Kinetics of the esterification reaction between adipic acid and 1,6-hexanediol with tetrabutyl titanate as a catalyst

Abstract

In this paper, the esterification reaction for a batch reactor between adipic acid (AA) and 1,6-hexanediol (1,6-HD) catalyzed by tetrabutyl titanate ($Ti(OBu)_4$) was studied in the temperature range of 413-443K. A kinetic model based on the assumption of 3.5-order reaction was proposed to describe the variation of carboxyl group concentration with time. The kinetic data demonstrated that the model was suitable to the esterification reaction. The rate constant was obtained through global optimization method-genetic algorithm procedure and the activation energy ($E_a = 80.16 \pm 4.41 kJ / mol$) of the esterification reaction was calculated through the Arrhenius equation. The effects of initial 1,6-HD/AA molar ratio (α) and the amount of catalyst on the esterification was also investigated. The results showed that (i) the conversion of carboxyl group increases obviously when the α value increases from 1.1 to 1.2, but it does not change much when the α value is larger than 1.2; and (ii) the rate constant of the esterification increases with the concentration of $Ti(OBu)_4$ in the range of 0.36-5.66mmol/kg.

Keywords：kinetics; esterification; catalyst; 1,6-hexanediol; adipic acid; tetrabutyl titanate.

1. INTRODUCTION

Aliphatic polyester polyols with molecular weight of 1000-3000g/mol are playing a quite important role in the production of polyurethane rubber, polyurethane foam, polyurethane adhesive, polyurethane elastomer [1]. They are generally synthesized through the esterification of organic dicarboxylic acid with excess diols, followed by polycondensation. As one of the most important aliphatic polyester polyols, polyhexanediol adipate, synthesized by adipic acid (AA) and 1,6-hexanediol (1,6-HD) has been reported in documents over the past few decades [2,3], while no work was done on the kinetics of the esterification reaction between AA and 1,6-HD. In general, the kinetics is important to the synthesis process and can be used to guide the reactor design and industrial production. The kinetics of esterification between dicarboxylic acid and glycols have been widely discussed, especially in the cases where the esterification is catalyzed by hydrogen ion. And the basic rate equation is considered to be [4]:

$$-d[COOH]/dt = k_0[COOH][OH][H^+] \tag{1}$$

Flory [5-7] proposed that all functional groups were equally reactive in the esterification reaction and the hydrogen ions came from the ionization of the carboxyl group. And the rate equation of equimolar system in the absence of a foreign acid was simplified as:

$$-d[COOH]/dt = k_1[COOH]^2[OH] \tag{2}$$

Lin and Hsieh [4] proposed that in the absence of foreign acid, the hydrogen ions came from the ionization of the hydroxyl group and the kinetic equation was expressed as:

$$-d[COOH]/dt = k_2[COOH][OH]^2 \tag{3}$$

Quite different from those equations proposed by Flory and Lin, Tang and Yao [8] proposed a quite new kinetic equation in the absence of foreign acid:

$$-d[COOH]/dt = k_3[COOH]^{1.5}[OH] \tag{4}$$

Tang and Yao [8] reexamined the experimental data of Flory and Lin and found that all the data conformed to their 2.5-order model. However, the effect of the water removal on the esterification reaction hasn't been taken into consideration in Tang and Yao's model.

There are lots of other works dealing with the kinetic equation, Chen [9,10] pointed out that the unremoved water and the reverse reaction took great effect on the rate equation while their model were only suitable to self-catalyzed or acid-catalyzed system. Chen and Xu [11] proposed that different functional groups had different reaction activities and obtained the production distribution of esterification reaction. The expressions of these equations were quite complicated, but they may be unable to describe the kinetics of the polycondensation stage accurately. Taking Chen and Xu's [11] research as a example, they proposed an eight-step mechanism of esterification and established a kinetic model of diesters under the assumption that polycondensation process would not carry out until the esterification ratio reaches to 90%. These models have limitations on the description of the whole process of esterification reaction. In order to describe the kinetics of the whole process of esterification reaction more comprehensively, it is necessary to improve the kinetic model proposed before.

In recent years, more and more attention have been paid on the catalysts of esterification reaction. The catalysts that have been studied extensively were organic acid [12], inorganic salt or organometallic compound containing tin [13-15], zinc [16,17], aluminum [18,19], and titanium [20-22], etc. Organic acid, as a catalyst, will result in the yellowing of polyester polyols and then affect the brightness of the product. Tin, zinc and aluminum may do harm to human health and cause damage to environmental system [23]. The titanium catalyst such as tetrabutyl titanate ($Ti(OBu)_4$) could improve the brightness of the product and do no damage to environmental and biological systems [11], which means that titanium catalyst has an extensive prospect. Skrzypek [21] worked on the kinetics of esterification of phthalic anhydrides with 2-ethylhexanol in the presence of $Ti(OBu)_4$, and the results showed that all reaction orders for $Ti(OBu)_4$, mono-ester and alcohol were 1. Hsu [20,22] studied the transesterification catalyzed by $Ti(OBu)_4$, used three different methods to estimate the rate constant and proved the validity of the equal reactivity hypothesis for functional groups within a wide range of experimental condition. However, the kinetics of esterification reaction between AA and 1,6-HD haven't been reported .

In this paper, the esterification reaction for a batch reactor between AA and 1,6-HD was studied in the presence of $Ti(OBu)_4$ under atmospheric pressure, and the kinetic data was obtained in the temperature range of 413K-443K. A kinetic model based on the assumption of 3.5-order reaction was established to fit the kinetic data and the results were compared with those of the model reported before [4,21]. In addition, the effects of reaction temperature, 1,6-HD/AA molar ratio (α) and catalyst dosage on esterification reaction were investigated as well.

2. KINETIC MODEL

According to the discussion above, the reaction order of esterification in the absence of catalyst may be 1, 1.5 or 2 for carboxyl group and 1 or 2 for hydroxyl group, respectively. For the esterification process in the presence of catalyst, the kinetic model will be more complicated. In this paper, three assumptions to the esterification reaction with $Ti(OBu)_4$ as a catalyst (Scheme 1) are proposed as follow:

$$\begin{array}{ccccc} -\mathrm{COOH}+ & -\mathrm{OH} & \xrightarrow{\text{catalyst}} & -\mathrm{COO}- & +\mathrm{H_2O} \\ (A) & (B) & (C) & (D) & (W) \end{array}$$

Scheme 1. Equation for esterification reaction

(1) all the carboxyl group existing in the diacids, monoester and polyester have the same reactivity, and all the hydroxyl group existing in the dihydric alchol, monoester and polyester have the same reactivity as well;

(2) the orders of reaction are 1.5, 1 and 1 with respect to carboxyl group, hydroxyl group and catalyst respectively;

(3) under the condition of atmospheric pressure and final conversion of carboxyl group being lower than 95%, most of the water produced by the reaction was removed and the water concentration in the liquid phase is always sufficiently small so that hydrolysis reactions (reverse of Scheme 1) can be neglected.

When water evaporates, the mass of the liquid phase in the batch reactor decreases, which has an influence on the concentrations of the carboxyl and hydroxyl groups, so the effect of water removal should be taken into consideration. The concentrations of each functional group are expressed by the mass molar concentration (mol/kg). If the initial concentrations (mol/kg) of carboxyl group, hydroxyl group and catalyst are denoted by c_{A0}, c_{B0}, c_{C0}, respectively, and their concentration at time t by c_A, c_B, c_C, while the initial mass of the mixture are denoted by m_0, and the mass at time t by m, then the moles of water (N_W) removed from the system at time t can be calculated from:

$$N_W = c_{A0}m_0 - c_A m = c_{B0}m_0 - c_B m \tag{5}$$

And the relationship between m_0 and m is described as:

$$m_0 = m + M_W N_W \tag{6}$$

$$c_{C0}m_0 = c_C m \tag{7}$$

where M_W (0.018 kg/mol) stands for the molar mass of water.

From Eqs. (5)-(7), the following equations can be easily derived:

$$\frac{m}{m_0} = \frac{1-M_W c_{A0}}{1-M_W c_A} \tag{8}$$

$$c_B = c_A + (c_{B0} - c_{A0})\frac{1-M_W c_A}{1-M_W c_{A0}} = \frac{(1-M_W c_{B0})c_A + (c_{B0}-c_{A0})}{1-M_W c_{A0}} \tag{9}$$

$$c_C = \frac{m_0}{m} c_{C0} = \frac{1\text{-}M_W c_A}{1\text{-}M_W c_{A0}} c_{C0} \tag{10}$$

Based on the assumption of 3.5-order reaction, the rate of reaction shown in Scheme 1 can be written as:

$$\text{-}\frac{\mathrm{d}c_A}{\mathrm{d}t} = k' c_C c_A^{1.5} c_B \tag{11}$$

Eq. (11) can be changed into:

$$\text{-}\frac{\mathrm{d}\sqrt{c_A}}{\mathrm{d}t} = \frac{k'}{2} c_C c_A c_B \tag{12}$$

where k' is the reaction constant.

Substitution of Eq. (9) and Eq. (10) into Eq. (12), gives

$$\frac{\text{-}\,\mathrm{d}\sqrt{c_A}}{c_A(\frac{1}{M_W} - c_A)(c_A + \frac{c_{B0}-c_{A0}}{1-M_W c_{B0}})} = \frac{k}{2}\frac{M_W(1-M_W c_{B0})}{(1-M_W c_{A0})^2}\mathrm{d}t \tag{13}$$

where $k = k' c_{C0}$.

Let $A = \frac{1}{M_W}$, $B = \frac{c_{B0}-c_{A0}}{1-M_W c_{B0}}$,

according to mathematical identity transformation shown as follow [24,25]:

$$\frac{1}{c_A(A-c_A)(c_A+B)} = \frac{1}{(A+B)A}\left[\frac{A+B}{B}(\frac{1}{c_A} - \frac{1}{c_A+B}) + \frac{1}{A-c_A} + \frac{1}{c_A+B}\right] \tag{14}$$

Eq. (13) can be changed to:

$$-\mathrm{d}\sqrt{c_A}\,\frac{M_W^2\left(1-M_Wc_{B0}\right)}{1-M_Wc_{A0}}\left(\frac{1-M_Wc_{B0}}{M_W\left(c_{B0}-c_{A0}\right)}\frac{1}{c_A}-\frac{1}{\frac{1}{M_W}-c_A}+\frac{1-M_Wc_{B0}}{M_W\left(c_{B0}-c_{A0}\right)}\frac{1}{c_A+\frac{c_{B0}-c_{A0}}{1-M_Wc_{B0}}}\right)=\frac{k}{2}\frac{M_W\left(1-M_Wc_{B0}\right)}{\left(1-M_Wc_{A0}\right)^2}\mathrm{d}t \tag{15}$$

Interacting Eq. (15) subject to the condition that $c_A = c_{A0}$ at $t = 0$ leads to

$$\frac{1-M_Wc_{A0}}{M_W(c_{B0}-c_{A0})}\frac{1}{\sqrt{c_A}}-\frac{\sqrt{M_W}}{2}\ln\frac{1+\sqrt{M_Wc_A}}{1-\sqrt{M_Wc_A}}+\frac{(1-M_Wc_{B0})^{1.5}}{(c_{B0}-c_{A0})^{1.5}M_W}arctg\sqrt{\frac{(1-M_Wc_{B0})c_A}{c_{B0}-c_{A0}}}=\frac{k}{2M_W(1-M_Wc_{A0})}t+f(c_{A0}) \tag{16}$$

where $f(c_{A0})$ is a constant and can be determined by Eq. (17):

$$f(c_{A0})=\frac{1-M_Wc_{A0}}{M_W(c_{B0}-c_{A0})}\frac{1}{\sqrt{c_{A0}}}-\frac{\sqrt{M_W}}{2}\ln\frac{1+\sqrt{M_Wc_{A0}}}{1-\sqrt{M_Wc_{A0}}}+\frac{(1-M_Wc_{B0})^{1.5}}{(c_{B0}-c_{A0})^{1.5}M_W}arctg\sqrt{\frac{(1-M_Wc_{B0})c_{A0}}{c_{B0}-c_{A0}}} \tag{17}$$

The usability of the Eq. (16) will be verified by our experimental data. Based on the experimental data of c_A at different time t, the rate constant (k) of esterification reaction can be obtained through global optimization method-genetic algorithm procedure [26,27] and the objection function is defined as follow:

$$S=\sum_{i=1}^{N}\left(c_{Ai}^{\exp}-c_{Ai}^{cal}\right)^2 \tag{18}$$

where N identifies the numbers of experimental points, $c_{Ai}^{\exp}$ identifies the experimental concentration and c_{Ai}^{cal} identifies the theoretical concentration.

Absolute average deviation (AAD%) is used to evaluate the goodness-of-fit and defined as:

$$AAD\%=\frac{1}{N}\sum_{i=1}^{N}\left(\frac{\left|c_{Ai}^{\exp}-c_{Ai}^{cal}\right|}{c_{Ai}^{\exp}}\right)\times100\% \tag{19}$$

3. EXPERIMENTAL

3.1 Materials

AA and 1,6-HD obtained from Shanghai Tipao Biotechnology Co., Ltd., China were base stock and used without further purification. $Ti(OBu)_4$ obtained from Shanghai Aladdin

Bio-Chem Technology Co . , Ltd ., China was used as a catalyst. Toluene and Ethanol obtained from Shanghai Titan Technology Co., Ltd. China were analytical reagent.

3.2 Apparatus and procedure

A 250ml flask, equipped with a platinum sensor, a stirring paddle (200rpm) and a fractionating column was used as the batch reactor to carry out the experiments under atmospheric pressure. The fractionating column was applied to allow the immediate removal of water from the system, reduce the hydrolysis reactions, and minimize the loss of reactant. Oil jacket was used as the reactor's heat source to keep a constant reactor temperature (maintained within ±0.5K).

A certain quantity of AA (approximately 33.2g) was placed into the 250ml flask and then heated to desired temperature (413-443K). The mixture of 1,6-HD (30-45g) and catalyst ($Ti(OBu)_4$) (8-128mg) are placed together in another 250ml flask and preheated to the same temperature before they are mixed with the AA. The initial time of the experiment is the time when the two reactants are mixed together. The samples were withdrawn from the mixture through the sampling port at each time interval, then immediately cooled down by ice water bath to stop the subsequent reaction, weighed, dissolve with the mixed solvent (ethanol and toluene equivolume) and titrated with 0.1mol/L alcoholic potassium hydroxide, where phenolphthalein was used as an indicator to signal the endpoint of the titration. A clear endpoint was always easily observed.

The measurement uncertainty for experimental data of carboxyl group which comes from the uncertainties in measuring the weight of the samples, the purity of reactant and the endpoint of the titration was less than 3 %. To confirm consistency of the data obtained, all the experiments were duplicated and the results showed that the reproducibility was excellent.

4. RESULTS AND DISCUSSIONS

4.1 Effect of reaction temperature

The effect of the reaction temperature on the esterification reaction was studied ranging from 413K to 443K at a specified initial 1,6-HD/AA molar ratio ($\alpha = c_{B0} / c_{A0} = 1.2$) and the concentration of Ti(OBu)$_4$ (c_{C0}) was about 0.71mmol/kg. On the basis of the procedure (Section 3.2), the concentrations of carboxyl groups (c_A) at time t were gotten for different temperature and shown in Fig. 1 (dots). Using the global optimization method-genetic algorithm procedure (Roulette wheel selection; crossover operator: 0.8; mutation operator: 0.001), the rate constants (k) of different temperature are obtained and listed in Table 1. The theoretical values (c_A) at different time t can be calculated based on the rate constants (k), and the relationships of c_A *vs* t are also shown in Fig. 1(solid lines). Meanwhile, the *AAD*% values calculated by Eq. (19) are listed in Table 1. From Fig. 1 and the values of *AAD*% (0.83-3.00%), the kinetic model describes the process of the esterification reaction between AA and 1,6-HD catalyzed by Ti(OBu)$_4$ quite well, so the above three assumptions are acceptable.

Fig. 2 shows the linear relationship between $1/T$ and $\ln k$. By fitting the experimental data with the Arrhenius equation:

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln k_0 \tag{20}$$

the activation energy (E_a) can be figured out to be 80.16±4.41 kJ/mol, enabling rate constant (k) to be expressed as:

$$k = 1.062 \times 10^{7} \exp\left(-\frac{80162 \pm 4414}{RT}\right) \tag{21}$$

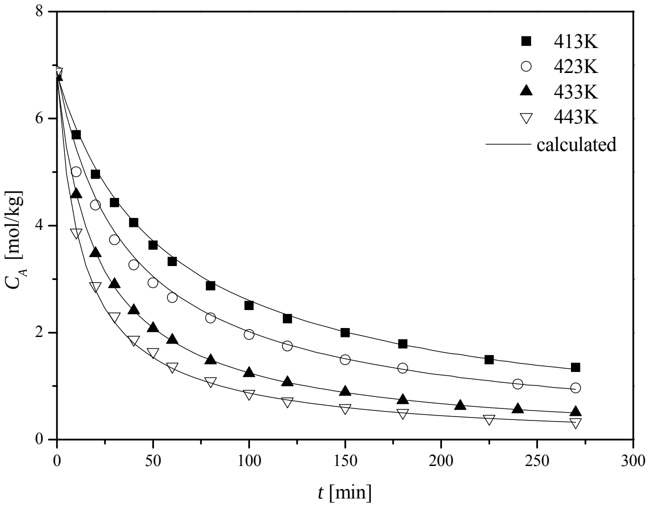

Figure 1 Plots of c_A versus t in the temperature range of 413K-433K

Table 1 Regression coefficients of different temperature

T/K	$10^{3}k$ / $\mathrm{kg^{1.5} \cdot mol^{-1.5} \cdot min^{-1}}$	*AAD*%
413	0.83	1.85%
423	1.28	3.00%
433	2.31	0.83%
443	3.78	2.46%

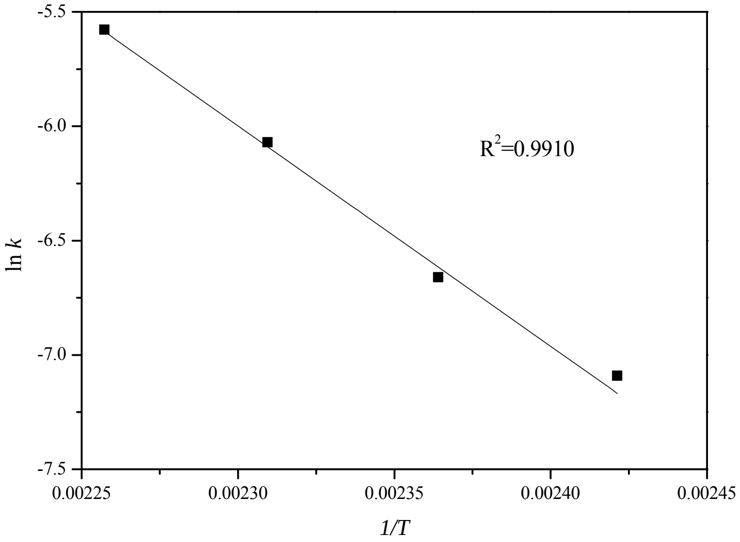

Figure 2 Arrhenius plot with Ti(OBu)$_4$ as catalyst in the temperature range of 413-443K

4.2 Effect of initial molar ratio of reactants

The effect of the initial reactant molar ratio of reactants on the esterification reaction was investigated at various initial 1,6-HD/AA molar ratios (α=1.1, 1.2, 1.5) where the reaction temperature was 433K and the concentration of Ti(OBu)$_4$ was 0.71mmol/kg. The conversion of carboxyl group (X) is calculated from:

$$X = \frac{c_{A0}m_0 - c_A m}{c_{A0}m_0} \tag{22}$$

Substitution of Eq. (8) into Eq. (22), gives:

$$X = \frac{c_{A0} - c_A}{(1 - M_W c_A)c_{A0}} \tag{23}$$

From Eq. (23), we can see that the effect of water removal on the conversion X is described as $\frac{1}{1 - M_W c_A}$.

Assuming that the conversion without consideration of the water removal is X_0, the fractional error between X and X_0 can be expressed as:

$$\delta = \frac{X - X_0}{X_0} = \frac{M_W c_A}{1 - M_W c_A} \tag{24}$$

On the basis of Eq. (24), the error δ is smaller than 1% when the carboxyl group concentration is quiet small ($c_A < 0.55 mol/kg$) , while it is larger than 10% when $c_A > 5.05 mol/kg$. In our experimental scale, the value of c_{A0} ranges from 6.04 to 7.08mol/kg. And the δ value will range from 12.20% to 14.61%, indicating that the water removal should be taken into consideration especially at the initial time.

The relationship of $X \sim t$ for esterification reaction between 1,6-HD and AA is presented in Fig. 3. What can be seen from Fig. 3 is that the X values increases obviously between $\alpha = 1.1$ and $\alpha = 1.2$, while there are few changes on X when $\alpha > 1.2$.

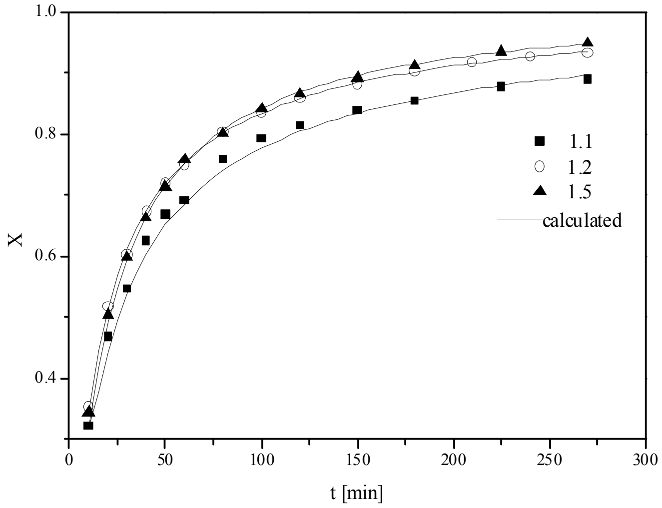

Figure 3 Plots of X versus t at various 1,6-HD/AA molar ratio

4.3 Effect of concentration of $Ti(OBu)_4$

The effect of the concentration of $Ti(OBu)_4$ (c_{C0}) on the esterification reaction was studied (0.36-5.66mmol/kg) under such conditions where $\alpha = 1.2$, $T = 433K$. On the basis of the procedure (Section 3.2), the concentrations of carboxyl groups (c_A) at time t were obtained for different concentration of $Ti(OBu)_4$ (c_{C0}) and shown in Fig. 4 (dots). Using the global optimization method-genetic algorithm procedure, the rate constant (*k*) are obtained and listed in Table 2. Then, the theoretical values of c_A at different time t are calculated and shown in Fig. 4(solid lines). Meanwhile, the *AAD*% values calculated by Eq. (19) are listed in Table 2. From Table 2, the rate constant of the esterification increases with the concentration of $Ti(OBu)_4$ in the range of 0.36-5.66mmol/kg.

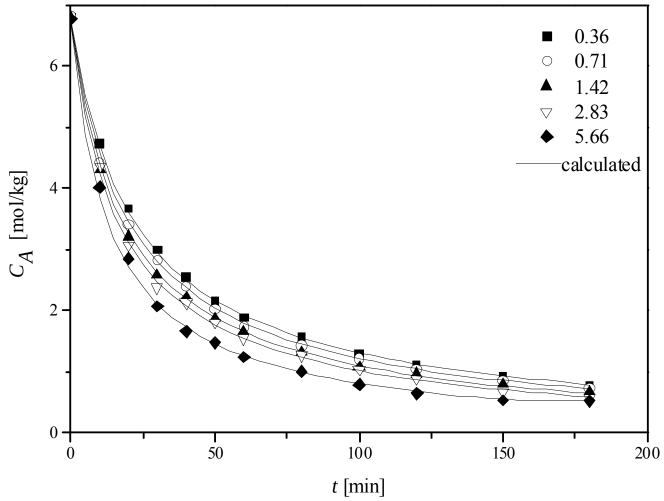

Figure 4 Plots of c_A versus t in the catalyst range of 0.36-5.66mmol/kg

Table 2　Linear Regression coefficients of several catalyst concentration

$c_{C0}\,/\,\mathrm{mmol\cdot kg^{-1}}$	$10^3 k\,/\,\mathrm{kg^{1.5}\cdot mol^{-1.5}\cdot min^{-1}}$	*AAD*%
0.36	2.22	4.01%
0.71	2.31	0.83%
1.42	2.67	1.42%
2.83	2.99	2.49%
5.66	3.71	2.93%

5. FURTHER DISCUSSION ABOUT THE KINETIC MODEL

According to Eq. (1) [4,21], the rate equation here in the presence of $Ti(OBu)_4$ can be rewritten as:

$$-d[COOH]/dt = k[COOH][OH][Cat] \tag{25}$$

When the water removal is taken into consideration, the equation above can be integrated into following form under the condition that $c_A = c_{A0}$ at $t = 0$:

$$kc_{C0}t = \frac{(1-M_W c_{A0})^2}{c_{B0}-c_{A0}}\ln\frac{c_A - M_W c_A c_{B0} + c_{B0} - c_{A0}}{c_A(1-M_W c_{B0})} + M_W(1-M_W c_{A0})\ln\frac{(1-M_W c_A)(1-M_W c_{B0})}{M_W(c_A - M_W c_A c_{B0} + c_{B0} - c_{A0})} - g(c_{A0}) \tag{26}$$

where $g(c_{A0})$ is a constant and can be determined by Eq. (27):

$$g(c_{A0}) = \frac{(1-M_W c_{A0})^2}{c_{B0}-c_{A0}}\ln\frac{c_{B0}(1-M_W c_{A0})}{c_{A0}(1-M_W c_{B0})} + M_W(1-M_W c_{A0})\ln\frac{1-M_W c_{B0}}{M_W c_{B0}} \tag{27}$$

Taking the experimental data (Fig. 5 dots) under the condition of ($\alpha = 1.2$, $T = 433K$, $c_C = 0.71 mmol/kg$) as an example, a fitting curve according to Eq. (26) was obtained and shown in Fig. 5 (solid line) through global optimization method-genetic algorithm procedure. From Fig. 5, the experimental data point are not uniformly distributed on either side of the curve (*AAD*%=15.79%), which means the kinetics model doesn't satisfy the esterification reaction here quiet well.

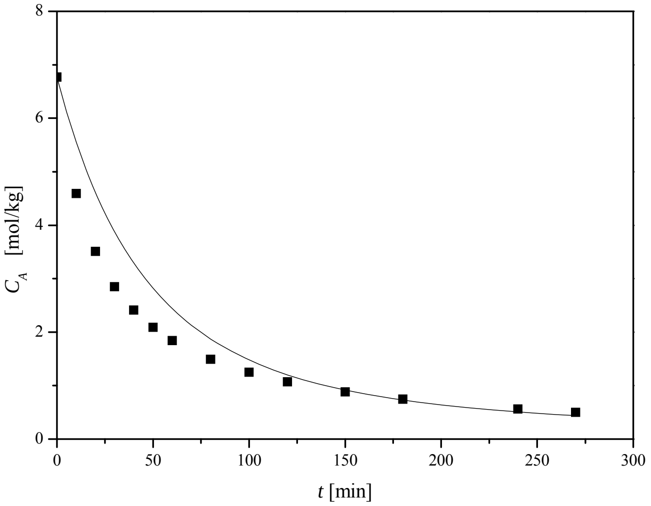

Figure 5 Plot of c_A **versus** t **under the condition of** $\alpha = 1.2$, $T = 433K$, $c_C = 0.71 mmol/kg$

6. CONCLUSION

In this paper, the kinetic data for the esterification for a batch reactor between AA and 1,6-HD catalyzed by $Ti(OBu)_4$ were measured in the temperature range of 413-443K under atmospheric pressure. A kinetic model based on the assumption of 3.5-order reaction was established to fit the kinetic data and the results were compared with those of the model reported in the literature. The results showed that the 3.5-order model is more suitable to the esterification reaction with *AAD*% value being less than 5.0%. The rate constant and the activation energy ($E_a = 80.16 \pm 4.41 kJ / mol$) of the esterification reaction were obtained by this model. The effects of initial 1,6-HD/AA molar ratio (α) and the amount of catalyst on the esterification was also investigated. The results showed that (i) the conversion of carboxyl group increases obviously when the α value increases from 1.1 to 1.2, but it does not change much when the α value is larger than 1.2; and (ii) the rate constant of the esterification increases with the concentration of $Ti(OBu)_4$ in the range of 0.36-5.66mmol/kg.

NOMENCLATURE

AA : adipic acid

1,6-HD : 1,6-hexanediol

$Ti(OBu)_4$: tetrabutyl titanate

c_{A0} : initial concentration of carboxyl group (mol/kg)

c_{B0} : initial concentration of hydroxyl group (mol/kg)

c_{C0} : initial concentration of catalyst (mol/kg)

c_A : concentration of carboxyl group (mol/kg)

c_B :concentration of hydroxyl group (mol/kg)

c_C : concentration of catalyst (mol/kg)

m_0 : initial mass of mixture (kg)

m : mass of mixture (kg)

N_W : moles of water removed (mol)

M_W : molar mass of water (0.018 kg/mol)

k' : rate constant ($\mathrm{kg}^{2.5} \cdot \mathrm{mol}^{-2.5} \cdot \mathrm{min}^{-1}$)

k : rate constant ($\mathrm{kg}^{1.5} \cdot \mathrm{mol}^{-1.5} \cdot \mathrm{min}^{-1}$)

T :reaction temperature (K)

t : reaction time (min)

$c_{Ai}^{\exp}$:experimental concentration of carboxyl group (mol/kg)

c_{Ai}^{cal} :theoretical concentration of carboxyl group (mol/kg)

AAD% : absolute average deviation

E_a : reaction activation energy (kJ/mol)

k_0 : pre-exponential factor

X : conversion of carboxyl group (%)

X_0 : conversion of carboxyl group without consideration of water removal (%)

δ : fractional error between β and β_0 (%)

α : initial1,6-hexanediol/adipic acid molar ratio

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