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Kinetics models to describe the synthesis of benzyl acetate

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ABSTRACT

Two types of kinetics equations have been applied on benzyl acetate system. One kinetics equation is the second order reaction by addition of strong acid cation exchange resin loaded Fe^{3+} as a catalyst. Another kinetics equation is the secondorder reaction by addition of silicotungstic acid as a catalyst under the condition of ultrasonic radiation. The results show that both kinetic equations may predict the distribution of product and the experimental value is in agreement with the quantitatively analytical conclusions drawn from the calculated value.

KEYWORDS

Kinetics model;
Synthesis;
Benzyl acetate;
Strong acid cation exchange resin;
Ultrasonic radiation.

INTRODUCTION

Benzyl acetateis a colourless oily liquid. It is naturally found in many flowers such as jasmine, ylang-ylang and tobira. Its molecular formula, melting point, boiling point, relative density (16 °C), refractive index n_D^{20} and flash point are $C_9H_{10}O_2$, 50 °C, 213 °C, 1.057, 1.5232 and 102 °C, respectively. Benzyl acetate is hard to dissolve in water, but benzyl acetate and other organic solvent such as alcohol and ester, etc. are completely miscible in all[1]. Due to floral fragrance and low price, it is widely used in different areas such as soap class essence and other industrial essence, etc[2]. Benzyl alcohol with concentrated sulphuric acid as a catalyst reacts with acetic acid to synthesisebenzyl acetate. Concentrated sulphuric acid has a lot of disadvantages also except several advantages, such as long reaction time, low yield and purity of benzyl acetate. Large amount of waste water is discharged to cause the problem of environmental pollution and equipments are seriously corroded at the same time[3].

In the present paper, two types of kinetics equations have been discussed. The second order reaction by addition of strong acid cation exchange resin loaded Fe^{3+} as the catalyst and addition of silicotungsticacid as the catalyst under the condition of ultrasonic radiation have also been pointed out.

DISCUSSION

The second order kinetics equation by addition of strong acid cation exchange resin loaded Fe^{3+} as the catalyst

Jiang Hongzhi[4] used strong acid cation exchange resin loaded Fe^{3+} as the catalyst and benzyl alcohol and acetic acid as feedstocks. He studied effects of different reaction conditions such as the reaction temperature and the amount of strong acid cation exchange resin loaded Fe^{3+} on the yield ofbenzyl acetate. TABLE 1 showed that the initial reaction rate increased with an increase in the weight ratio of strong acid cation exchange resin loaded Fe^{3+} to acetic acid at the same reaction temperature. On the other hand, the initial reaction rate increased with an increase in the reaction temperature at the same weight ratio of strong acid cation exchange resin loaded Fe^{3+} to acetic acid.

TABLE 1 the relationship between the initial reaction rates and different reaction conditions

Note: C_c and r_0 mean the weight ratio of strong acid cation exchange resin loaded Fe^{3+} to acetic acid and the initial reaction rate, respectively.

It is supposed that the reaction of benzyl acetate is the second order reaction. Its reaction rate (Eqn. (1)) is written as follows.

$$-r_A=\varphi(C_c)k_0 e^{-\frac{E_a}{RT}}(C_A C_B-\frac{C_E C_W}{K}) \quad (1)$$

Where r_A - the reaction rate, $mol\cdot L^{-1}\cdot min^{-1}$.

φ - the function of the catalyst.

C_c - the weight ratio of strong acid cation exchange resin loaded Fe^{3+} to acetic acid, $g\cdot g^{-1}$.

k_0 - the pre-exponential factor, $L\cdot mol^{-1}\cdot min^{-1}$.

E_a - the activation energy, $J\cdot mol^{-1}$.

R -the gas constant, $8.314 J\cdot mol^{-1}K^{-1}$.

T -the reaction temperature, K.

C_A - the acetic acid concentration, $mol\cdot L^{-1}$.

C_B - the concentration of benzyl alcohol, $mol\cdot L^{-1}$.

C_E - the concentration of benzyl acetate, $mol\cdot L^{-1}$.

C_W - water concentration, $mol\cdot L^{-1}$.

K - the equilibrium constant.

Eqn. (1) is transferred to Eqn. (2) at a given temperature. Eqn. (2) is written as follows.

$$-r_A=\varphi(C_c)k_0 e^{-\frac{E_a}{RT}}(C_{A0}C_{B0}) \quad (2)$$

It is supposed that $A=k_0 e^{-\frac{E_a}{RT}}$ and $f=-\frac{r_0}{(C_{A0}C_{B0})}$. Eqn. (2) is simplified to Eqn. (3).

$$f=A\times\varphi(C_c) \quad (3)$$

The relationship (Eqn. (4)) between the initial reaction rate and the amount of the catalyst is obtained based on TABLE 1.

$$-r_0=0.01495C_c^{0.7992} \quad (4)$$

Eqn. (4) is simplified to Eqn. (5) when the amount of the catalyst is a constant.

$$f=\frac{-r_{A0}}{C_{A0}B_{A0}}=\varphi(C_c)k_0 e^{-\frac{E_a}{RT}}=C_c^{0.7992}k_0 e^{-\frac{E_a}{RT}} \quad (5)$$

It is supposed that $a=C_c^{0.7992}k_0$ and $b=-\frac{E_a}{R}$. Eqn. (5) is transferred to Eqn. (6).

$$f=ae^{\frac{b}{T}} \quad (6)$$

$\frac{b}{T}$ is calculated with the linear regression based on TABLE 1. Their results are obtained as follows.

$$a=137293.19 \quad (7)$$

TABLE 1 : The relationship between the initial reaction rates and different reaction conditions

C_c ($g\cdot g_A^{-1}$)	Temperature (K)	r_0 ($mol\cdot L^{-1}\cdot min^{-1}$)
0.0333	353.2	0.0333
0.0667	353.2	0.0609
0.1000	353.2	0.0848
0.1333	353.2	0.1062
0.1667	353.2	0.1214
0.0333	323.2	0.0060
0.0333	333.2	0.0116
0.0333	343.2	0.0202
0.0333	363.2	0.0573

$$b=6634.5 \quad (8)$$

The final kinetics Eqn. (9) is written as follows.

$$-r_A=2.081\times10^6\times C_c^{0.7992}e^{-\frac{6634.5}{T}}\times(C_A C_B-\frac{C_E C_W}{4.31}) \quad (9)$$

Figure 1 shows the relationship between the calculated value and the experimental value. The experimental value is in agreement with the quantitatively analytical conclusions drawn from the calculated value. Furthermore, the maximum relative error is less than 10 %, so it can predict the distribution of product.

The second order kinetics equation by addition of silicotungsticacid as the catalyst under the condition of ultrasonic radiation

Chen Xi[5] used H_2SO_4 as the catalyst and explained the reasons for its use. The reaction conditions were:

ultrasonic frequency (10 k Hz), ultrasonic intensity (1.0 W cm^{-2}) and the air velocity (0.3 L min^{-1}). The maximum yield of benzyl acetate was 65.8 %. He supposed that the reaction of benzyl acetate is the second order kinetics reaction. Its kinetics reaction Eqn. (10) is written as follows.

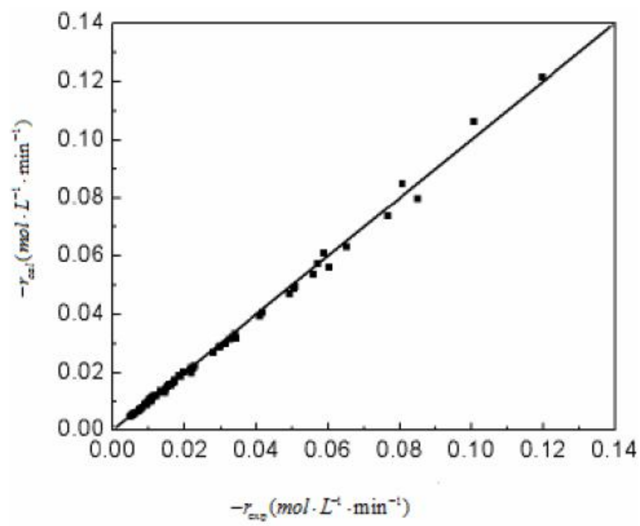

Figure 1 : The relationship between the calculated value and the experimental data

$$r=-\frac{dc_A}{dt}=kc_Ac_B \tag{10}$$

$$c_A=c_{A0}-x \tag{11}$$

$$c_B=c_{B0}-x \tag{12}$$

Where r - the reaction rate, $mol\cdot L^{-1}\cdot \min^{-1}$.

C_A - the acetic acid concentration, $mol\cdot L^{-1}$.

C_B - the concentration of benzyl alcohol, $mol\cdot L^{-1}$.

c_{A0} - an initial acetic acid concentration, $mol\cdot L^{-1}$.

c_{B0} - the initial concentration of benzyl alcohol, $mol\cdot L^{-1}$.

It si supposed that $Y=c_{B0}-c_{A0}$, so $Y=c_B-c_A$ or $c_B=c_A+Y$ is obtained.

Eqn. (10) is transferred to Eqn. (13).

$$-\frac{dc_A}{dt}=kc_A\times(Y+c_A) \tag{13}$$

Eqn. (13) is integrated to get Eqn. (14) and Eqn. (15).

$$kt=\frac{1}{Y}\times\ln(\frac{Y}{c_A}+1)+C \tag{14}$$

$$\frac{1}{Y}\times\ln(\frac{Y}{c_A}+1)=kt-C \tag{15}$$

t has a linear relationship with $\frac{1}{Y}\times\ln(\frac{Y}{c_A}+1)$, so this is used in Arrhenius Eqn. (16).

$$\ln k=-\frac{E}{RT}+\ln A \tag{16}$$

Where E - activation energy, $kJ\cdot mol^{-1}$.

A - the pre-exponential factor, $L\cdot mol^{-1}\cdot \min^{-1}$.

R -the gas constant, $8.314 J\cdot mol^{-1}K^{-1}$.

T -the reaction temperature, K.

$\ln k$ and $\frac{1}{T}$ are calculated with the linear aggression. The experimental results are listed in TABLE 2.

TABLE 2 : Parameters of reaction kinetics of benzyl acetate

T (K)	$\ln k$	E ($kJ\cdot mol^{-1}$)	$\ln A$	A ($10^4 L\cdot mol^{-1}\cdot h^{-1}$)
363	-9.026			
373	-8.531	59.12	10.555	3.863
383	-8.001			

The final kinetics Eqn. (17) with the addition of silicotungsticacid as the catalyst under the condition of ultrasonic radiation is written as follows.

$$-\frac{dc_A}{dt}=3.863\times10^4\times e^{-\frac{5.912\times10^4}{RT}}\times c_A\times c_B \tag{17}$$

CONCLUSION

Using benzyl alcohol and acetic acid as feedstocks and strong acid cation exchange resin loaded Fe^{3+} as the catalyst, the second order reaction by addition of strong acid cation exchange resin loaded Fe^{3+} as the catalyst and addition of silicotungstic acid as the catalyst under the condition of ultrasonic radiation have been discussed. In this paper, the author has found that two types of kinetics equations lead to and are closely in accordance with predicting the practical experimental values. The yield of benzyl acetate is accurately estimated. The two types of kinetics equations point out that a deeply comprehending reaction mechanism of benzyl acetate not only has a very important significance, but also provides a theoretical foundation for the chemical plant. It is important for the reaction of benzyl acetate to design and operate rightly and optimizes the reaction processing and may increase the plant's benefits. This mathematical method is effective, economic, simple and convenient and thus it is suitable for refineries in China.

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