



## Study on the Reaction Kinetics of Ultrasonic Radiation Non-homogeneous Phase Chitin Deacetylation

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### Abstract

Under the condition of ultrasonic radiation, in this article, we studied the reaction kinetics of non-homogeneous phase chitin deacetylation. The results indicated that the deacetylation degree of chitin was obviously enhanced under the condition of ultrasonic radiation, and the reaction process accorded with pseudo-first order kinetics relationship, and the reaction control is diffusion control, and the surface activation energy was  $E=23.45\text{kJ/mol}$ .

**Keywords:** Chitin, Kinetics, Activation energy, Ultrasonic radiation, Non-homogeneous phase

### 1. Introduction

With the increasing deficiency of mineral resources such as oil, the manufacture research of functional materials which take the natural macromolecule as raw materials becomes more and more important in the world. Chitin is a sort of natural macromolecule material of polysaccharide, which is also called as poly-N-acetylglucosamine, and its chemical name is beta-(1,4)-2-acetamido-2-deoxy-d-glucose, and it is the amylase linked with N-acetyl D-glucosamine through  $\beta$ -(1.4) indicant bond. The biological yield of chitin in the world can achieve tens billion ton, and the chitin is sort of natural renewable resource which reserve is only inferior to the cellulose (Jiang, 2001). The chitin could be prepared as various natural macromolecule derivatives with different purposes through chemical modification, and this sort of material possesses many good properties such as harmless, erosion-resistance, good biodegradability and biocompatibility, and it is extensively applied in many industries such as medication, food, textile, paper making, agriculture, printing and dyeing, cosmetic, biomedicine, enzyme preparation and health products (B. Hexing, 2006, p.3069 & Li, 2006, p.374-381). Therefore, in recent years, many domestic colleges and scientific research institutions begin to study it, and many production enterprises with competitive force occur one after the other. The research about functional material development taking natural macromolecule as raw materials has fueled a boom. Someone thought that the chitin will be one pillar industry as synthetic resin and plastic in the 21'st century.

Because strong hydrogen bond function exists in the chitin molecule, so the deacetylation needs longtime function of lye with high concentration, but the products with this method have low deacetylation degree and low viscosity, and so applied performance will be influenced. Many people studied the problem, for example, they adopted precipitation method, pure medium method and microwave method (Cao, 2005, p.120-124 & Cui, 2004) to study the problem and obtained certain effects. Though people have studied the chitin for many years and applied it in many aspects of the industry, but there is still not a complete theory for the preparation of chitosan, especially there are few basic theory researches about the deacetylation of chitin. There are no articles to utilize the ultrasonic radiation technology to study the basic theory of deacetylation, so according to the structure of chitin and the function principle of ultrasonic, we explore the deacetylation to offer the reference for the production of industrialization.

### 2. Experiment and Testing

#### 2.1 Experimental materials and instruments

Experimental materials and instruments include chitin (made by Zhanjiang Botai Biology Chemical and Industrial as Well as Scientific and Technological Co., Ltd), ethanol (95% AR), sodium hydroxide (AR), acetic acid (AR), ultrasonic generator (Branson2200), Ubbelohde viscosity meter, constant temperature water-bathing trough, shear high speed disintegrator and electronic balance.

## 2.2 Chitin deacetylation reaction

Crush the chitin after drying as powders by the disintegrator, respectively take 5g to into three flasks, and add 40% sodium hydroxide solution or add sodium hydroxide-ethanol mixed liquid. Under the condition of circumfluence in the ultrasonic field, control the temperature respectively as 80°C, 100°C, 120°C, and control the time in 1h, 3h, 5h, 7h, and 9h. When the reaction completes, take out flasks, cool, filtrate and wash to neutrality, then drying.

## 2.3 Measure of deacetylation degree (Chen, 1998, p.419-422)

In the experiment, we adopt the acid-based titration method to measure. The chitosan is electrolyte, and to make the measured result exact, we add 0.5% sodium chloride into the acetic acid solution dissolving chitosan.

$$D.D \% = \frac{(C_1 V_1 - C_2 V_2) \times 0.016}{G \times (100 - W) \times 0.0994} \times 100$$

Where, D.D is the degree of deacetylation (%), C1 is the standard solution concentration of hydrochloric acid (mol/L), C2 is the standard solution concentration of sodium hydroxide (mol/L), V1 is 30ml standard solution quantity of 0.1 hydrochloric acid, V2 is the quantity that titration consumes standard solution of sodium hydroxide (ml), G is the quantity of sample (g), W is the water content of sample (%), 0.016 is the amine content equal to 1ml 1mol/L hydrochloric acid solution (g), and 0.0994 is the theoretic amidocyanogen content in chitosan (16/161).

## 2.4 Measure of Characteristic viscosity and molecular weight (Jiang, 2001)

Take 0.5g chitosan into the breaker, add certain acetic acid (0.1mol/L) and sodium acetic acid (0.2mol/L) mixed solution, mix round to make them fully dissolving, and under 25°C in the constant temperature trough, use Ubbelohde viscosity meter to measure the viscosity of chitosan solution.

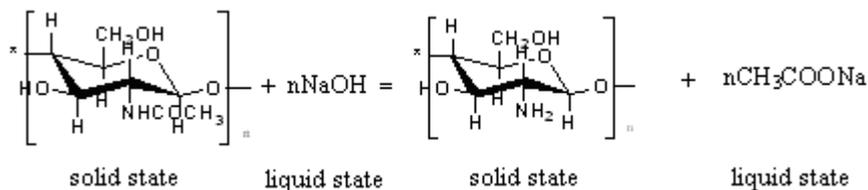
$$[\eta] = K M \alpha$$

Where,  $k=1.81 \times 10^{-3}$ ,  $\alpha=0.93$ .

## 3. Results and Discussion

### 3.1 Diffusion control chitin deacetylation model

The deacetylation of chitin is liquid solid chemical reaction, and with the emersion of acetyl, OH- gradually move to the interior of chitin though the reaction interfaces. In this process, the emersion of acetyl is slow, so the reaction process mainly consider the diffusion control, and we could think the diffusion speed equal to the reaction speed (Cai, 1998, p.352-355, Takanori, 1997, p.649-651, Loth, 1997, Xie, 1996, p.30-33, Chen, 1992, p.1008-1010). The equation of reaction process is



The chitin through crashing could be regard as plate which length, height and thickness respectively are A, B and L, and  $AB \gg L$ , the diffusion area of OH-  $S=AB$ , so the diffusion behavior of OH- in the chitin is seen in Figure 1.

According to the Fick's laws of diffusion (Novikov, 1990, p.64-67 & Zhang, 2000, p.23-26), the diffusion flux of unit area in unit time through vertical diffusion direction is  $\Phi = -D \frac{dC}{dx}$ .

So, the diffusion speed of OH- in chitin is

$$\frac{dG}{dt} = -D S \frac{dC}{dx}$$

Where, D is the diffusion coefficient, S is the transparence area of diffusion direction,  $dc/dx$  is the concentration grads along the diffusion direction. Because the reaction is controlled by the diffusion, so the deacetylation speed (reaction speed) could be thought to equal to the diffusion speed. Implement integral to the above formula, we can get  $-dG/dt = -D S C_0/x$ , where,  $C_0$  is the concentration of sodium hydroxide solution (g/ml) and X is the advance distance of OH-diffusion (cm).

In the deacetylation process of chitin, the interior reaction surface gradually shifts inside, and the shift speed is  $dN = dG = \rho S dx$ .

Combine the diffusion speed with shift speed, and we can obtain  $x dx = DC_0/\rho dt$ .

Solve the above equation, we can get  $x = (2DC_0t/\rho)^{1/2}$ .

Slice-shape chitin is in the sodium hydroxide solution, and the diffusion of OH<sup>-</sup> is seen in Figure 1. So, we can suppose the degree of deacetylation is  $D.D \% = 100 \times 2x/L = 200/L \times (2DC_0t/\rho)^{1/2}$ , where,  $\rho$  is the density of chitin ( $\text{g/cm}^3$ ),  $L$  is the thickness of chitin (cm),  $C_0$  is the concentration of sodium hydroxide (g/ml),  $t$  is the time of reaction (h), and  $D$  is the diffusion speed.

From the formula of deacetylation degree, we can see that under the condition of constant temperature, the deacetylation degree of chitin is directly proportional to the concentration of sodium hydroxide and reaction time, and the function relationship is  $D.D = f(D, C_0, t, \rho, L)$ . The experiment research showed that the experiment result basically inosculate with the theory. The establishment of the mathematical model possesses certain instructive meaning for actual production.

### 3.2 Reaction kinetics of chitin deacetylation

The molecules of chitin are generally arranged in the crystal lattice of highly crystal micro-fiber, and they are divided into three types such as  $\alpha$ ,  $\beta$  and  $\gamma$  according to their crystal structure, and the  $\alpha$  structure is the most stable structure, and it is the common structure in the nature. Strong -O...H-O- and -O...H-N- hydrogen bond functions exist among chitin molecules, and the function force among big molecules is very strong, which make the chitin molecules present ordered structure and induce the non-melt and highly difficult non-dissolving property of chitin, and the chitin is not dissolved in water and other most solvents (Keeme, 1980, p.293-296, Huang, 1995, Zhou, 1995, p.93-96, Qian, 1998, p.100-104 & Liu, 2002, p.31-34). The structure of chitin is seen in Figure 2. Figure 3 is the structure of chitosan through deacetylation.

The basic hydrolysis of acid amide is a nucleophilic substitution reaction (Zhang, 2004, p.511-515). Under the concentrated alkali, because carbonyl takes positive charge and OH<sup>-</sup> has strong nucleophilicity and small bulk, chitin will first attach carbonyl to make original plane deltoid amides become into tetrahedral transition state, and part of negative charge will be on the oxygen. The tetrahedral transition state will change into the tetrahedral midbody, and the positive charge is on the oxygen. That is the first step of reaction, and it is the addition of OH<sup>-</sup> to the amides, and the balance exists from reaction material to the midbody, so it is reversible. The second step is the leaving of alkalescence group. The reaction course is seen in Figure 4.

The whole reaction process is controlled by the first step, and the reaction could be thought as the first order reaction, so the first order dynamical equation could be denoted as

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Where,  $a$  is the initial concentration of acetylamine, and  $X$  is the amidogen concentration formed after  $t$  time of hydrolyzation.

From the above formula, we can obtain

$$k = \frac{2.303}{t} \log \frac{1}{1-x/a}$$

Suppose  $D.D = x/a$ , where  $X$  is the transformation rate of chitin deacetylation which corresponds with the deacetylation degree of chitin. So we can obtain  $\text{Ln}[1/(1-D.D)] = k t$ , where  $K$  is the reaction surface speed constant, and  $D.D$  is the degree of deacetylation.

From Figure 5 and Figure 6, under constant sodium hydroxide concentration and reaction temperature, the deacetylation degree of static reaction chitin is far smaller than the deacetylation degree under dynamic condition, which indicates that the mixing condition enhance the diffusion intension of OH<sup>-</sup>. The condition of ultrasonic radiation could make compact crystal chitin loosen, which makes for the diffusion of OH<sup>-</sup> in the body of chitin, improves the enhancement of deacetylation degree and further proves that the deacetylation reaction of chitin is controlled by diffusion.

In the deacetylation reaction process of chitin, the influence of reaction temperature is very important. From Figure 7, the temperature increases, the deacetylation degree of chitin obviously increase, and with the increase of reaction time, the degree of deacetylation increases. The chitin deacetylation reaction from above hypothesis is the first order reaction dynamics which accords with the experiment research, i.e. the equation of  $\text{Ln}[1/(1-D.D)] = k t$  comes into existence.

Under the condition of ultrasonic radiation, the concentration of sodium hydroxide is 40%, and the reaction temperatures respectively are 60°C, 80°C, 100°C and 120°C. Construct  $\text{Ln}[1/(1-D.D)]$  to the reaction time  $t$ , we can obtain Figure 8, and parameters all present good linear relationship, and all correlative coefficients exceed 0.995. The

result shows that the deacetylation reaction dynamics of chitin is the first order reaction.

Figure 9 is the relationship between the slope of the first order reaction equation  $\ln[1/(1-D)] = kt$  under different temperatures  $\ln k$  with the time reciprocal  $1/T$ , and both are linear relationship, and the correlative coefficient of beeline is 0.9964. So we can compute the surface activity energy of deacetylation of chitin under ultrasonic radiation,  $E = 23.45 \text{ kJ/mol}$ . The value is obviously smaller than the activity energy  $92.05 \text{ kJ/mol}$  in Sannan's report (Zhang, 2004, p.511-515) which took the homogeneous phase as the hypothesis, which indicates both reaction mechanisms are very different, and the non-homogeneous phase deacetylation of chitin is diffusion control. Chen Bingnian's researches about the deacetylation dynamics to chitin under the mixing condition indicated that the surface activity energy is  $35.63 \text{ kJ/mol}$ . Under the condition of ultrasonic radiation, its surface activity energy is smaller, which shows that the ultrasonic radiation could strengthen the diffusion of  $\text{OH}^-$ , strongly shake the acetyl groups on chitin, and make for the hydrolysis nucleophilic substitution reaction for alkali.

Figure 10 is the fitting curve between deacetylation degrees of chitin with time. The fitting equation is  $D \cdot D\% = -1.15t^2 + 20.17t + 3.04$ ,  $R^2 = 0.992$ . The experiment values basically accord with the computation values from the fitting equation. Under the condition of ultrasonic radiation, the concentration of sodium hydroxide is 40%, and with the process of time, the deacetylation degree continually increases, and when the deacetylation degree achieves 80%, the deacetylation begins to be slow, and when the degree exceeds 90%, the deacetylation goes parallel, and the resistance of diffusion is large. To enhance the degree of deacetylation, we must further crush the chitin.

Figure 11 shows the comparison of average molecular weight of same deacetylation degree prepared under conditions of ultrasonic radiation, static state and mixing, which indicates the ultrasonic radiation could not induce degradability for chitosan.

#### 4. Conclusions

(1) The deacetylation degree of chitin increases obviously under the condition of ultrasonic radiation, and the deacetylation is the pseudo-first-order reaction dynamic relationship, and the surface activation energy of deacetylation is  $E = 23.45 \text{ kJ/mol}$ , which is smaller than the activation energy which takes the homogeneous phase reaction as the hypothesis, and that indicates both reaction mechanisms are very different, and the non-homogeneous phase deacetylation reaction of chitin is diffusion control.

(2) In the deacetylation reaction process of chitin, the influence of reaction temperature is very important, and the temperature increases, the deacetylation of chitin obviously increases. The ultrasonic radiation also has very important influence to the deacetylation of chitin, and under same conditions, the deacetylation degree is enhanced obviously, which indicated that the condition of ultrasonic radiation could make the compact crystal of chitin loosen, and it is propitious to the diffusion of  $\text{OH}^-$  in the chitin and deacetylation.

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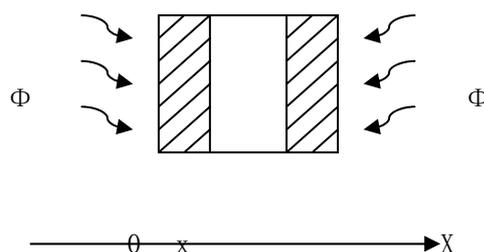


Figure 1. OH-proliferation Direction Schematic Drawing

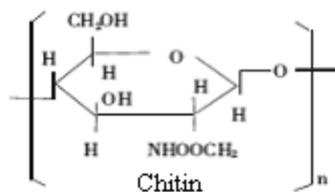


Figure 2. Carapace Element (Chitin) Structural Formula

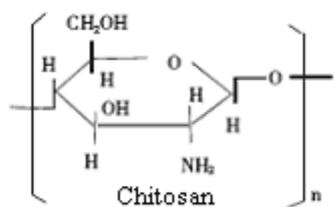


Figure 3. Shell Polyose (Chitosan) Structural Formula

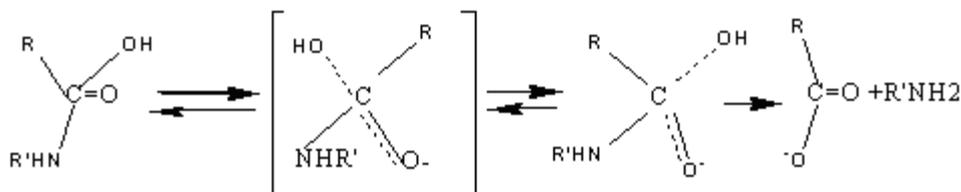


Figure 4. The Drawing of Carapace Element Escape Acetylyze Response under Thick Alkali's Function

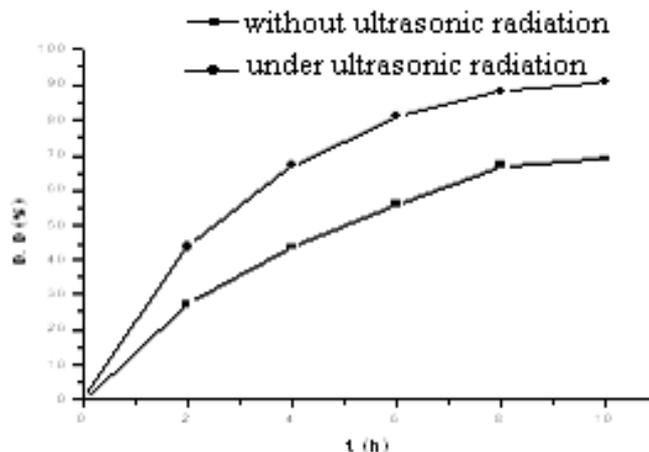


Figure 5. Contrast of Escape Acetyl Influence under Supersonic Radiation Condition

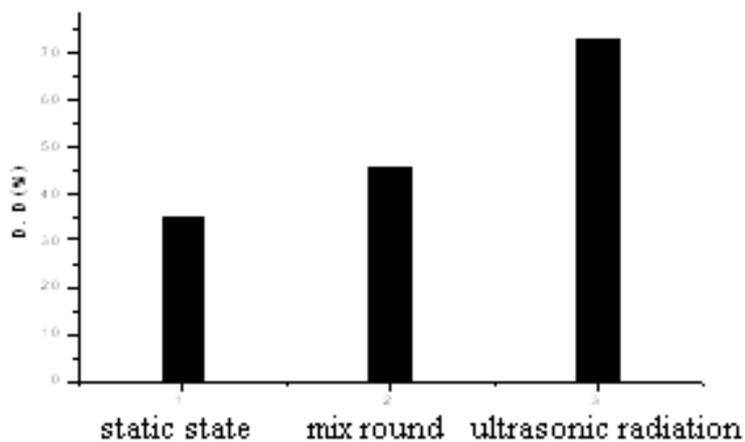


Figure 6. Contrast of Escapes Acetyl under Tendency and Static Condition

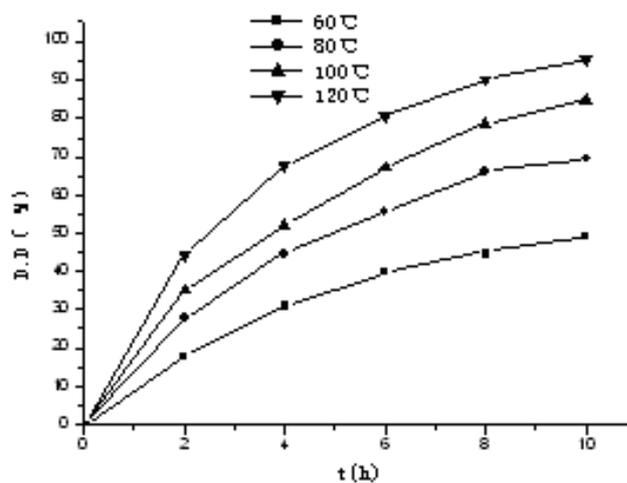


Figure 7. Influence of Temperature to Escapes Acetyl of Carapace Element

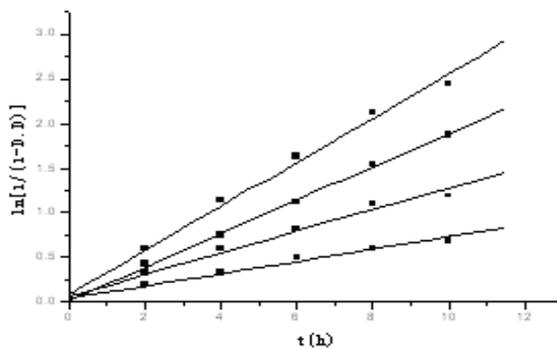


Figure 8. Ln [1/(1-D.D)] with Time t Relational

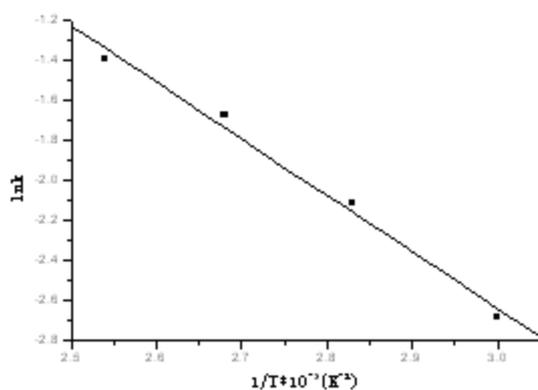


Figure 9. Lnk with 1/T Relational

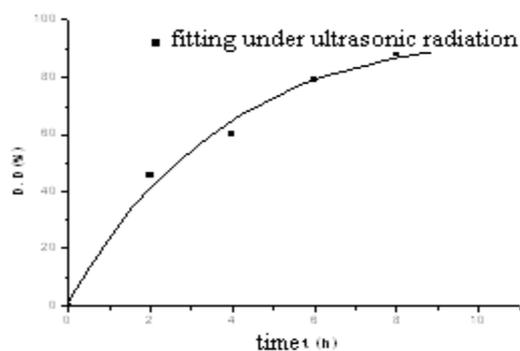


Figure 10. Escape Acetyl with Time Relationship Fitted Curve

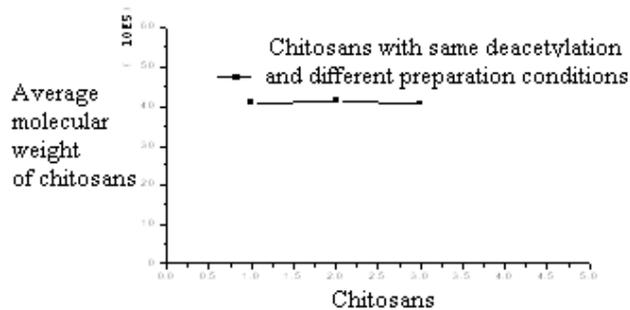


Figure 11. Change of Escapes Acetyl Same Shell Polyose Molecular Weight