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Kinetics of polyvinyl butyral hydrolysis in ethanol/water solutions

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Abstract−The hydrolysis kinetics of polyvinyl butyral (PVB) was studied in ethanol/water mixed solvents in the temperature range of 339.15-355.15 K, and a three-step hypothesis was proposed to describe the hydrolysis process. The influences of stirring speed, ethanol content and temperature on the hydrolysis of PVB were investigated, and an induction period (IP) phenomenon was found in the process of PVB hydrolysis. The ethanol content in the mixed solvents has a great influence on IP, which is due to the formation of the two kinds of water-ethanol clusters in the system. Temperature influences the IP by changing the catalytic activity of hydroxylamine hydrochloride (HH) on the hydrolysis of PVB. The shrinking core models with three controlling steps were used to fit the kinetic data, and the results indicate that the model controlled by chemical reaction is suitable to describe the kinetic behavior of PVB hydrolysis.

Keywords: Kinetics, Polyvinyl Butyral, Induction Period, Water-ethanol Clusters, Shrinking Core Model

INTRODUCTION

Polyvinyl butyral (PVB), which is an important ingredient of the interlayer material of laminated glass, has been expensively used in the field of automobiles, architecture, aerospace and photovoltaic cells, due to its high adhesion, sound insulation, UV protection, and excellent mechanical properties [1-5]. In recent years, PVB has attracted widespread attention in chemical engineering because of its growing applications in nanofibers [6,7], ultrafiltration membranes [8,9] and protective coatings [10,11]. Acetalization degree (AD) is one of the important quality indicators to measure the application performance of PVB resin [12]. It can be determined by hydroxylamine hydrochloride (HH) method, titrating the hydrochloric acid (HCl) produced from the reaction of HH and n-butanal, the hydrolysis product of PVB [13]. Obviously, the hydrolysis reaction kinetics plays an important role in the optimization of the test method of AD, but most of the existing research on PVB focuses on the synthesis and application, and rarely on the hydrolysis. Therefore, it is necessary to carry out some research to fill the gaps in this area.

Under acidic condition, the hydrolysis of PVB is the reverse process of the synthesis, which is similar to that of the small molecule acetals [14-16]. However, there is a huge difference in the hydrolysis kinetic model between them, which is owing to the special dissolution phenomenon of PVB. PVB is a high molecular weight nonionic polymer composed of acetal groups (AG), hydroxyl groups and a small amount of acetate groups, but it cannot be dissolved well in ethanol/water mixed solvents during the whole hydrolysis process. Since, the molecular chains of PVB cannot stretch freely in the mixed solvents and a number of nearly spherical coils will be formed [17,18]. The hydrolysis of acetal groups proceeds layer by layer from the outer to the inner of the PVB coil, which is similar to the process of grafting reaction of walnut shell [19]. Therefore, the shrinking core models controlled by external diffusion, internal diffusion, and chemical reaction are very suitable to describe the kinetics of PVB hydrolysis [20,21].

In this paper, the hydrolysis reaction of PVB was performed in ethanol/water mixed solvents with the presence of HH, and the influence of stirring speed, ethanol content in mixed solvents (x_e) and temperature (T) on the hydrolysis of PVB was studied. The kinetic experimental data of PVB hydrolysis were determined within the temperature range of 339.15-355.15 K, and they were fitted by the shrinking core models with three controlling steps.

EXPERIMENT

1. Reagents

The reagents used in this work were PVB (M.W. 40,000-70,000, acetalization degree (AD)=80%, Shanghai Aladdin Biochemical Technology Co., Ltd.), HH (98.5%, Shanghai Titan Scientific Co., Ltd.), ethanol (99.5%, Shanghai Macklin Biochemical Co. Ltd.), n-butanal (98.0%, Shanghai Macklin Biochemical Co., Ltd.). and Sodium hydroxide (97.0%, Shanghai Aladdin Biochemical Technology Co., Ltd.). The bromophenol blue indicator solution used in the titration was prepared by the laboratory.

2. Kinetic Experiment

The hydrolysis reaction of PVB was conducted in a 250-mL three-neck flask equipped with a condenser, a stirrer and a mercury thermometer. First, a certain amount of PVB was added to the flask containing a certain volume of ethanol and heated to dissolve it under vigorous stirring. When the temperature reached the preset value, a certain volume of HH aqueous solution (the molar ratio of HH to theoretical acetal groups: n_{HH}/n_{AG}=15 mol/mol, determined by the preliminary experiment shown in the Supporting Informa-

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tion) was added to the above solution, and the hydrolysis reaction was timed from then on. Samples were taken out in specific intervals by the injector and were titrated by standard sodium hydroxide solution with the addition of bromophenol blue indicator. In all experiments, the ratio of the feeding amount of PVB to the total volume of ethanol/water mixed solvents (w/V) was fixed as 0.678 g/100 mL. The hydrolysis conversion rate of PVB can be calculated according to Eq. (1):

$$Y(\%)=\frac{0.142\times V\times C_{NaOH}\times m_t}{m_{PVB}\times AD\%\times m_i}\times 100\% \quad (1)$$

where m_t, m_{PVB} and m_i are the mass of the total system, PVB feeding and the sample taken out, respectively (g); C_{NaOH} is the concentration of sodium hydroxide (mol mL^{-1}); V is the volume of sodium hydroxide solution consumed by samples taken out (mL) and AD% refers to the acetalization degree of PVB.

The above procedures were repeated at different temperatures (339.15 K, 344.15 K, 349.15 K, 355.15 K) with other reaction conditions fixed, and the kinetic experimental data of the hydrolysis of PVB were obtained.

3. Characterization

After the hydrolysis reaction was completed, 5 mL of the solution was taken out, then 20 mL of ethanol was added to it to precipitate the end product, PVA. The solids were centrifugally separated, washed and dried. Finally, the solid samples were characterized by Fourier transform infrared spectroscopy (FTIR), and the difference in peaks of PVA and PVB was analyzed as follows.

As shown in Fig. 1, PVA and PVB have several common vibration absorption peaks: a relatively strong absorption peak of -OH appears near 3,311 cm^{-1} in the spectrum of PVA and PVB, indicating that both of them contain -OH. However, the peak intensity of -OH at 3,311 cm^{-1} of PVA is much stronger than that of PVB at 3,486 cm^{-1}, which is caused by the hydrolysis of acetal groups in the PVB molecules. The two absorption peaks at 2,950 cm^{-1} and 2,902 cm^{-1} are attributed to the stretching vibration of C-H, and the intensity of the two peaks in the PVA spectrum is weaker than that in PVB, which may be because the acetal groups in PVB contain a large amount of C-H. The weak peak appearing at 1,716 cm^{-1} is the stretching vibration of C=O of acetate group. There are two peaks at 1,144 cm^{-1} and 998 cm^{-1} in the PVB spectrum assigned to the asymmetric and symmetric stretching vibration of C-O-C of acetal groups, while they do not appear in PVA spectrum, confirming that almost all acetal groups in PVB have been hydrolyzed [13].

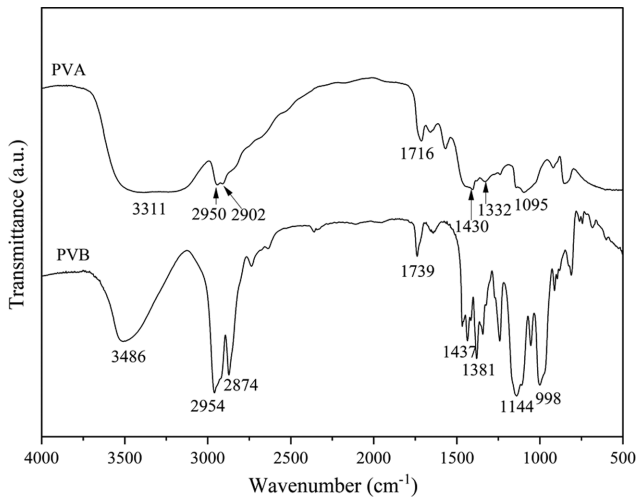

Fig. 1. FTIR spectrum of PVB and the end hydrolyzed product, PVA (T=355.15 K, stirring speed: 400 rpm, x_e=0.4339, w/V=0.678 g/100 mL and n_{HH}/n_{AG}=15 mol/mol).

HYDROLYSIS MECHANISM and KINETIC MODEL

1. Hydrolysis Mechanism

AD of PVB is usually determined by hydroxylamine hydrochloride (HH) method, titrating the HCl produced by the reaction of HH and n-butanal with the sodium hydroxide solution. Preliminary experiments were carried out to study the role of HH in the hydrolysis of PVB and the details are given in Supporting Information. The results show that without adding HH in advance, PVB did not hydrolyze even if it was kept at high temperature for a long time. The reason may be that the hydrolysis reaction of PVB occurs under acidic condition, and the H^+ released from HH can promote the hydrolysis of PVB. It can be concluded that HH can not only react with n-butanal producted by PVB hydrolysis, but also play a catalytic role in the hydrolysis reaction.

Here, we propose a hypothetical reaction mechanism of PVB hydrolysis based on its synthesis reaction mechanism [22] and the hydrolysis mechanism of aliphatic acetals [14-16]. The detailed multistep hydrolysis mechanism of an acetal unit (i) is shown in Fig. 2, and it is described as follows. First, the oxygen atom on the acetal

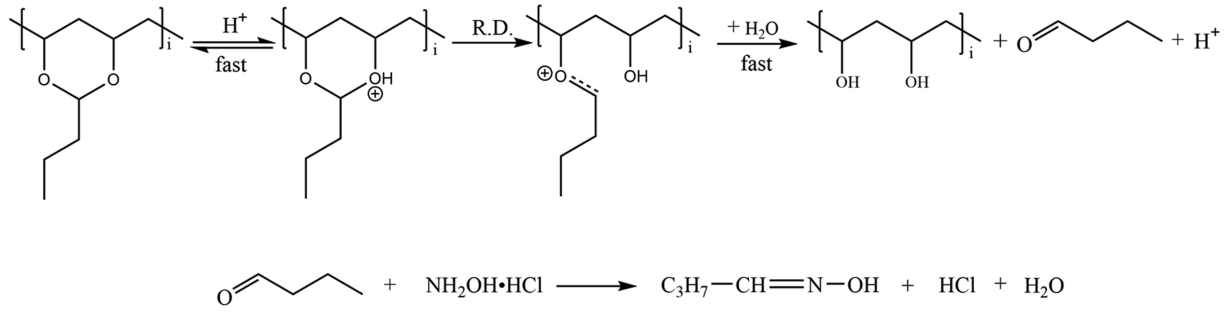

Fig. 2. Reaction mechanism of PVB hydrolysis.

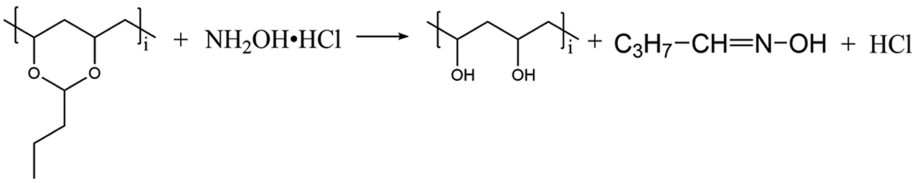

Fig. 3. Overall reaction of PVB hydrolysis.

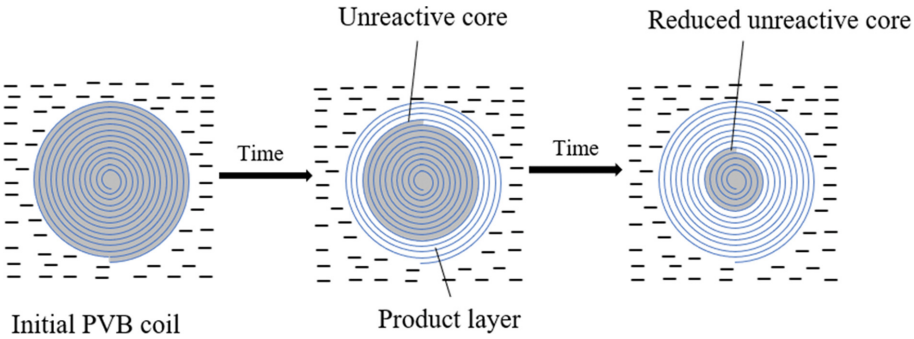

Fig. 4. Shrinking core model assumed for the hydrolysis of PVB.

ring is attacked by H^+ released from HH, and electropositivity of the carbonyl carbon is enhanced by the protonated oxygen atom. Subsequently, the carbon-oxygen bond between them breaks and the hemiacetal group is formed. Finally, the nucleophilic addition reaction takes place between the carbon-oxygen bond and a water molecule, and n-butanal leaves the PVB molecule, then it quickly reacts with HH to generate HCl (verified in the Supporting Information).

As shown in Fig. 3, water has been offset in the overall reaction formula and does not appear as a reactant, but it is still an important component in the hydrolysis reaction of PVB. According to Fig. 3 and the above hydrolysis mechanism, 1 mol acetal unit can react with 1 mol HH, so the reaction of PVB hydrolysis can be simplified as:

$$A + B \rightarrow \text{product} \tag{2}$$

where A is a molecule of HH and B is a acetal unit.

2. Kinetic Model

PVB is easily soluble in ethanol and insoluble in water, while its final hydrolysate polyvinyl alcohol (PVA) is more soluble in water than ethanol. Therefore, it is suitable to select the mixture of ethanol and water as the solvent in the kinetic experiments of PVB hydrolysis. As the hydrolysis reaction proceeds, the ratio of the acetal group and the hydroxyl group on PVB molecules is constantly changing, but these high polymer molecules cannot be dissolved well in the mixed solvents all the time. The molecular chains cannot stretch freely, and they always exist in the form of nearly spherical coils. In the process of PVB hydrolysis, the acetal groups on the molecular chain fall off after being hydrolyzed, and product layer is formed with the coil shape unchanged. According to pre-experiment (Supporting Information), the rate of the reaction between n-butanal and HH is very fast; thus, the reaction between acetal groups and H_2O catalyzed by H^+ can represent the chemical reaction on the outer surface of the coil. Therefore, macrodynamic process of PVB hydrolysis can be simply described as follows:

1. External diffusion: H_2O molecules and H^+ released from HH diffuse from the liquid phase through the liquid film to the outer surface of the PVB coil.

2. Surface chemical reaction: Once they reach the outer surface of PVB coil, H_2O molecules react with the acetal groups on it under the catalysis of H^+ and a product layer will be formed.

3. Internal diffusion: H_2O molecules and H^+ diffuse through the product layer onto the surface of the unreacted core and react with acetal groups on it.

As the hydrolysis reaction proceeds, the product layer gradually increases and the unreacted core becomes smaller until the end of the hydrolysis. Therefore, it can be assumed that the hydrolysis of PVB starts from the outer layer of the PVB coil and gradually advances to the center, which can be described by the shrinking core models shown in Fig. 4. The hydrolysis rate of PVB depends on the sum of the above three steps of external diffusion, internal diffusion and surface reaction. To quantitatively describe the hydrolysis reaction kinetics of PVB, it could be regarded that the hydrolysis rate of PVB is determined by only one of the above three steps. The three kinetic models are discussed in detail in the following sections.

2-1. Model Controlled by External Diffusion

The hydrolysis process of PVB controlled by external diffusion means that the internal diffusion resistance is negligible and the rate of chemical reaction is very fast. In this case, the concentration of component A (Eq. (2)) on the surface of the spherical coil could be regarded as zero. The mass transfer rate of component A during the reaction can be defined as [23]

$$-\frac{dN_A}{dt} = 4\pi r_0^2 k_l C_{Ab} \tag{3}$$

where r_0 is initial coil radius, k_l is the mass transfer coefficient, and C_{Ab} is the concentration of component A in the bulk liquid phase.

If the feeding amount of A far exceeds that of B, C_{Ab} could be considered as a constant. Assuming that the molar density of the PVB coil is ρ (mol m^{-3}), the decrease of component B is manifested as the decrease of unreacted core (r_c). So, the reaction rate of component B can be expressed as [21]

$$-\frac{dN_B}{dt}=-4\pi\rho r_c^2\frac{dr_c}{dt} \tag{4}$$

Based on Eq. (2), the stoichiometric relationship will be

$$-\frac{dN_A}{dt}=-\frac{dN_B}{dt} \tag{5}$$

Substituting Eqs. (3) and (4) into Eq. (5) gives

$$-r_c^2\frac{dr_c}{dt}=\frac{r_0^2k_lC_{Ab}}{\rho} \tag{6}$$

Integrating Eq. (6) under the condition of $r_c=r_0$ at t=0 leads to

$$t=\frac{\rho r_0}{3k_lC_{Ab}}\left[1-\left(\frac{r_c}{r_0}\right)^3\right] \tag{7}$$

While the hydrolysis conversion fraction of PVB can be defined as [20]

$$Y=1-\left(\frac{r_c}{r_0}\right)^3 \tag{8}$$

So, Eq. (7) can be simplified to

$$Y=k_{ED}t \tag{9}$$

in which

$$k_{ED}=\frac{3k_lC_{Ab}}{\rho r_0} \tag{10}$$

2-2. Model Controlled by Internal Diffusion (Product Layer)

Internal diffusion can be regard as the rate-controlling step of PVB hydrolysis, if the external diffusion resistance is very small and the rate of chemical reaction is fast. During the reaction process, both the liquid phase component A and the reaction surface are moving to the center of the spherical coil, and the transfer speed of reactant A is much faster than the moving speed of the reaction surface in this case. Therefore, in a short time, the reaction surface can be approximately regarded as static, and the transfer rate of component A can be regarded as constant:

$$-\frac{dN_A}{dt}=4\pi r^2D_A\frac{dC_A}{dr}=\text{constant} \tag{11}$$

where D_A is the diffusion coefficient in the product layer of PVB coil.

Integrating Eq. (11) under the condition that $r=r_0$, $C_A=C_{Ab}$, and $r=r_c$, $C_A=0$, we get

$$-\frac{dN_A}{dt}\left(\frac{1}{r_c}-\frac{1}{r_0}\right)=4\pi D_AC_{Ab} \tag{12}$$

Substituting Eqs. (4) and (5) into Eq. (12), and integrating it based on the condition of $r_c=r_0$ at t=0 gives

$$t=\frac{\rho r_0^2}{6D_AC_{Ab}}\left[1-3\left(\frac{r_c}{r_0}\right)^2+2\left(\frac{r_c}{r_0}\right)^3\right] \tag{13}$$

From Eq. (8), Eq. (13) can be simplified

$$k_{ID}t=\left[1-3(1-Y)^{\frac{2}{3}}+2(1-Y)\right] \tag{14}$$

in which

$$k_{ID}=\frac{6D_AC_{Ab}}{\rho r_0^2} \tag{15}$$

2-3. Model Controlled by Chemical Reaction

If the hydrolysis process is controlled by a chemical reaction, the internal diffusion and external diffusion can be ignored. The hydrolysis reaction rate of PVB is represented by the number of acetal groups which is proportional to the surface area of the unreacted core, thus

$$-\frac{dN_A}{dt}=-\frac{dN_B}{dt}=4\pi r_c^2kC_{Ab} \tag{16}$$

Replacing Eq. (4) into Eq. (16) gives

$$-4\pi\rho r_c^2\frac{dr_c}{dt}=4\pi r_c^2kC_{Ab} \tag{17}$$

Integrate Eq. (17) based on the condition $r_c=r_0$ at t=0, we can get

$$t=\frac{\rho}{kC_{Ab}}(r_0-r_c) \tag{18}$$

Substituting Eq. (8) into Eq. (18) gives

$$k_Rt=\left[1-(1-Y)^{\frac{1}{3}}\right] \tag{19}$$

in which

$$k_R=\frac{kC_{Ab}}{\rho r_0} \tag{20}$$

According to the experimental data at different temperatures, the kinetics parameters (k_{ED}, k_{ID}, k_R) of Eqs. (9), (14), and (19) can be calculated by the least-squares method and the objective function is expressed as Eq. (21):

$$S=\sum_{i=1}^{N}(Y_i^{exp}-Y_i^{cal})^2 \tag{21}$$

where N is the number of experimental points, Y_i^{exp} refers to experimental data, Y_i^{cal} is the theoretical conversion rate calculated by Eqs. (9), (14), and (19), respectively.

RESULTS AND DISCUSSION

1. Influence of Stirring Speed

The influence of stirring speed on the hydrolysis of PVB was investigated in the range of 200 rpm to 600 rpm, and other experimental parameters were fixed as follows: T=355.15 K, x_e=0.4339, w/V=0.678 g/100 mL and n_{HH}/n_{AG}=15 mol/mol. As the experimental results show in Fig. 5, the hydrolysis conversion rate of PVB increases significantly from 200 rpm to 400 rpm, while the hydrolysis conversion rate at 600 rpm is almost the same as that at 400 rpm. The possible reason for this phenomenon could be as fol-

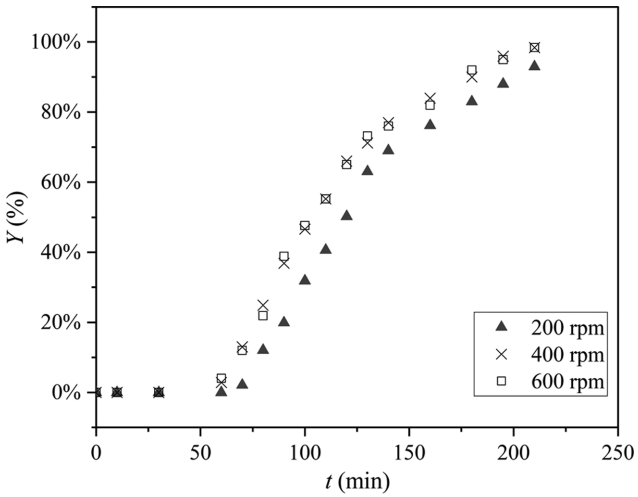

Fig. 5. The influence of stirring speed on the hydrolysis of PVB (T=355.15 K, x_e=0.4339, w/V=0.678 g/100 mL and n_{HH}/n_{AG}=15 mol/mol).

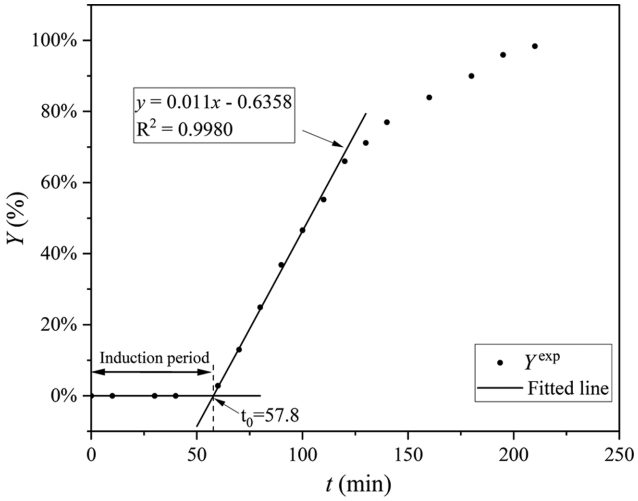

Fig. 6. Calculation of duration of IP (T=355.15 K, stirring speed: 400 rpm, x_e=0.4339, w/V=0.678 g/100 mL and n_{HH}/n_{AG}=15 mol/mol).

lows. At a low stirring speed, increasing the stirring speed will promote the hydrolysis of PVB by increasing the mass diffusion rate of the reactants in the liquid phase. When the stirring speed exceeds 400 rpm, the external diffusion resistance basically disappears and the stirring speed no longer affects the rate of hydrolysis. All the subsequent experiments were carried out at 400 rpm.

As shown in Fig. 5, an interesting induction period (IP) phenomenon was found in the hydrolysis reaction of PVB. IP represents a critical time when PVB really begins to hydrolyze. To quantify the IP [24,25], the tangent method is used to calculate the duration of IP, t_0, which is the x-coordinate of the intersection point of the line of x=0 and the straight line fitted with the first three points after PVB starts to hydrolyze (Fig. 6).

2. Influence of Ethanol Content

The experiment of PVB hydrolysis in pure water was performed

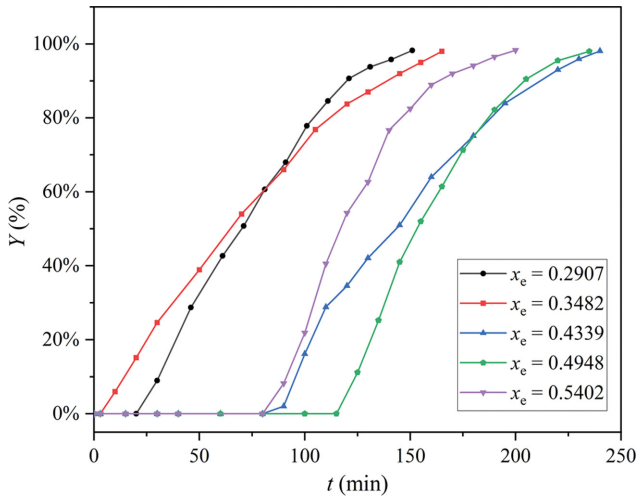

Fig. 7. Influence of ethanol content on PVB hydrolysis (T=353.15 K, stirring speed: 400 rpm, w/V=0.678 g/100 mL and n_{HH}/n_{AG}=15 mol/mol).

Table 1. The duration of IP (t_0) in ethanol/water mixed solvents with different ethanol content

x_e	t_0 (min)
0.2907	21.9
0.3482	3.7
0.4339	88.4
0.4948	117.9
0.5402	85.3

Reaction conditions: T=353.15 K, stirring speed: 400 rpm, w/V=0.678 g/100 mL and n_{HH}/n_{AG}=15 mol/mol

(Supporting Information), and the result indicates that PVB is difficult to hydrolyze in pure water. Therefore, it is suitable to select the mixture of ethanol and water as the solvent in the kinetic experiments of PVB hydrolysis. Experiments were performed to investigate the influence of the ethanol content on PVB hydrolysis within the range of 0.2907-0.5402, while the other parameters were fixed as follows: T=353.15 K, stirring speed: 400 rpm, n_{HH}/n_{AG}=15 mol/mol, w/V=0.678 g/100 mL. As seen in Fig. 7, ethanol content has a considerable influence on the IP of PVB hydrolysis, and the duration of IP of the above five experiments was calculated and shown in Table 1.

As can be seen from Table 1, with the increase of x_e, the duration of IP decreases first, then rises, and finally decreases again. The special variation behavior could be explained by the formation of two kinds of water-ethanol clusters, which has been used successfully to explain the variation of solubility of the transition metal tosylates in mixed ethanol/water solvents [26-28]. According to the hydrolysis mechanism of PVB, the reaction between acetal group and water is relatively slow, so the content of free water is an important factor affecting the IP of the hydrolysis reaction, which is largely affected by the water-ethanol clusters. In addition, the dissolution state of PVB in the system can also affect IP by affecting the interaction between acetal groups and water molecules.

Therefore, the ethanol content in the mixed solvents will influence the IP of PVB hydrolysis by affecting the dissolution of PVB and the content of free water in the system, respectively. A detailed analysis about the evolution of the duration of IP with ethanol content is as follows.

As reported in the above literature [28], when x_e>0.105, some $(water)_2$-ethanol clusters are starting to take shape in the mixture, which will reduce the content of free water in the system. Within the low ethanol content range, the interaction between acetal groups and water is relatively weak and the content of $(water)_2$-ethanol clusters is very low; in this case, the dissolution of PVB has a greater effect on IP. Thus, in the range of 0.2907-0.3482, the increase of ethanol content will be conducive to the dissolution of PVB and reduce the duration of IP correspondingly. With increasing in x_e, more $(water)_2$-ethanol clusters will be formed and the free water content will become the main influence on IP. Therefore, in the range of 0.3482 to 0.4948, the duration of IP increases continuously with the increase of x_e. The second kind of cluster water-$(ethanol)_3$ will appear when x_e>0.535, which can increase the content of the free water, so the duration of IP decreases with the increase of x_e in the range of 0.4948 to 0.5402.

3. Influence of Temperature

The influence of temperature on the hydrolysis of PVB was investigated in the range of 339.15-355.15 K, while the other parameters were fixed as follows: x_e=0.4339, stirring speed: 400 rpm, w/V=0.678 g/100 mL and n_{HH}/n_{AG}=15 mol/mol. As shown in Fig. 8, temperature has a significant effect on IP and hydrolysis rate, which will be discussed in the following parts.

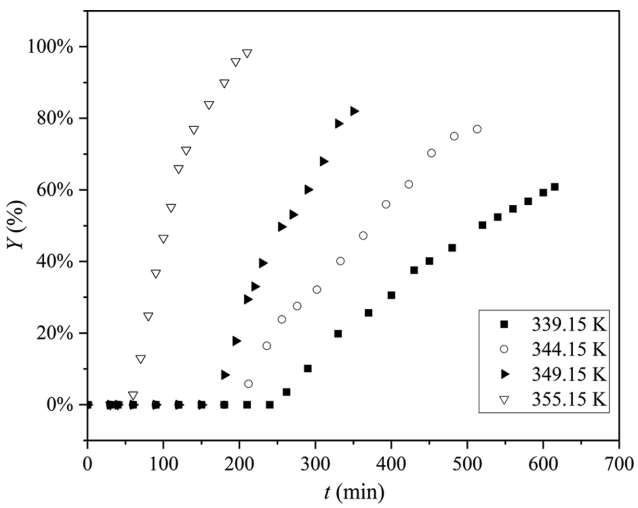

Fig. 8. Influence of temperature on PVB hydrolysis (x_e=0.4339, stirring speed: 400 rpm, w/V=0.678 g/100 mL and n_{HH}/n_{AG}=15 mol/mol).

Table 2. The duration of IP at different temperature

T/K	t_0 (min)
339.15	247.7
344.15	197.2
349.15	169.2
355.15	57.8

Reaction conditions (x_e=0.4339, stirring speed: 400 rpm, w/V=0.678 g/100 mL and n_{HH}/n_{AG}=15 mol/mol)

From Table 2, it is found that the duration of IP decreases with the increase of temperature. The possible reason for the significant influence of temperature on IP is given as follows. HH plays a catalytic role in the hydrolysis of PVB, which has been mentioned in the hydrolysis mechanism of PVB. As temperature increases, the catalytic activity increases significantly, resulting in the decrease of the duration of IP of the PVB hydrolysis reaction.

Correlating the kinetic experimental data of Y at real hydrolysis time ($t-t_0$) with the above three kinetic models (Eqs. (9), (14), and (19)) and the fitting results is given in Fig. 9-11. As shown in above three pictures, the rate of PVB hydrolysis increases with the increase of temperature. Three parameters k_{ED}, k_{ID}, and k_R can be calculated by optimizing the above objective function Eq. (21), and the absolute average deviation (AAD%) of three kinetic models can be cal-

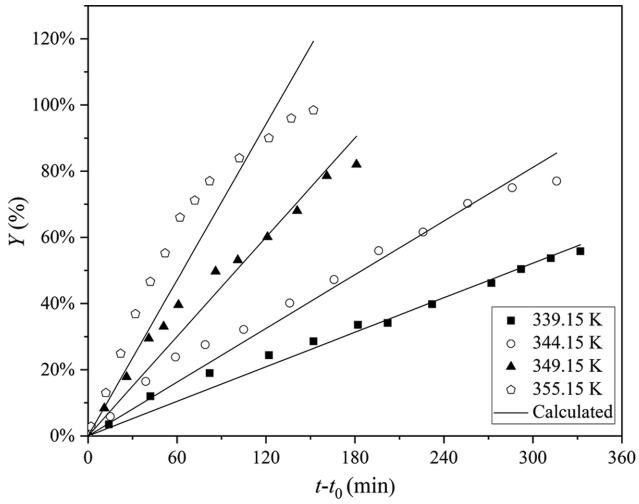

Fig. 9. Variation of Y_i^{exp} and Y_i^{cal} calculated by Eq. (9) with real hydrolysis time ($t-t_0$) at different temperatures.

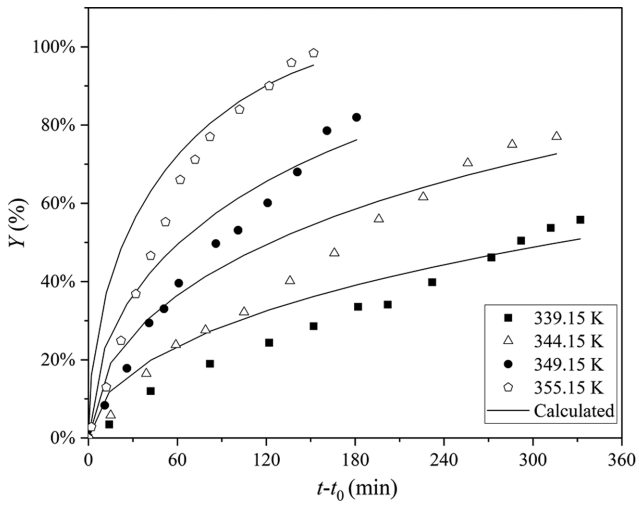

Fig. 10. Variation of Y_i^{exp} and Y_i^{cal} calculated by Eq. (14) with real hydrolysis time ($t-t_0$) at different temperatures.

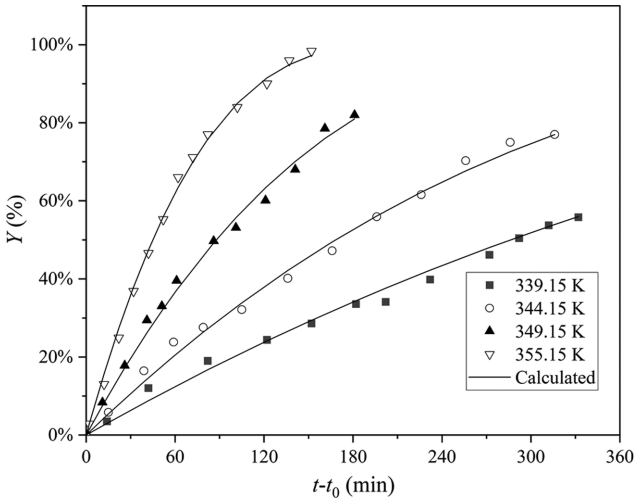

Fig. 11. Variation of Y_i^{exp} and Y_i^{cal} calculated by Eq. (19) with real hydrolysis time ($t-t_0$) at different temperatures.

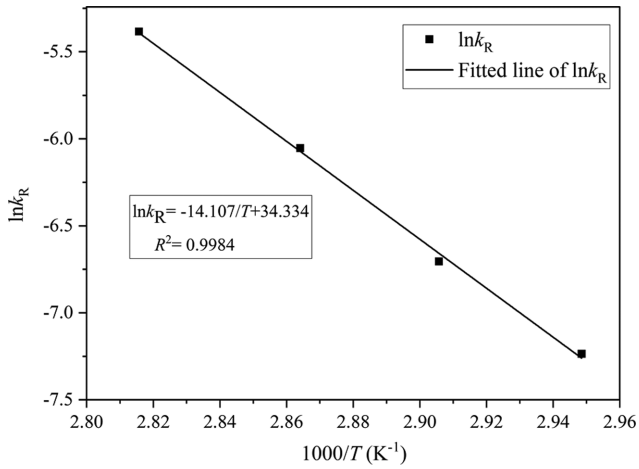

Fig. 12. Arrhenius plot.

culated as follows:

$$\mathrm{AAD\%}=\frac{1}{N}\left(\sum_{i=1}^{N}\frac{\left|Y_i^{exp}-Y_i^{cal}\right|}{Y_i^{exp}}\right)\times 100\% \tag{22}$$

The values of k_{ED}, k_{ID}, k_R, and AAD% are listed in Table 3. As seen in Table 3, the average AAD% of Eq. (19) (4.93%) is the lowest, compared with those of Eq. (9) (15.84%) and Eq. (14) (44.44%). Therefore, the shrinking core model controlled by chemical reaction is more suitable to describe the reaction kinetics of PVB hydrolysis.

Based on the rate constant of PVB hydrolysis, k_R at four temperatures, the activation energy of the hydrolysis reaction can be calculated by the Arrhenius equation:

$$\ln k_R=\frac{-E_a}{RT}+C \tag{23}$$

where E_a is activation energy and R is a constant of ideal gas. Fig. 12 shows the plot of $\ln k_R$ versus T^{-1} for Eq. (23), the activation energy is estimated to be 117.29 kJ mol^{-1} based on the slope of the fitting line. The activation energy of PVB hydrolysis is much higher than that of some low molecular acetals investigated by Yuta et al. [29]. They studied the hydrolysis reaction of 4,6-O-benzylidene acetal group and obtained the hydrolysis activation energies of benzylidene acetal groups of six monosaccharides based on the Arrhenius equation, and their values are in the range of 72.4-79.3 kJ mol^{-1}. The big difference in hydrolysis activation energy between PVB and low molecular weight acetals may be explained as follows. PVB is a long chain polymer containing many strong hydrophobic acetal groups, and has large steric hindrance. It may disturb the access of proton and water molecules, which is unfavorable to the hydrolysis of PVB.

CONCLUSIONS

The kinetics of PVB hydrolysis was studied in ethanol/water mixed solvents within the temperature range of 339.15-355.15 K, and a three-step hydrolysis hypothesis was proposed to describe the hydrolysis mechanism. The influence of stirring speed, ethanol content in mixed ethanol/water solvents and temperature on the hydrolysis of PVB was investigated. The experimental results show that the influence of stirring speed on the hydrolysis of PVB can be ignored when it is greater than 400 rpm. During the experiments, an interesting IP phenomenon was found in the hydrolysis reaction of PVB and the duration of IP can be calculated by the tangent method. The ethanol content in mixed solvents has a great influence on IP and it can be explained by the formation of the two kinds of water-ethanol clusters in the system. The duration of IP decreases with the increase of temperature, owing to the influence of temperature on the catalytic activity of HH on PVB hydrolysis reaction. The kinetic experimental data of PVB hydrolysis after the IP were correlated by shrinking core models, and the

Table 3. The regression parameters of the three kinetic models

T (K)	Kinetic model					
	External diffusion control		Internal diffusion control		Chemical reaction control	
	k_{ED}	AAD%	k_{ID}	AAD%	k_R	AAD%
339.15	1.740×10^{-3}	10.18%	3.463×10^{-4}	36.60%	7.207×10^{-4}	6.23%
344.15	2.706×10^{-3}	12.92%	8.957×10^{-4}	41.38%	1.226×10^{-3}	5.16%
349.15	5.004×10^{-3}	19.01%	1.791×10^{-3}	36.05%	2.350×10^{-3}	4.57%
355.15	7.849×10^{-3}	21.26%	4.639×10^{-3}	63.73%	4.596×10^{-3}	3.74%
Average		15.84%		44.44%		4.93%

results show that the shrinking core model controlled by chemical reaction is suitable to describe the kinetics of PVB hydrolysis with average AAD% less than 5%. The hydrolysis conversion rate of PVB can reach about 98.40% under the reaction conditions of x_e=0.4339, T=355.15 K, 400 rpm of the stirring speed, w/V=0.678 g/100 mL and n_{HH}/n_{AG}=15 mol/mol. The activation energy of the hydrolysis reaction of PVB was calculated to be 117.29 kJ mol^{-1}.

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NOMENCLATURE

PVB : polyvinyl butyral
PVA : polyvinyl alcohol
HH : hydroxylamine hydrochloride
AD : acetalization degree
IP : induction period
AG : acetal group
x_e : mole fraction of ethanol in mixed ethanol/water solvents
t_0 : the duration of the induction period [min]
Y_i^{exp} : experimental conversion rate
Y_i^{cal} : calculated conversion rate
k_{ED} : kinetic parameter of the model controlled by external diffusion
k_{ID} : kinetic parameter of the model controlled by internal diffusion
k_R : kinetic parameter of the model controlled by chemical reaction
S : objective function
AAD : absolute average deviation
T : temperature [K]
E_a : activation energy [kJ mol^{-1}]
R : a constant of ideal gas [J mol^{-1} K^{-1}]

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Kinetics of polyvinyl butyral hydrolysis in ethanol/water solutions

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1. Selection of the amount of Hydroxylamine Hydrochloride (HH) in the Kinetic Experiments

At 339.15 K, the reaction between HH and n-butanal is a fast reaction when the molar ratio of them is 15 : 1. The n-butanal can be completely converted within 3 minutes, indicating that the conversion rate of PVB hydrolysis can be calculated by titrating the HCl produced by n-butanal and HH. When the amount the molar ratio decreased to 10 : 1, it took more than 40 minutes to completely convert the same amount of n-butanal. Therefore, all further experiments of PVB hydrolysis were carried out under the condition that the molar ratio of HH to theoretical acetal group (AG) is 15 : 1 (n_{HH}/n_{AG}=15 mol/mol).

2. The Role of HH in PVB Hydrolysis

At room temperature, a certain amount of HH and n-butanal (n_{HH}/n_{AG}=15 mol/mol) were added to the ethanol/water solution. After reacting for 10 minutes, the above mixture was titrated by the sodium hydroxide standard solution with the addition of bromophenol blue indicator. The result showed that the conversion rate of n-butanal can reach about 85% under this condition.

A certain amount of PVB was added to a three-necked flask containing a certain volume of ethanol/water mixture, then heated to the reflux temperature for 7 h with constant stirring. Then, cooled to room temperature, and HH (n_{HH}/n_{AG}=15 mol/mol) was added to the mixture. After 10 min, the bromophenol blue was added to the above solution, but the color of the titration end point had been reached without adding sodium hydroxide solution. The result showed that there was no HCl generated in the experiment, which means that PVB will not hydrolyze at high temperature for a long time without the addition of HH in advance.

3. The Hydrolysis of PVB in Pure Water

The experiment of PVB hydrolysis was performed in pure water, and other conditions were set as: T=355.15 K, stirring speed: 400 rpm, n_{HH}/n_{AG}=15 mol/mol, w/V=0.678 g/100 mL. After heated for 2 hours, almost all of PVB solids were not dissolved. A small amount of the solution was taken out for titration, and the result shows that there is no HCl generated in the solution, indicating that it is difficult for PVB to hydrolyze in pure water.

4. The Integration Process of Eq. (11)

Here, the equation of (S1) is the equation of (11) in the manuscript.

$$-\frac{dN_A}{dt}=4\pi r^2 D_A\frac{dC_A}{dr}=\text{constant} \tag{S1}$$

Assume the constant as a, so,

$$-\frac{dN_A}{dt}=4\pi r^2 D_A\frac{dC_A}{dr}=a \tag{S2}$$

Integrate Eq. (S2) under the condition that $r=r_0$, $C_A=C_{Ab}$, and $r=r_c$, $C_A=0$,

$$4\pi D_A\int_{C_{Ab}}^{0} dC_A=a\int_{r_0}^{r_c}\frac{1}{r^2}dr \tag{S3}$$

$$4\pi D_A C_{Ab}=a\left(\frac{1}{r_c}-\frac{1}{r_0}\right) \tag{S4}$$

$$a=\frac{4\pi D_A C_{Ab}}{\left(\frac{1}{r_c}-\frac{1}{r_0}\right)} \tag{S5}$$

Substituting Eq. (S5) into Eq. (S2), and integrating it gives

$$-\frac{dN_A}{dt}\left(\frac{1}{r_c}-\frac{1}{r_0}\right)=4\pi D_A C_{Ab} \tag{S6}$$