initial derivative method).

6) The general overall growth rate expression show that super saturation is the most significant variable. While the positive dependence of the stirrer speed demonstrates the importance of the

diffusional step in the growth rate model. Moreover, the positive dependence of the seed size demonstrates the importance of the surface integration step in the growth rate model. Eventually, all the studied variables tend to suggest that the growth rate characteristics of ammonium perchlorate from aqueous solution commenced in a batch crystallizer are diffusion kinetic controlled process.

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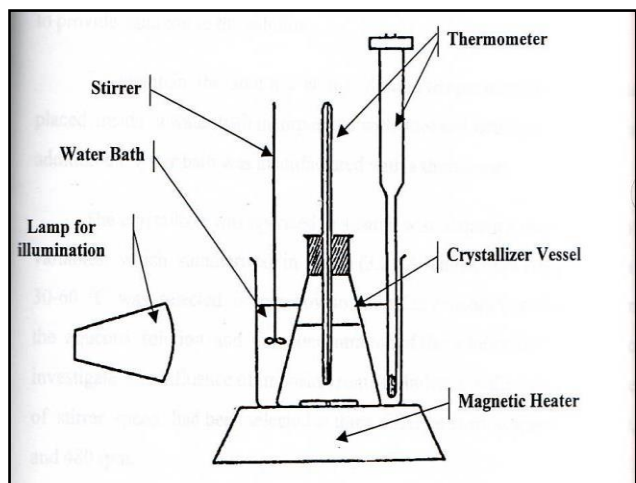


Fig. (1) Apparatus for the determination of the metastable limits and the kinetics of nucleation

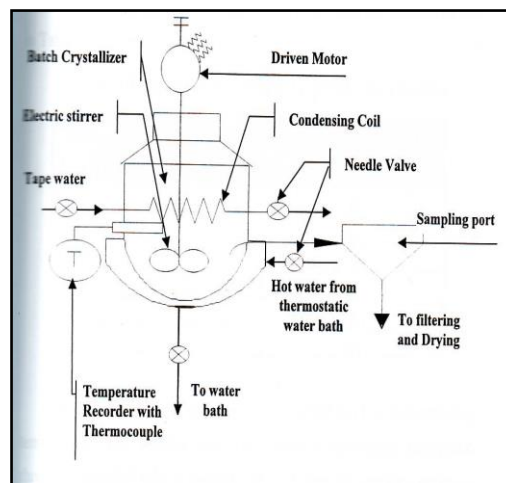


Fig. (2) Layout of the apparatus

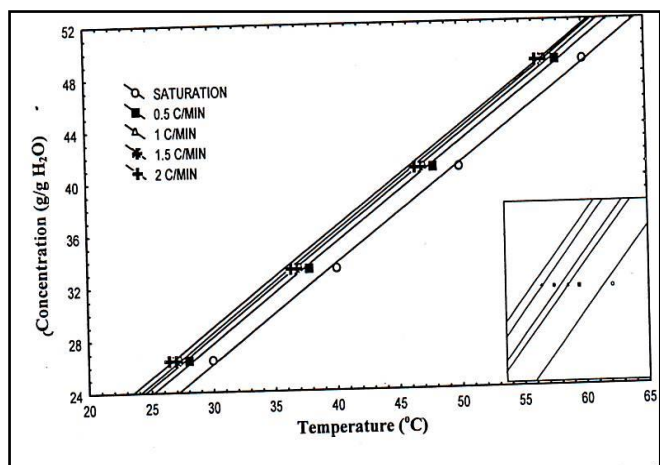


Fig. (3) Metastable limits at different rate of cooling (unseeded solution)

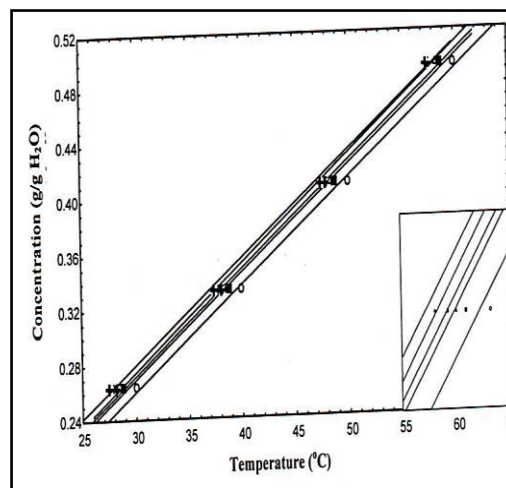


Fig. (4) Metastable limits at different rate of cooling (seeded solution)

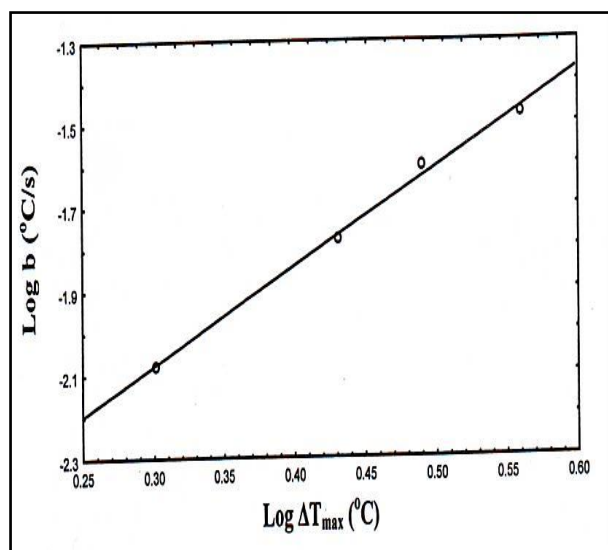


Fig. (5) Effect of cooling rate, b , on the maximum allowable undercooling temperature, ΔT_{\max} for unseeded solution (saturation temperature 30 °C)

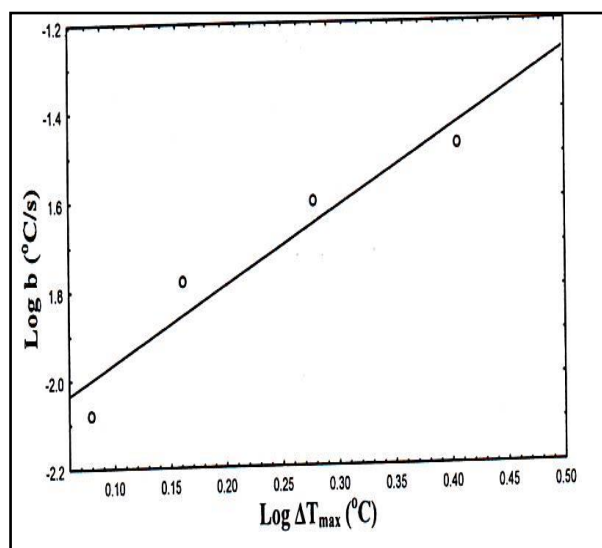


Fig. (6) Effect of cooling rate, b , on the maximum allowable undercooling temperature, ΔT_{\max} for seeded solution (saturation temperature 30 °C)

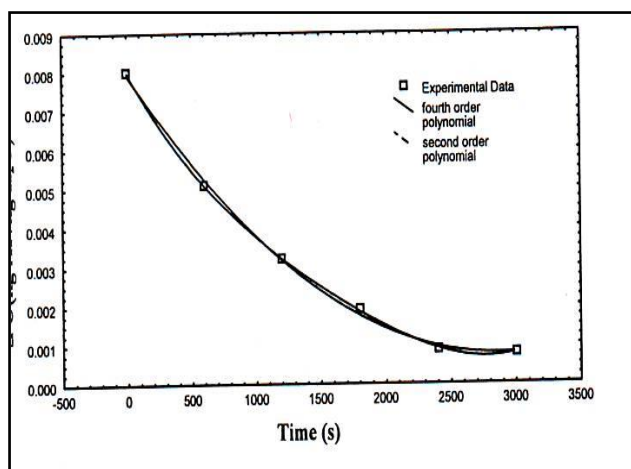


Fig. (7) Desupersaturation curve of ammonium perchlorate at 40 °C, 160 rpm and 0.275 mm seed size (experiment 2)

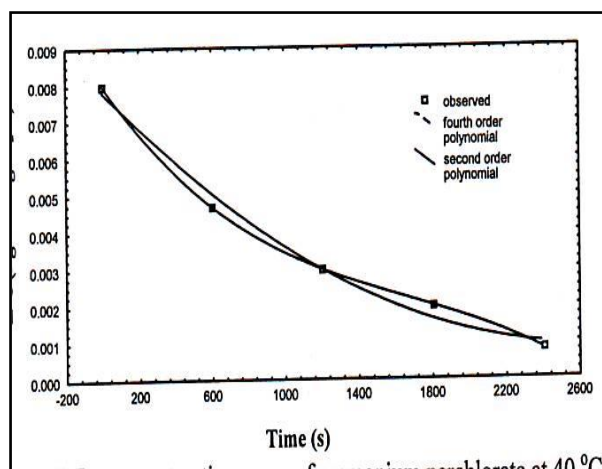


Fig. (8) Desupersaturation curve of ammonium perchlorate at 40 °C, 480 rpm and 0.275 mm seed size (experiment 6)

حركية بلورة بيركلورات الامونيوم في خزان خلط

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جامعة تكريت

الجامعة التكنولوجية

تم التحقق من حركية النمو البلوري لمادة بيركلورات الامونيوم في خزان خلط لمبلور وجبات من تجارب مختبرية و أنجزت بنظام تكاملي.

تم دراسة تأثير درجات الحرارة بين 30-60°م و حجم حبيبات مزروعة 0.070, 0.12, 0.275 ملم و سرعة خلط 160, 340, 480 دورة بالدقيقة.

استخدمت طريقتين لتمثيل النتائج العملية لحركية النمو البلوري و هي طريقة متعددة الحدود و طريقة التفاضل البدائي و قد أعطت الطريقتين نتائج مقاربة من بعضهما. في جميع الأحوال لم تتعد درجة النمو البلوري أعلى من الدرجة الثانية.

استخرجت طاقة التنشيط للنمو البلوري لبلاورات بيركلورات الامونيوم و كانت تساوي 5.8 كيلو جول / مول.

أخيراً، أعطت دراسة تأثير العوامل المؤثرة على النمو البلوري معادلة عامة أشارت بشكل واضح تأثير كل عامل من هذه العوامل و كانت بالشكل التالي:

$$R_G = 0.00224 \exp\left(\frac{5.80}{8.314T}\right) N^{0.19} L^{0.79} \Delta C^{1.38}$$

أظهرت معادلة النمو البلوري العامة أن فوق الإشباع كان له تأثيراً كبيراً كما أوضح الاعتماد الايجابي لسرعة الخلط أهمية خطوة الانتشار. بالإضافة الى ذلك اظهر الاعتماد الايجابي لمعدل النمو للحجم الحبيبي أهمية خطوة الانتشار. كما اظهر الاعتماد الايجابي لمعدل النمو للحجم الحبيبي أهمية خطوة التكامل السطحي لميكانيكية النمو البلوري. أخيراً عملت كل المتغيرات المدروسة على اقتراح صفات النمو البلوري لمادة بيركلورات الامونيوم للمحاليل المائية في مبلور وجبات هي عملية انتشار و بناء (حركية) في وقت واحد.