Mechanism and kinetics of esterification of adipic acid and ethylene glycol by tetrabutyl titanate catalyst

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Abstract−An eight-step mechanism of esterification reaction between adipic acid (AA) and ethylene glycol (EG) catalyzed by tetrabutyl titanate [Ti(OBu)$_4$] was studied in detail. The kinetic data for the esterification reaction between AA and EG catalyzed by tetrabutyl titanate [Ti(OBu)$_4$] were measured in the temperature range of 403 K-433 K. A second-order kinetic model was established, and the model parameters were obtained through an optimization procedure by minimizing the value differences between the simulated component concentrations in the reaction system with the experimental ones. The results demonstrate that the model is suitable for the esterification reaction between AA and EG catalyzed by tetrabutyl titanate [Ti(OBu)$_4$]. Furthermore, the esterification reaction rate increases with the increase of reaction temperature, concentration of catalyst and the initial reactant ratio of EG to AA.

Keywords: Mechanism, Kinetics, Esterification, Adipic Acid, Ethylene Glycol

INTRODUCTION

As one of the main raw materials used in the synthesis of polyurethane, polyethylene glycol adipate (PEA) with molecular weight of 1,000-3,000 g/mol is widely used in the production of flexible or rigid polyurethane foam, polyurethane rubber, polyurethane elastomer and polyurethane adhesive [1,2]. PEA is prepared by the esterification and polycondensation between AA and EG in the presence of catalyst. The polycondensation process will not take place successfully until the esterification ratio reaches a higher level (90%), and the esterification ratio is closely related to the kinetics of esterification reaction, which means it is necessary to investigate the kinetics of esterification reaction in the presence of an appropriate catalyst.

There are some works related to the kinetics of esterification reaction between acid and polyols [3-10]. Chang et al. [11] investigated the synthesis of adipic acid-based polyesters through esterification catalyzed by organotin catalyst. However, organotin is toxic and does serious harm to the human liver, nervous system, endocrine system, skin and mucous membranes; also, it may do damage to the ecological environment [12]. Thus, it is necessary to use a kind of green catalyst instead of organotin. Being characteristic of high catalytic activity, high efficiency, and non-pollution, titanium catalysts [13] can improve the brightness and transparency of polyester and are widely used in catalyzing the esterification reaction between acid and polyols [14,15]. Tian et al. [16] investigated the kinetics of the mono-esterification between terephthalic acid and 1,4-butanediol using tetrabutyl titanate [Ti(OBu)$_4$] as catalyst.

Thus, in this work, tetrabutyl titanate [Ti(OBu)$_4$] was used to cat-alyze the esterification reaction and the reaction mechanism was studied in detail to accurately establish the kinetic model. The reaction kinetics was studied based on a second-order kinetic model. The effects of the reaction temperature, concentration of catalyst and the initial reactant ratio of EG to AA on the kinetics of the esterification reaction were also studied.

REACTION MECHANISM

The esterification between AA and EG catalyzed by [Ti(OBu)$_4$] is assumed as a consecutive reaction. Based on coordination theory [17,18], we may propose the esterification reaction mechanism as shown in Fig. 1, and it is described as follows. First, AA reacts with the catalyst to quickly generate a complex (I) by the coordinate bond between the titanium atom (low electronegativity) in [Ti(OBu)$_4$] and the carbonyl oxygen (high electronegativity) in AA and the hydrogen bond between the hydrogen atom in the carboxyl and the oxygen atom in [Ti(OBu)$_4$]. In the complex (I), the electronegativity of carbonyl carbon reduces due to the electrophilic effect of the coordinate bond, so when it reacts with EG, a new complex (II) is gradually formed by the coordinate bond between the carbonyl carbon and the hydroxyl oxygen in EG and the hydrogen bond between the hydroxyl oxygen in AA and the hydroxyl hydrogen in EG.

Afterwards, the monoester quickly forms via the rearrangement of the coordinate bond and the hydrogen bond in complex II; meanwhile, complex II loses one molecule of water. Finally, the diester forms via the reaction of monoester and EG catalyzed by [Ti(OBu)$_4$] following the same mechanism as above.

KINETICS MODEL

According to the mechanism shown in Fig. 1, the reaction pro-

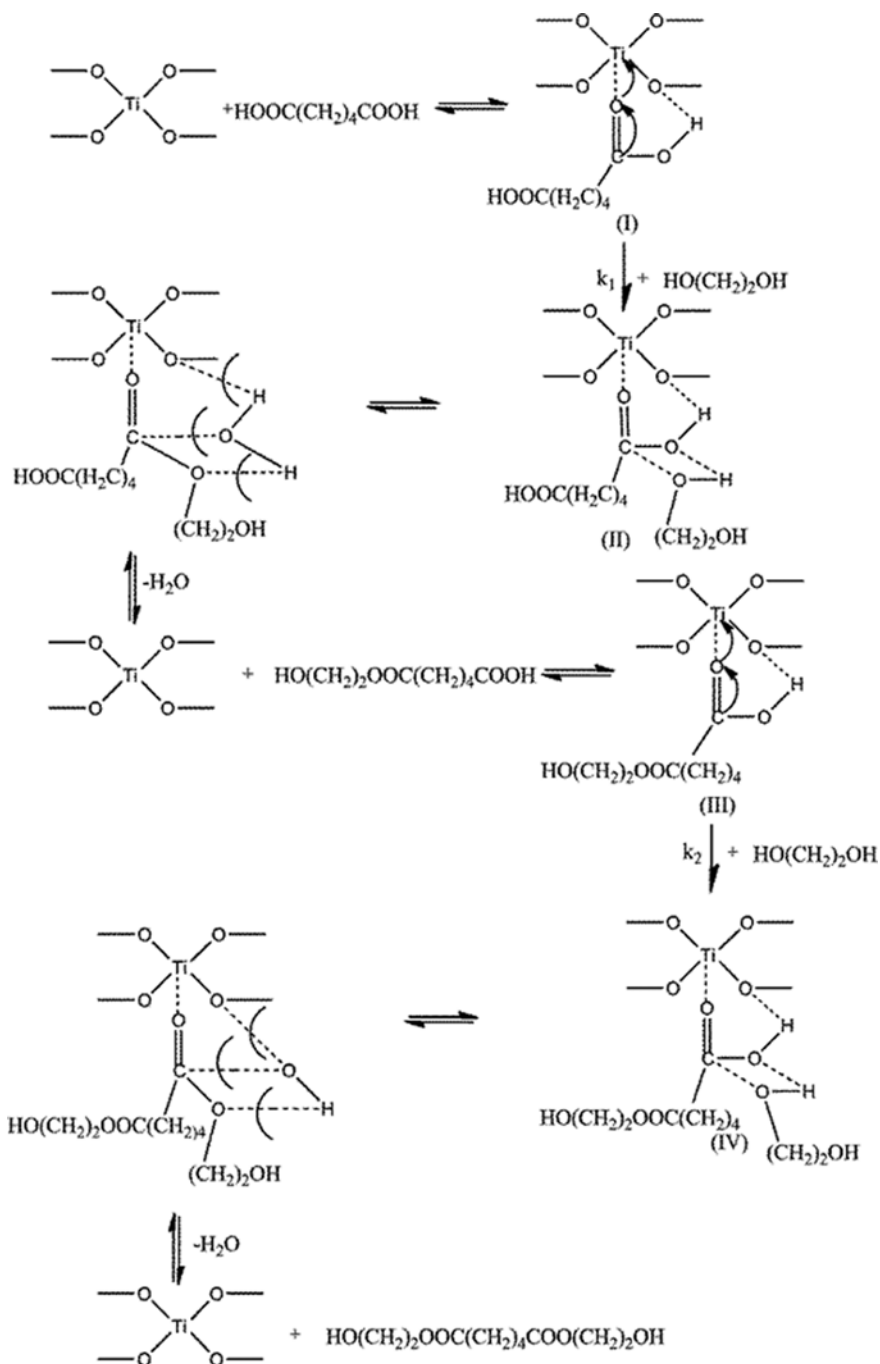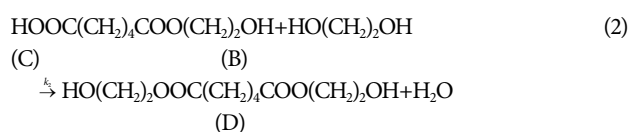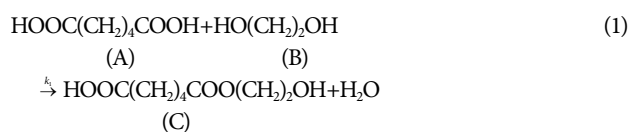[†]To whom correspondence should be addressed.
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Fig. 1. The mechanism of the esterification between AA and EG catalyzed by Ti(OBu)$_4$.

cess can be simplified as follows:

$$HOOC(CH_2)_4COOH + HO(CH_2)_2OH \qquad (1)$$
$$\qquad (A) \qquad\qquad\qquad (B)$$
$$\xrightarrow{k_1} HOOC(CH_2)_4COO(CH_2)_2OH + H_2O$$
$$\qquad\qquad (C)$$

$$HOOC(CH_2)_4COO(CH_2)_2OH + HO(CH_2)_2OH \qquad (2)$$
$$(C) \qquad\qquad\qquad\qquad (B)$$
$$\xrightarrow{k_2} HO(CH_2)_2OOC(CH_2)_4COO(CH_2)_2OH + H_2O$$
$$\qquad\qquad (D)$$

Let C_A, C_B, C_C and C_D (mol/kg) represent the concentration of A, B, C and D in the samples at time t (min) respectively, C_{A0}, C_{B0}, C_{C0} and C_{D0} (mol/kg) represent the initial concentration of A, B, C and D. In addition, k_1 and k_2 are the reaction rate constants.

In this work, as the water produced is removed from the system, we assume the two steps reaction are both second-order reaction and irreversible, then the rate equations are obtained as follows:

$$-dC_A/dt = k_1 C_A C_B \qquad (3)$$

$$-dC_B/dt = k_1 C_A C_B + k_2 C_B C_C \qquad (4)$$

$$dC_C/dt = k_1 C_A C_B - k_2 C_B C_C \tag{5}$$

$$dC_D/dt = k_2 C_B C_C \tag{6}$$

Relating Eq. (3) with Eq. (5), we obtain

$$\frac{-dC_C}{dt} \Big/ \frac{dC_A}{dt} = \frac{k_1 C_A C_B - k_2 C_B C_C}{k_1 C_A C_B} = \frac{k_1 C_A - k_2 C_C}{k_1 C_A} \tag{7}$$

Eq. (7) can be simplified as follows:

$$\frac{dC_C}{dC_A} = \frac{k_2 C_C}{k_1 C_A} - 1 \tag{8}$$

Let $C_C = y C_A$

$$\ln y = \ln C_C - \ln C_A \tag{9}$$

Take the derivation of Eq. (9) with respect to $\ln C_A$, we obtain

$$\frac{1}{y}\frac{dy}{d(\ln C_A)} = \frac{d(\ln C_C)}{d(\ln C_A)} - 1 = \frac{C_A}{C_C}\frac{dC_C}{dC_A} - 1 \tag{10}$$

Combining Eqs. (8), (9) with Eq. (10), we obtain

$$\frac{dy}{d(\ln C_A)} = (K-1)y - 1 \quad \text{and} \quad K = \frac{k_2}{k_1} \tag{11}$$

And its solution is

$$C_C = \frac{C_A}{K-1}\left[1 - \left(\frac{C_A}{C_{A0}}\right)^{K-1}\right] \tag{12}$$

The solution of C_B and C_D can be obtained as follows:

$$C_B = C_{B0} + \frac{C_A}{K-1}\left[2K - 1 - \left(\frac{C_A}{C_{A0}}\right)^{K-1}\right] - 2C_{A0} \tag{13}$$

$$C_D = C_{A0} - \frac{C_A}{K-1}\left[K - \left(\frac{C_A}{C_{A0}}\right)^{K-1}\right] \tag{14}$$

Substitution of Eq. (13) into Eq. (3) gives

$$-dC_A/dt = k_1 C_A\left\{C_{B0} + \frac{C_A}{K-1}\left[2K - 1 - \left(\frac{C_A}{C_{A0}}\right)^{K-1}\right] - 2C_{A0}\right\} \tag{15}$$

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

$$\ln\frac{C_{A0}}{C_A} = \int_0^t k_1\left\{C_{B0} + \frac{C_A}{K-1}\left[2K - 1 - \left(\frac{C_A}{C_{A0}}\right)^{K-1}\right] - 2C_{A0}\right\}dt \tag{16}$$

Eq. (16) can be changed to

$$C_A = C_{A0}e^{-f(t)} \tag{17}$$

where $f(t) = \int_0^t k_1\left\{C_{B0} + \frac{C_A}{K-1}\left[2K - 1 - \left(\frac{C_A}{C_{A0}}\right)^{K-1}\right] - 2C_{A0}\right\}$ and

the integral value of $f(t)$ can be calculated by the Simpson integral method.

Eqs. (17), (13), (12) and (14) can be used to describe the variation of the concentrations of C_A, C_B, C_C and C_D with time and temperature. Hereinafter the applicability of the above four equations will be validated via the experimental data.

Based on a series of experimental data of C_A, C_B, C_C and C_D at time t, the kinetics parameters of the esterification reaction can be determined via global optimization method - genetic algorithm

procedure [19,20] and the objective function is defined as follows:

$$S = \sum_{i=1}^{N}\left[\left|C_{Ai}^{exp} - C_{Ai}^{cal}\right| + \left|C_{Bi}^{exp} - C_{Bi}^{cal}\right| + \left|C_{Ci}^{exp} - C_{Ci}^{cal}\right| + \left|C_{Di}^{exp} - C_{Di}^{cal}\right|\right]^2 \tag{18}$$

where N refers to the number of experimental points, C_{Ai}^{exp}, C_{Bi}^{exp}, C_{Ci}^{exp} and C_{Di}^{exp} are the experimental concentrations, C_{Ai}^{cal}, C_{Bi}^{cal}, C_{Ci}^{cal} and C_{Di}^{cal} are the theoretical concentrations calculated by Eqs. (17), (13), (12) and (14), respectively.

The value of the absolute average deviation (AAD%) is defined as follows:

$$AAD\% = \frac{1}{4N}\left(\sum_{j=1}^{N}\sum_{i=A}^{D}\frac{\left|C_i^{cal} - C_i^{exp}\right|}{C_i^{exp}}\right) \times 100\% \tag{19}$$

where i identifies the components and runs over all components of the mixture (A, B, C, D).

EXPERIMENTAL

1. Reagents

Adipic acid (AA, Sinopharm, ethylene glycol) EG, Wuxi Jani chemical Co. LTD, $Ti(OBu)_4$ (Shanghai Chemical Reagent Co. China), methylbenzene (Yangzi chemical), ethyl alcohol l(Shanghai Xiangling Chemical Co. LTD) were all chemically pure reagents. Ethylene glycol monoester [$HOOC(CH_2)_4COO(CH_2)_2OH$] (99.9%) and ethylene glycol adipate [$HO(CH_2)_2OOC(CH_2)_4COO(CH_2)_2OH$] (99.9%) were prepared by gel filtration chromatography.

2. Experimental Method

The experiments were carried out in a 250 ml flask equipped with a single-blade stirrer (200 rpm), a platinum sensor, a fractionating column allowing the withdrawal of water during the reaction. The reactor was heated with the oil jacket, and the reaction temperature was controlled automatically by adjusting the oil temperature, which was maintained within ±0.5 K.

A known amount (about 20-30 g) of EG and proper amount of (about 0.05-0.15 mg) catalyst ([$Ti(OBu)_4$]) were added into the 250 ml flask and heated to the desired temperature (403 K-433 K). The esterification reaction was started by adding AA (about 60-65 g), which was preheated to the same temperature. The sample was withdrawn from the mixture at each time interval by using a sampling port, and then cooled with ice-water immediately to avoid a further reaction.

3. Analytic Method

The concentration of AA, EG, monoester [$HOOC(CH_2)_4COO(CH_2)_2OH$] and diester [$HO(CH_2)_2OOC(CH_2)_4COO(CH_2)_2OH$] in the samples was determined by a high performance liquid chromatograph (HPLC, Waters-1515, USA) with a refractive index detector. Pinnacle II C_{18} (150 mm×4.6 mm) was used as the column. The optimal operation conditions of HPLC are as follows: flow phase, tetrahydrofuran (A) - potassium dihydrogen phosphate buffer solution (B) (40 : 60); flow rate, 0.6 ml/min; column temperature, 40 °C.

RESULTS AND DISCUSSION

1. Effect of Temperature

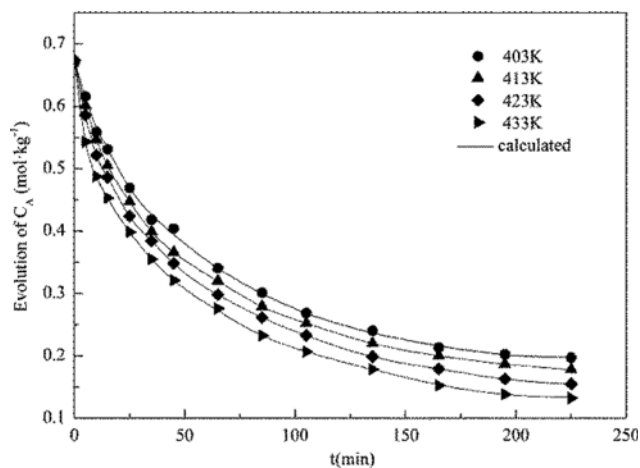The effect of the temperature on the esterification reaction rate

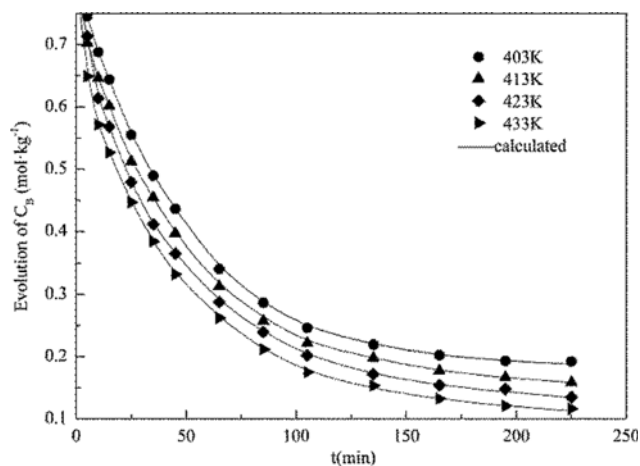**Fig. 2. Evolution of experimental and simulated concentrations of C_A.**

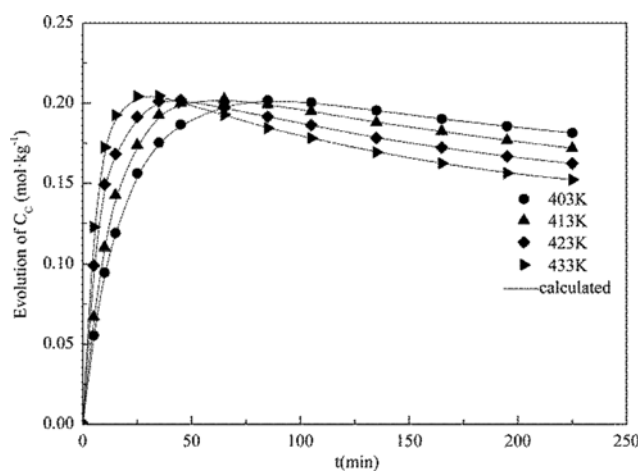**Fig. 3. Evolution of experimental and simulated concentrations of C_B.**

Fig. 4. Evolution of experimental and simulated concentrations of C_C.
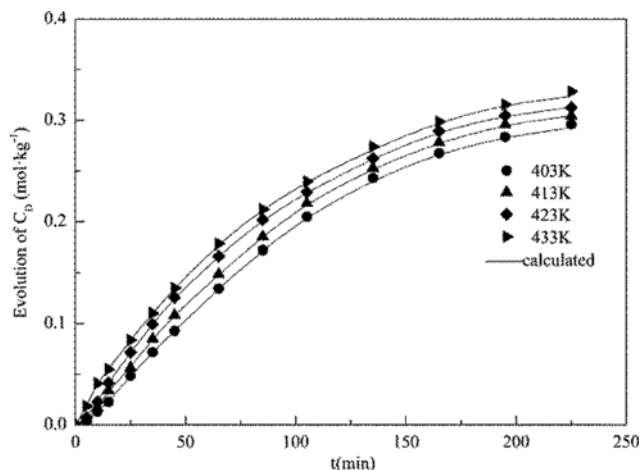

Fig. 5. Evolution of experimental and simulated concentrations of C_D.

Table 1. The regression parameters values of different reaction temperature

T/K	$k_1 \times 100$	$k_2 \times 100$	AAD
	$kg \cdot mol^{-1} \cdot min^{-1}$	$kg \cdot mol^{-1} \cdot min^{-1}$	%
403	0.533	0.782	4.13
413	0.692	0.951	3.07
423	0.873	1.091	2.36
433	1.062	1.256	2.58

perature range of 403-433 K. The experimental concentration variations of components with time are shown in Figs. 2-5. Substituting the experimental data and the theoretical concentrations calculated by Eqs. (12), (13), (14) and (17) into Eq. (18), the values of the kinetic constants (k_1 and k_2) were estimated by global optimization method - genetic algorithm procedure (Roulette wheel selection; crossover operator: 0.8; mutation operator: 0.001) [19,20] and listed in Table 1. The comparisons between the experimental data with theoretical ones are also shown in Figs. 2-5, from which it may be seen that the obtained agreement is generally satisfactory. From Table 1, it is clear that all values of absolute average deviation (AAD%) are less than 5%, suggesting that the esterification reaction between AA and EG catalyzed by [Ti(OBu)$_4$] is a second-order reaction.

Based on Table 1, it is clear that the reaction rate increases with the increase of the temperature. The reason is that the collision probability between the molecules is larger due to the higher energy of the reactant molecules at a higher temperature. Besides, we can find that the value of k_1 is less than k_2, indicating that the first step is the rate-limiting step in the whole series reaction.

By plotting $1/T$ *vs* $-\ln k$, we can correlate the rate constant with the temperature as shown in Fig. 6, and the results show a linear relationship between $-\ln k$ and $1/T$. Thus, the fitting equations (R^2=0.997, 0.992) can be obtained as follows:

$$\ln k_1 = 4.7885 - 4037.1/T \tag{20}$$
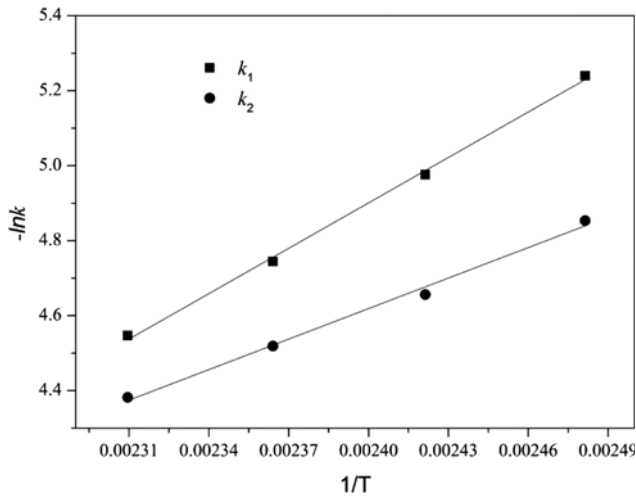
$$\ln k_2 = 1.8920 - 2712.9/T \tag{21}$$

of EG/AA catalyzed by [Ti(OBu)$_4$] (0.023 mol/kg) was studied at a specified initial reactant molar ratio ($\beta = C_{B0}/C_{A0}$=1.2) in the tem-

Fig. 6. Arrhenius plots for esterification of AA with EG catalyzed by [Ti(OBu)$_4$] in the temperature range of 403-433 K (β=1.2, $C_{Ti(OBu)4}$=0.023 mol/kg).

Table 2. Activation energy and preexponential factor

Reaction step	E$_a$	k$_0$
	kJ·mol^{-1}	kg·mol^{-1}·min^{-1}
1	33.56	120.12
2	22.56	6.63

Table 3. The regression parameters of different concentration catalyst at 413 K

Concentration	k$_1$×100	k$_2$×100	AAD
mol/kg	kg·mol^{-1}·min^{-1}	kg·mol^{-1}·min^{-1}	%
0.023	0.692	0.951	2.51
0.046	0.792	1.181	3.69
0.069	0.874	1.317	3.49
0.092	0.891	1.324	3.44

Based on the Arrhenius Equation, the values of E$_a$ and k$_0$ for the reaction can be obtained and listed in Table 2. From Table 2, the activation energy of the first step is higher than the second step, indicating that the reaction of AA to the monoester (HOOC(CH$_2$)$_4$COO(CH$_2$)$_2$OH) is more sensitive to the temperature variation. Besides, the activation energy (33.56 kJ/mol) is lower than that of autocatalytic reaction (56 kJ/mol) [21] between AA and EG, indicating that [Ti(OBu)$_4$] can greatly reduce the activation energy of the esterification reaction between AA and EG.

2. Effect of Concentration of Catalyst

The catalyst [Ti(OBu)$_4$] was used at four different concentration (mol/kg) levels of 0.023, 0.046, 0.069, 0.092 to investigate the effect of catalyst concentration on the reaction rate constant of (β=1.2) at 413 K. Relating the experimental data to the kinetic model, the reaction rate constants (k$_1$, k$_2$) and AAD were obtained and listed in Table 3, suggesting that the reaction rate constants increase with the increase of catalyst concentration up to about 0.07 mol/kg, and then tend to level off. The reason could be the saturation of the
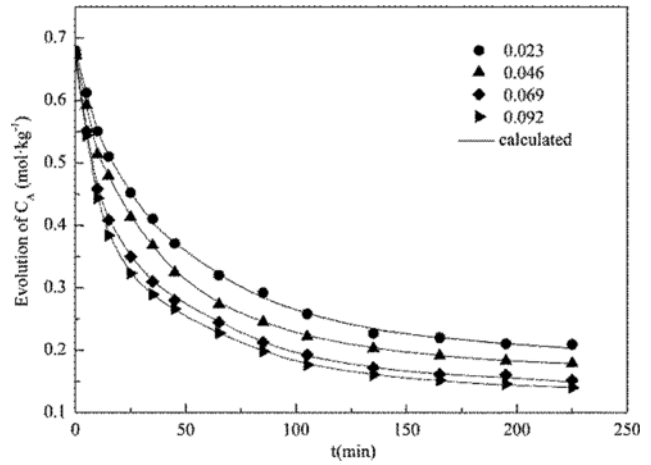

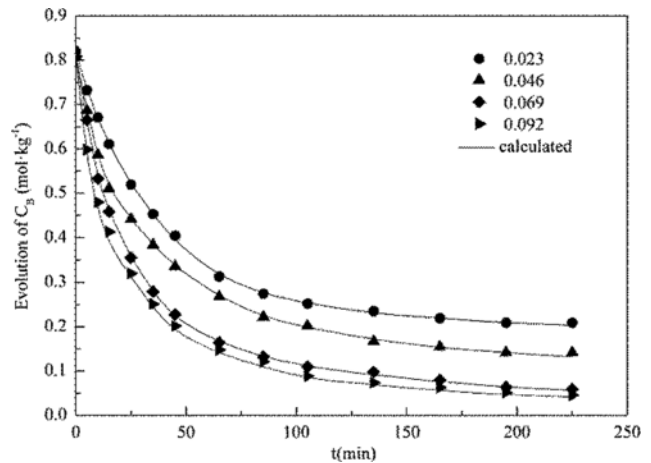Fig. 7. Evolution of experimental and simulated concentrations of C$_A$.

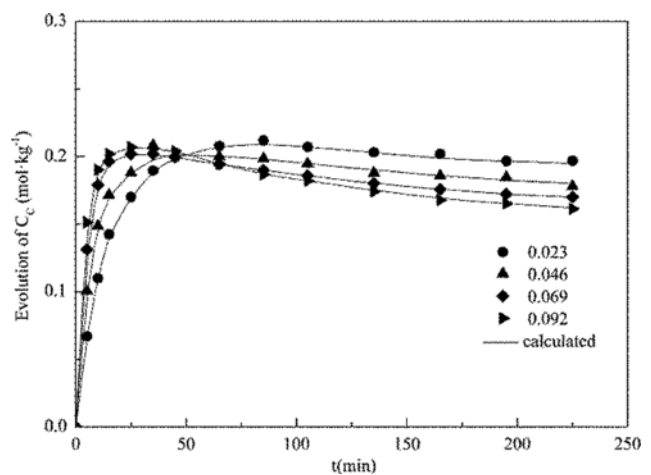Fig. 8. Evolution of experimental and simulated concentrations of C$_B$.

Fig. 9. Evolution of experimental and simulated concentrations of C$_C$.

solution with catalyst particles. From Table 3, it is clear that all values of AAD are less than 4%; the comparisons between the exper-
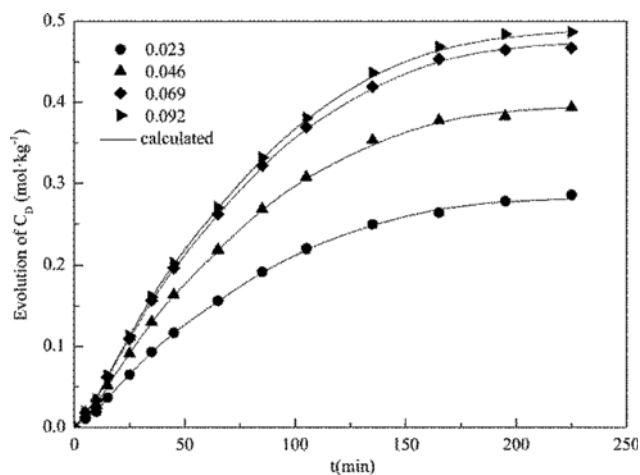
Fig. 10. Evolution of experimental and simulated concentrations of C_D.

imental data (C_i vs t) with theoretical ones are shown in Figs. 7-10, indicating that the kinetic model proposed here retains a level of process description detailed enough to characterize the evolution of product concentrations when changing the catalyst concentration within a relatively wide range.

3. Effect of Initial Reactant Molar Ratio

The experiments were carried out with four different initial molar ratios of EG to AA (β=1.1, 1.3, 1.5, 1.7) to investigate the effect of initial molar ratio of EG to AA on the kinetics of the esterification reaction when the reaction conditions were as follows: reaction temperature 413 K, $C_{Ti(OBu)4}$=0.069 mol/kg. The experimental values of the conversion of AA are shown in Fig. 11 (points), where the conversion of AA at the same time increases with the increase of β, indicating that the reaction rate increases with the increase of β.

Based on the fundamentals of chemical reaction engineering, when the reaction temperature and the concentration of catalyst remain constant, the reaction rate constants are the same for dif-
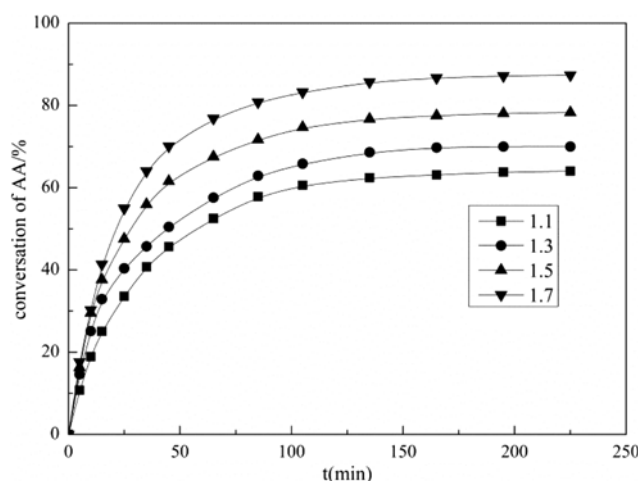
ferent initial reactant molar ratio, so the reaction rate constant (k_1, k_2) here can be obtained from Table 3 (k_1=0.874 kg·mol^{-1}·min^{-1}, k_2=1.317 kg·mol^{-1}·min^{-1}). Then the time evolution of conversion of AA can be predicted based on Eq. (17) and shown in Fig. 11 (solids). From Fig. 11, the predicted conversion of AA is generally consistent with the experimental ones (AAD: 1.16%, 1.13%, 1.72%, 1.45%), indicating that when changing the initial reactant ratio of EG to AA within a relatively wide range, the kinetic model proposed here retains a level of process description detailed enough to characterize the evolution of product concentrations.

CONCLUSIONS

The kinetics of AA/EG esterification reaction was studied. The reaction pathway, which includes two reactions in series, can exactly describe the reaction process. A second-order kinetic model was established to describe the variation of the component concentration with time. Based on the kinetics data obtained, the reaction rate constants and the activation energy of the two steps in the temperature range of 403 K-433 K were determined and discussed. The results show that the kinetic model is suitable for the reaction, and the values of AAD% are all less than 5%. It was concluded that the first step is more sensitive to the change of the temperature.

The effects of the concentration of catalyst and the initial reactant molar ratio of EG to AA on the kinetics of the esterification reaction were studied. It was found that the reaction rate constant increases with the concentration of catalyst, especially at a low level.

NOMENCLATURE

PEA : polyethylene glycol adipate
AA : adipic acid
EG : ethylene glycol
C_A : concentration of adipic acid [mol/kg]
C_{A0} : initial concentration of adipic acid [mol/kg]
C_B : concentration of ethylene glycol [mol/kg]
C_{B0} : concentration of ethylene glycol [mol/kg]
C_C : concentration of monoester [mol/kg]
C_{C0} : concentration of monoester [mol/kg]
C_D : concentration of diester [mol/kg]
C_{D0} : concentration of diester [mol/kg]
$C_{Ti(OBu)4}$: concentration of catalyst [mol/kg]
AAD : absolute average deviation [%]
t : reaction time [min]
T : reaction temperature [K]
k_1, k_2 : reaction rate constant [kg·mol^{-1}/min]
k_0 : preexponential factor
E_a : activation energy [kJ/mol]
β : initial reactant molar ratio of EG to AA

Fig. 11. Plots for conversion of AA vs reaction time (t) with different β (413 K, $C_{Ti(OBu)4}$=0.069 mol/kg).

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