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Study on Reactive Extraction Kinetics of 1,3-Propanediol in Dilute Aqueous Solutions

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Abstract: In this work, the separation of 1,3-propanediol (1,3-PD) from dilute fermentation broth coupling the reversible reaction 1,3-PD with acetaldehyde to form 2-methyl-1,3-dioxane (2MD) and a synchronous extraction of 2MD by o-xylene was studied experimentally. The equilibrium and reaction kinetics of the reactive extraction were established catalyzed by cation exchange resin HD-8. After eliminating the influence of internal and external diffusion, the rate constants of positive and reverse reaction were obtained by fitting the experimental data to a pseudo-homogeneous model. The results indicated that the reaction was a weakly exothermal reaction. The kinetics was found to be first-order in the concentrations of the reactants and the products. The results can help to design the reactor of reactive extraction of 13,-PD.

Keywords: Reactive extraction, 1,3-propanediol, dilute aqueous solutions, kinetics

INTRODUCTION

1,3-propanediol (1,3-PD) is an important chemical intermediate used in organic synthesis and as one of the monomers of one new type polyesters—polypropylene terephthalate (PTT), and PTT has excellent characteristic than the polyester—polyethylene terephthalate (PET) produced using ethylene glycol as monomer (1).

As for manufacturing of 1,3-PD, two routes are promising in large-scale commercialization: hydration and hydrogenation of acrylaldehyde, and

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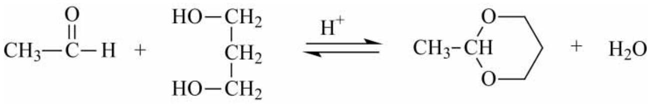
carbonylation and hydrogenation of ethylene oxide. The method of ethylene oxide was commercialized by Shell Co. in 1996 with scale 2 kt/a, and the method of acrylaldehyde was commercialized by Degussa Co. in 1998, scale also 2 kt/a (2). Because the cost of 1,3-PD produced by chemical synthesis is higher, the production of 1,3-PD from renewable resources has attracted substantial research efforts in the past decade. 1,3-PD can be produced by fermentation of glycerol by bacteria from several genera including *Klebsiella pneumoniae*, *Citrobacter freundii*, and *Clostridium butyricum* (3–5). A maximum 1,3-PD concentration of about 0.724-0.921 mol/L was usually achieved (6). Cameron et al. (7) reported a maximum 1,3-PD concentration of 1.316 mol/L.

Recovery of 1,3-PD, relatively high boiling point (higher than water 114°C) and strongly hrdrophilic compounds, from the complex and dilute fermentation is a challenging task, critical for the development of a commercially viable bioconversion process. Conventional distillation techniques applied to the separation 1,3-PD fermentation broth require a substantial energy input. It is not an economic technique. Liquid-liquid extraction represents a means of achieving more energy efficient separation of the product from dilute solutions, if a suitable solvent can be found. Xiang et al. (8) tested the extraction of 1,3-PD from a dilute solution, the results indicated that normal physical or complex extraction does not effectively separate 1,3-PD from dilute solutions. Malinowski (9) performed solvent screening using UNIFAC method, experimental verification of the predictions revealed that the distribution of 1,3-propanediol into organic solvents was not good enough to make simple extraction efficient. 1,3-Propanediol is so difficult to recover from aqueous solution because of its hydrophilic properties, caused by the presence of two hydroxyl groups, allowing the formation of multiple hydrogen bonds with surrounding water molecules. Zhou and Fang (10) summarized all kinds of separation methods of 1,3-propanediol from dilute fermentation broth. A feasible way to tackle this problem is to convert 1,3-PD into a substance without hydroxyl groups or other highly polar groups. A suitable reaction should be a reversible chemical reaction. One such reaction is 1,3-PD with acetaldehydes to form substituted 2-methyl-1,3-dioxane (2MD), catalyzed by an acid catalyst, presented as follows:



Malinowski (11) and Xiang et al. (8) studied the process combining reversible reaction of 1,3-PD with acetaldehyde to 2MD and a simultaneous extraction of the product by organic solvent. The 2MD yield was 91–92%, the overall conversion of 1,3-PD was 98–99%, and recovery of 2MD into the organic extractant was about 75% by one step extraction. But no information is available on the kinetics of this important reaction.

The present work was undertaken to study the reactive extraction kinetics of the reaction 1,3-PD with acetaldehydes in a dilute aqueous solution in the presence of acidic ion exchange resins as catalyst. A pseudo-homogeneous model could be later to fit the experimental data.

EXPERIMENTAL

Chemicals

Acetaldehyde (40% concentration), 1,3-propanediol (99.5%), o-xylene (99.5%) were purchased from commercial suppliers. 2MD (99.5%) was produced by ourselves according to literature (11), and HD-8 ion-exchange resin was provided by Shanghai Huazheng Technology Co. Ltd., a strongly acidic cation-exchange resin. The physical properties of the catalyst used are given in Table 1.

Apparatus and Procedure

The reaction of 1,3-PD with acetaldehyde was completed in a 500 ml jacketed reactor with a motor stirrer. Temperature was maintained to within ±0.5°C of the desired value. 100 ml acetaldehyde solution (acetaldehyde concentration 30%), 100 ml o-xylene and HD-8 ion-exchange resin of 40 g/L were first charged into the reactor with a agitating speed of 723 r/min, and preheated to the desired temperature by recycled hot water and then, 2.09 g 1,3-PD was introduced directly into the reactor. The time of introduction of 1,3-PD into the reactor was considered as the starting point for the reaction. Samples of the two-phase mixture were analyzed on a gas chromatograph at a fixed time interval. 2MD was analyzed in both phases, and 1,3-PD was determined in the aqueous phase only. The analysis was performed on a 7890F series gas chromatograph (GC) supplied by Shanghai Techcomp Instrument Ltd, and the results were processed on a GC workstation. The column of the GC was a 15 m SE-54 column (0.25 mm diameter, 0.33 μm film thickness) supplied by Lanzhou Institue of Chemical Physics Chinese

Table 1. Physical properties of the catalyst used

Property	HD-8
Shape	Beads
Bead size distribution (mm) (min 95%)	0.3–1.0
Internal surface area (m^2/g)	55
Exchange capacity (mmol/g)	4.6
Temperature stability (°C)	130

Academy of Science. The detector was a FID with nitrogen as the carrier gas. The injector and detector were set at 230°C, and the oven temperature was 90°C. The external standard method was used as quantitative analysis method.

RESULTS AND DISCUSSION

Elimination of Mass Transfer Resistances

The mass transfer resistance including internal diffusion and external diffusion must be eliminated in the study of the intrinsic kinetics of heterogeneous reaction. In a continuous stirring reactor, the mass transfer rate will increase as the increasing of the speed of agitation. The effect of external diffusion will decrease till elimination. The effect of the speed of agitation on the conversion of 1,3-PD was shown in Fig. 1. It can be seen that external diffusion was found to be absent above 423 r/min as there was no effect of the speed of agitation on the rate of reaction above 423 r/min. So, all the experiments were carried out later at 723 r/min ensuring that the reaction was free from external diffusion resistance. To check whether intraparticle diffusion resistance was the controlling factor, the reaction was carried out with two different particle sizes of HD-8 catalyst, rounded beads and crushed powder, respectively. The experimental results were shown in Fig. 2. It was observed that with difference in the diameter of the catalyst particle, there was no effect on the conversion of 1,3-PD to the corresponding 2MD. These observations corroborate the conclusion of Widdecke (12) that pore diffusion is not a rate-limiting factor in most catalytic applications of resin catalysts, and of Chakrabarti (13) that the pseudo-homogeneous approach is particularly applicable in cases where one of the reactants or solvent is highly polar when using

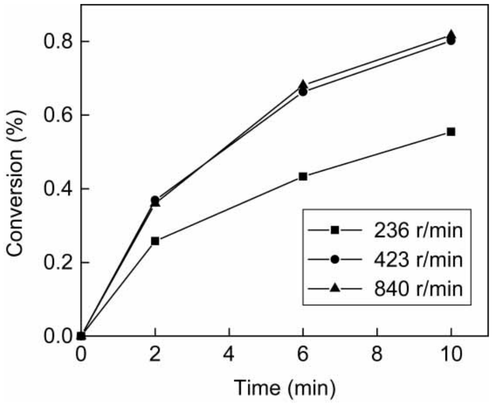


Figure 1. Effect of the speed of agitation on the conversion of 1,3-PD. T, 13 K; catalyst loading, $40 \text{g} \cdot \text{L}^{-1}$.

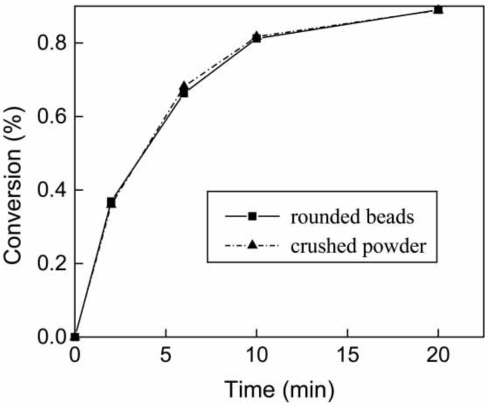


Figure 2. Effect of the size of catalyst on the conversion of 1,3-PD. T, 313K; catalyst loading $40\text{g} \cdot \text{L}^{-1}$; agitating speed: 723 r/min.

a resin catalyst. As 1,3-PD is a highly polar and hydrophilic reactant, a pseudohomogeneous model would be used for representing the rate of the reaction.

Effect of Catalyst Loading

Effect of catalyst loading on the conversion of 1,3-PD was shown in Fig. 3. It was observed that, in the case of 1,3-PD conversion to 2MD with HD-8 catalyst, with an increase in the catalyst loading from 9.3 g/L to 37.6 g/L, the rate of reaction increased but, with further increase in catalyst loading to 65.3 g/L, there was no obvious change in the rate of the reaction. So, in the

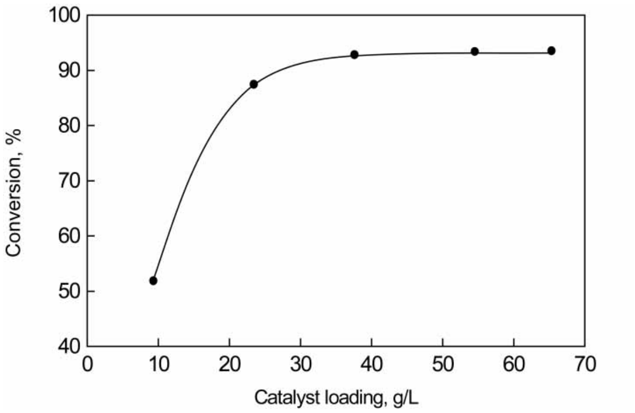


Figure 3. Effect of catalyst loading on the conversion of 1,3-PD. T, 303K; catalyst, HD-8; t, 45 min.

case of lower catalyst loading, the kinetics should take into account the effect of the catalyst loading. However, in cases where there is higher catalyst loading, the rate of reaction becomes independent of catalyst concentration. All kinetics experiments were carried out with 40 g/L loading of the catalyst.

Extraction Experiment

The initial experiment was carried out without extractant to the 2MD formation. In all cases conversion was in the range of 81%–85%. Extractive reaction experiments have been performed using the selected o-xylene as extractant. As could be expected, the extraction shifted the equilibrium position, and this resulted in the larger conversion. As can be seen from Fig. 4, when phase ratio (organic solvent volume/1,3-PD solution volume) larger than 0.6, there were notable differences in the equilibrium conversion of 1,3-PD. It can be concluded, therefore, that the rate of reaction becomes independent of phase ratio in cases of higher phase ratio. Hence, in order to simplify the kinetics, all kinetics experiments were carried out with phase ratio 1. The degree of recovery of 2MD by the solvent o-xylene was 72.4%, 73.2%, 75.5%, 76.9% and 80.6% at 293K, 303K, 313K, 323K and 343K.

Kinetic Model

The experiment was carried out to examine the kinetics of the 2MD formation at 293K, 303K, 313K, 323K and 343K. The time plots of the 2MD and 1,3-PD concentrations during the run are shown in Fig. 5. As can be seen, the reaction is a chemical equilibrium reaction, the near-equilibrium time reduces as the

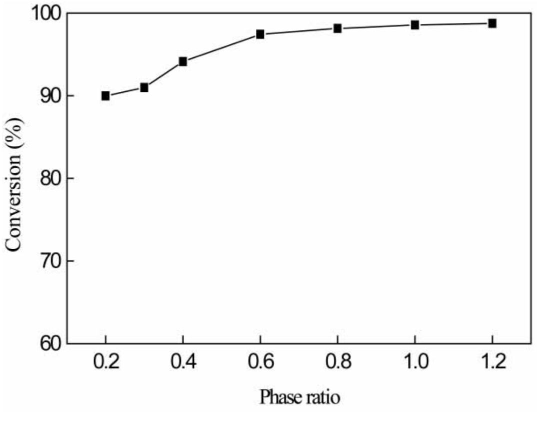


Figure 4. Effect of phase ratio on the conversion of 1,3-PD. T, 303K; catalyst, HD-8; t, 80 min.

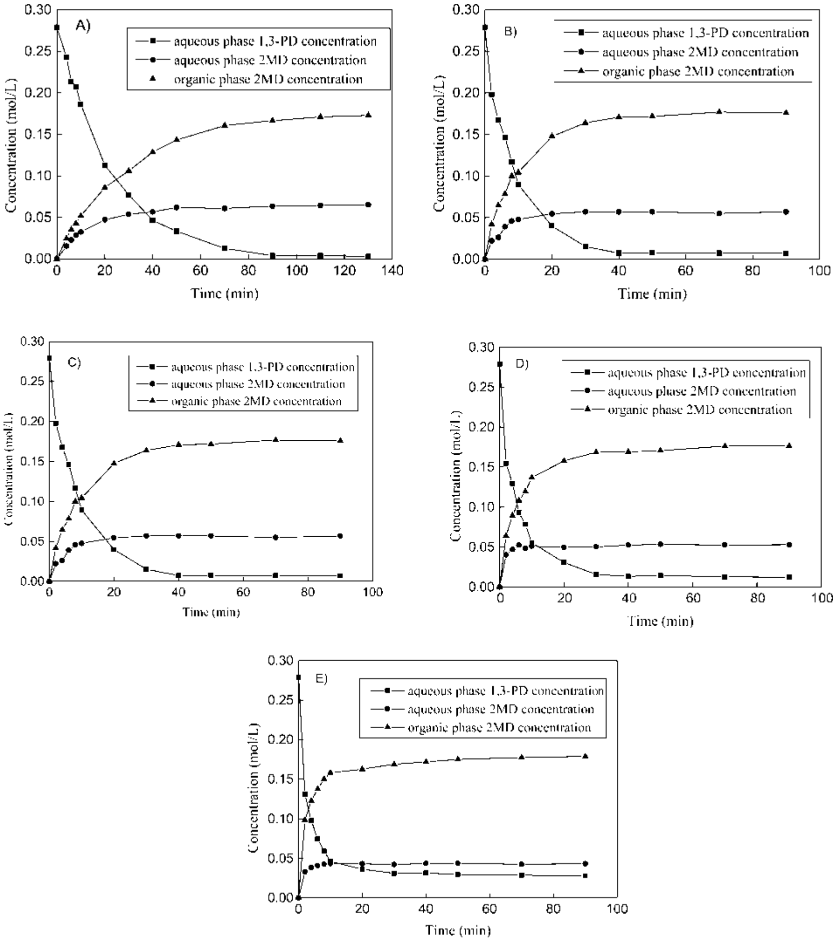


Figure 5. Times courses of the reactive extraction of 1,3-PD with acetaldehyde. Reactive temperature: (A) 293K; (B) 303K; (C) 313K; (D) 323K; (E) 343K.

reaction temperature increases, and this behavior is typical for exothermic reactions. The overall conversion of 1,3-propanediol is 90%–98.8%. The reactive extraction equilibrium constant can be calculated as Equation (1):

$$K_c = \frac{C_{2MD} \times C_{H_2O}}{C_{1,3-PD} \times C_{C_2H_4O}} \tag{1}$$

The equilibrium constants at different temperature are shown in Table 2. Table 2 shows that the equilibrium constant decreases with the reaction temperature increasing. These results show that the reactive extraction process is an exothermal reaction. Temperature dependence of the equilibrium coefficient

Table 2. The reactive extraction equilibrium constant at different temperature

T(K)	K_c
293	1.77×10^3
303	1.13×10^3
313	770
323	506
343	183

as determined based on the concentration in the liquid phase is as follows:.

$$\frac{\partial \ln K_C}{\partial T} = \frac{\Delta U^0}{RT^2} \tag{2}$$

where, ΔU^0 is the internal energy change of the reaction system. However, the volume of the liquid phase can be considered constant, $\Delta U^0 \cong \Delta H^0$. Hence, K_C can be related to the concentration of the components in the liquid phase, and expressed as follows by integrating Equation (2):

$$lnK_C = -\frac{\Delta H^\theta}{RT} + C \tag{3}$$

So, it will be a straight line in lnK_C vs $1/T$ figure. K_C can be obtained from liquid concentration of various components when reaction reaches equilibrium at different temperature. The relationship of lnK_C with $1/T$ is shown in Fig. 6.

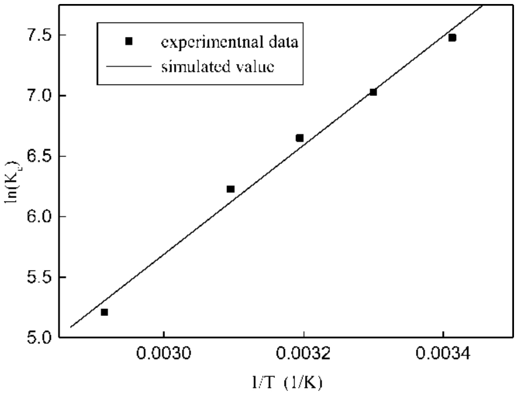


Figure 6. Relationship of lnK_c with $1/T$.

Table 3. The calculated positive reaction rate constant k_+ at different temperature

T(K)	k_+
293	0.049
303	0.090
313	0.150
323	0.242
343	0.365

It can be seen that $\ln K_c$ changes linearly with $1/T$ with a correlation given by:

$$\ln K_c = \frac{4506.2}{T} - 7.8298 \tag{4}$$

Accordingly, the reaction heat, ΔH^0, is calculated to be $-37.46\,\mathrm{kJ/mol}$, in a good agreement with the calculated result of $-34.74\,\mathrm{kJ/mol}$, based on the published chemical thermodynamic data (14, 15).

From the experimental data, the reaction rate of 1,3-PD can be calculated. The simplex method is used to determine the kinetic parameters. The kinetics constants are optimized by minimizing the objective function (OF):

$$OF = \sum_{i=1}^{N} \left(r^{\exp}_{1,3-PD\ i} - r^{cal}_{1,3-PD\ i}\right)^2 \tag{5}$$

where N is the number of data points, $r^{\exp}_{1,3-PD\ i}$ is the experimental reaction rate, and $r^{cal}_{1,3-PD\ i}$, the calculated reaction rate. As the reverse reaction rate constant $k = k_+/K_c$, and K_c has been determined as illustrated by Eq. (4),

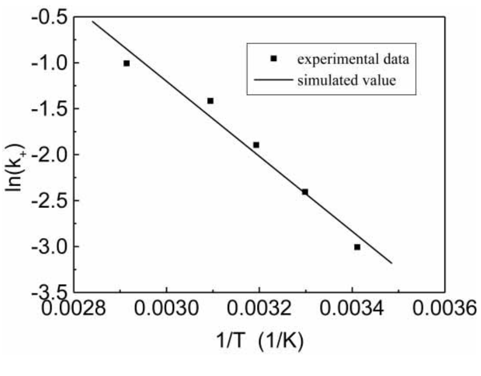


Figure 7. Relationship of k_+, with temperature.

Table 4. Estimated value of kinetic constants

	Activation energy ($\mathrm{kJ \cdot mol^{-1}}$)	Rate constants ($\mathrm{min^{-1} \cdot (mol \cdot L^{-1})^{-1}}$)
Positive reaction	33.9	$k_+ = 6.22 \times 10^4\, e^{-3.39 \times 10^5}/RT$
Reverse reaction	70.8	$\mathrm{k}_- = 1.20 \times 10^8\, e^{-7.08 \times 10^4}/RT$

the correlating kinetic equation is described by Eq. (6). The positive reaction rate constants k_+ at different temperature are shown in Table 3, and the correlations of k_+ with temperature is shown in Fig. 7. The estimated kinetic constants are displayed in Table 4.

$$r_{1,3-PD} = k_+ \cdot \left(C_{1,3-PD} C_{C_2H_4O} - \frac{1}{K_c} C_{2MD} C_{H_2O}\right) \tag{6}$$

The comparison of experimental values and calculated values of 1,3-PD reactive extraction rate is shown in Table 5. It can be seen that most relative deviation are less than 15%, the calculated results show a good agreement with the experimental ones. The kinetic equation can describes the process of 1,3-PD reactive extraction well.

Table 5. Comparison of experimental values and calculated values of 1,3-PD reactive extraction rate

		No.				
T(K)		1	2	3	4	5
	r_{exp}	0.011	0.009	0.003	0.002	0.001
293	r_{cal}	0.014	0.009	0.004	0.002	0.001
	Relative deviation	0.157	0.008	0.072	0.078	0.154
	r_{exp}	0.023	0.020	0.012	0.005	0.001
303	r_{cal}	0.025	0.017	0.013	0.004	0.001
	Relative deviation	0.068	−0.141	0.070	−0.066	0.044
	r_{exp}	0.040	0.028	0.014	0.009	0.004
313	r_{cal}	0.041	0.024	0.012	0.008	0.003
	Relative deviation	0.018	−0.152	−0.191	−0.152	−0.106
323	r_{exp}	0.062	0.015	0.013	0.010	0.007
	r_{cal}	0.067	0.017	0.012	0.010	0.007
	Relative deviation	0.071	0.097	−0.047	0.024	−0.011
	r_{exp}	0.074	0.014	0.010	0.007	0.004
343	r_{cal}	0.081	0.014	0.010	0.006	0.004
	Relative deviation	0.086	0.008	0.015	−0.138	−0.034

CONCLUSION

The reactive extraction kinetics of 1,3-PD with acetaldehydes from a dilute aqueous solution is investigated. From the experimental and calculated results, we could draw the following conclusions:

1. It is technically feasible to convert 1,3-propanediol to 2-methyl-1,3-dioxane by reactive extraction to separate 1,3-propanediol from the dilute fermentation broth. The overall conversion of 1,3-propanediol is greater than 98%.
2. The reactive extraction is a weakly exothermal reaction with the experimental and the calculated reaction heat being a good agreement.
3. A pseudohomogeneous kinetic model based on experimental data was established. The kinetics was found to be first-order in the concentrations of the reactants and the products. This kinetic equation could help to design the reactor of reactive extraction to separate 1,3-propanediol from fermentation broth.

NOMENCLATURE

C	constant defined by Eq. (3)
C_i	concentration of component, subscript i = 2MD, H_2O, 1,3-PD, C_2H_4O, $\mathrm{mol \cdot L^{-1}}$
k_+	positive reaction rate constant, $\mathrm{min^{-1} \cdot (mol \cdot L^{-1})^{-1}}$
k_-	reverse reaction rate constant, $\mathrm{min^{-1} \cdot (mol \cdot L^{-1})^{-1}}$
K_C	equilibrium constant
$r_{1,3-PD}$	reaction rate according to 1,3-PD, $\mathrm{(mol/L) \cdot min^{-1}}$
r_{exp}	experimental reaction rate of 1,3-PD, $\mathrm{(mol \cdot L^{-1}) \cdot min^{-1}}$
r_{cal}	calculated reaction rate of 1,3-PD, $\mathrm{(mol \cdot L^{-1}) \cdot min^{-1}}$
T	temperature, K
t	time, min
ΔH^0	heat of reaction, $\mathrm{J \cdot mol^{-1}}$
ΔU^0	internal energy change of the reaction system

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