Thermodynamic and Kinetic Study on the Catalysis of Isoamyl Acetate by a Cation-Exchange Resin in an Intensified Fixed-Bed Reactor

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ABSTRACT: Kinetics and thermodynamics of esterification by a cation-exchange resin in an intensified fixed-bed reactor was studied systematically. The resin type, catalyst loading, volume flow rate, initial molar ratio, temperature, and catalyst reusability were studied and optimized. The nonideality of the reaction system was corrected by the UNIFAC group contribution method. The ΔH°, ΔS°, and ΔG° of the reaction were acquired by two methods. The pseudo-homogeneous (PH) model and the Langmuir–Hinshelwood–Hougen–Watson (LHHW) model were adopted to simulate the kinetic process. The result indicated that the LHHW model was better suited to simulate the kinetic process than the PH model.

1. INTRODUCTION

Isoamyl acetate, the common name of banana oil, is commonly found in fruits. Because of its special aroma, it is widely used as an additive in foods, tobacco, flavors and fragrances, daily chemical products, and other industries.1−5 Isoamyl acetate is synthesized from acetic acid and isoamyl alcohol, catalyzed by inorganic acids (such as sulfuric acid). To solve the problems of equipment corrosion and environmental pollution, in recent years, molecular sieves,6 solid superacids,7 inorganic acids (such as sulfuric acid). To solve the problems of equipment corrosion and environmental pollution, in recent years, molecular sieves,6 solid superacids,7 supercritical carbon dioxide,8−10 ionic liquids,11 zeolites,12−14 lipase,15 heteropoly acids,16−18 lipase,15 supercritical carbon dioxide,8−10 ionic liquids,11 zeolites,12−14 lipase,15 heteropoly acids,16−18 and many other new catalysts have been used in the synthesis of isoamyl acetate. Compared to liquid acids and solid acids, cation-exchange resins have considerable advantages, such as good chemical stability, easy separation and recovery, and high catalytic activity and selectivity, and cation-exchange resins such as CT175,19−21 IR-120,22−24 and T-63225, have been reported. However, the above research is confined to a stirred tank reactor. Long-term and intense mechanical agitation will cause severe wear to the resin and deactivation of the catalyst. Meanwhile, the intermittent operation also makes the separation and recovery of catalysts very hard, which will seriously affect the industrial production efficiency in actual industrial production. Compared with the stirred tank reactor, a fixed-bed reactor can effectively solve the mechanical wear problem of the solid catalyst and greatly simplify the process of catalyst recovery and utilization. Based on a traditional fixed-bed reactor, our research group designed a novel significantly intensified fixed-bed reactor (IFBR).23 Driven by a circulating pump, the liquid passes through the catalyst bed at high speed, which solves the problem that channel flow is easily formed in a conventional fixed-bed reactor due to its slow velocity. Previous studies have shown that the mass transfer coefficient in the IFBR can generally be increased by more than 30% compared with traditional reactors, and the mass transfer area between liquid phases can be more than double.24

In this work, the reaction process of synthesis of isoamyl acetate catalyzed by a cation-exchange resin was investigated in an IFBR, and the effects of resin type, the initial molar ratio of acetic acid to isoamyl alcohol, temperature, and other conditions on the reaction were mainly investigated, and the recovery performance of the catalyst was verified. After modifying the experimental results with the UNIFAC group contribution method, the thermodynamic results of the reaction were obtained. The kinetic parameters of the reaction were obtained by the simulation of PH and LHHW models.

2. RESULTS AND DISCUSSION

2.1. Effect of Resin Type. The catalytic effects of eight cation-exchange resins (A15, A35, A36, A39, NKC-9, CT175, CT275, and Lewatit2620) on the reaction are compared in Figure 1. Considering that the bed filling and disassembly operations are relatively complex, the catalytic performance of
the above resins was investigated by replacing the IFBR with a stirring kettle reaction device, other conditions being the same. The NKC-9 resin showed the highest catalytic activity. Presumably, the reason is that the esterification reaction conforms to the mechanism of positive carbon ion type. The NKC-9 resin has higher acidity, can provide more acidic active sites, and can produce more carbocation intermediates within the same time, so the reaction rate is fast. Hence, the NKC-9 resin was used as the catalyst for a series of subsequent reactions in the IFBR.

2.2. Effect of Catalyst Loading. Other conditions being the same, the influence of the amount of the NKC-9 resin on the reaction conversion was investigated, as shown in Figure 2. In a certain range, with the increase of the amount of catalyst, the number of active sites provided by the catalyst also increased; therefore, the reaction rate accelerated. However, when the amount of catalyst increased from 20 to 25 wt %, the reaction rate decreased significantly, and the utilization rate of the catalyst decreased. Considering that the increase of catalyst loading will bring higher costs, from the perspective of cost–performance ratio, the catalyst dosage of the reaction system was set as 20 wt %.

2.3. Effect of Volume Flow Rate. On the premise that the other reaction conditions are the same, the influence of liquid circulation flow on the reaction rate is shown in Figure 3. When the liquid circulating flow increased from 20 to 30 mL/min, the reaction rate increased slightly. After that, the liquid circulation flow continued to increase and the reaction rate tended to be stable, indicating that the effect of external diffusion on the reaction could be ignored. Considering that more energy needs to be consumed to increase the liquid circulating flow rate, the liquid circulating flow rate in the IFBR in the subsequent reaction process is set at 40 mL/min.

2.4. Effect of Molar Ratio. The influence of the initial molar ratio of raw materials on the reaction conversion is shown in Figure 4. Considering that isoamyl alcohol is more expensive than acetic acid and more difficult to separate, the amount of acetic acid should be appropriately increased. With the increase of the amount of acetic acid, the reaction rate and equilibrium conversion of isoamyl alcohol will increase, but the trend will gradually slow down, and the energy consumption of the subsequent separation and treatment of excessive acetic acid will
also increase. To sum up, from the perspective of economic benefit maximization, the ratio of raw materials was set at 1.2:1.

2.5. Effect of Reaction Temperature. The influence of temperature on the reaction conversion was investigated (Figure 5). As seen, the conversion of isoamyl alcohol gradually increased with the increase of temperature. However, when the temperature was higher than 323.15 K, the reaction was close to the equilibrium state for about 2 h, and the promotion effect of further heating on the reaction was not obvious. This esterification reaction is a typical exothermic process. In the fixed bed reactor, the resin catalyst is fixed and aggregated, while in the stirred tank reactor, the resin catalyst is dispersed, so the heat dissipation efficiency of the former is lower than that of the latter. In addition, there is also some friction between the fixed bed and the liquid fluid, leading to local overheating in the reactor. These factors speed up the reaction rate in the IFBR to some extent. Therefore, from the perspective of energy utilization efficiency, the temperature of the reaction in the IFBR is set at 323.15 K.

2.6. Reusability of Catalysts. The reusability of the NKC-9 resin in the optimal reaction conditions was investigated in the IFBR. (Figure 6). To ensure the accuracy of the results, the residual isoamyl alcohol and isoamyl acetate in the fixed bed were washed with acetic acid at the end of a single reaction. The experimental results showed that the conversion after 20 h hardly changed after the catalyst was recycled 10 times. The SEM results also showed that the resin had almost no wear after 10 repetitions in the IFBR (Figure 7). Furthermore, the activity and stability of the resin catalysts used in the IFBR and those of the resin catalysts used in a conventional stirred tank reactor (STR) and a packed bed reactor (PBR) are compared in Figures S1 and S2 (Supporting information). In summary, the NKC-9 resin showed stable activity in the synthesis of isoamyl acetate catalysis in the IFBR, which has certain practical application significance and potential industrial use.

2.7. Thermodynamic Study. The equilibrium states of the esterification reaction at different temperatures were determined under the optimal reaction conditions. When the conversion of isoamyl alcohol does not change with time, the reaction can be considered to be in equilibrium. Considering the nonideal state of the internal system of the IFBR, the equilibrium constant is corrected by substituting the activity of each component of the concentration. The activity of the substances involved could be calculated by the UNIFAC group contribution method.27 The UNIFAC group contribution method is based on the additive property of a molecule, that is, a certain property of the molecule is equal to the sum of the contributions of each structural unit of the molecule. The modified equilibrium constant is expressed as follows

\[
K_e = \frac{a_{IAc} \cdot a_{H_2O}}{a_{HAc} \cdot a_{IAA}} = \frac{x_{IAc} \cdot x_{H_2O}}{x_{HAc} \cdot x_{IAA}} = \frac{\gamma_{IAc} \cdot \gamma_{H_2O}}{\gamma_{HAc} \cdot \gamma_{IAA}}
\]

(1)

\[x_i \cdot \gamma_i \] and \( a_i \) stand for the mole fraction, activity coefficient, and activity of \( i \), respectively. The activity coefficient \( \gamma_i \) is divided into two parts

\[\ln \gamma_i = \ln \gamma_i^{(c)} + \ln \gamma_i^{(R)}
\]

(2)

\(\gamma_i^{(c)}\) represents the combined part activity coefficient and \(\gamma_i^{(R)}\) stands for the residual part activity coefficient, which can be figured out according to the corresponding parameters.28 And the corresponding parameters are listed in Tables S1 and S2. The calculation results of the activity coefficient and equilibrium constant are shown in Table 1.

Assuming that \(\Delta H^0\) and \(\Delta S^0\) do not change with temperature within the experimental temperature range, the relationship between the equilibrium constant and temperature can be obtained according to the van’t Hoff equation

\[\ln K_e = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}
\]

(3)

It can be seen from eq 3 that there is a linear relationship between \(\ln K_e\) and \(1/T\). Linear fitting of \(\ln K_e\) against \(1/T\) is carried out (Figure 8). From the slope and intercept of the fitted line, \(\Delta H^0\) and \(\Delta S^0\) can be obtained; then, \(\Delta G^0\) can be obtained according to eq 3, whose values are listed in Table 2.

However, \(\Delta H^0\) is a function of temperature, which varies with temperature, and the relationship between the enthalpy change and temperature can be described by the Kirchhoff equation

\[\frac{d\Delta H^0}{dT} = \sum_i v_i C_{p,i}
\]

(4)

where \(v_i\) stands for the stoichiometric number and \(C_{p,i}\) stands for the specific heat capacity of component \(i\). The principle of corresponding states shows that if two parameters of different
fluids have the same \( T_r \), \( P_r \), and \( V_r \), then the third parameter must be the same. The fluids in the same corresponding state have simple physical properties and the same functional relations. Therefore, \( C_{p,i} \) could be obtained by the Rowlinson−Bondi corresponding states method,24 as shown in eq 5

\[
C_{p,i} = a_i + b_i T + c_i T^2 + d_i T^3
\]  

(6)

The values of \( a_i, b_i, c_i, \) and \( d_i \) are listed in Table S3. The relationship between the reaction equilibrium constant \( \ln K_e \) and temperature \( T \) is illustrated by the van’t Hoff equation

\[
\frac{d \ln K_e}{dT} = \frac{\Delta_H}{RT^2}
\]  

(7)

The equation of \( C_{p,i} \) is substituted into eqs 4 and 7, and the expressions of \( \Delta_r H_0, \Delta_r S_0, \Delta_r G_0, \) and \( K_e \) varying with temperature are obtained as follows30

\[
\Delta_r H_0 = I_H - R \times I_H \times T - aT \ln T - \frac{b T^2}{2} - \frac{c T^3}{6}
\]  

(8)

\[
\Delta_r S_0 = \frac{12}{d} T^4
\]  

(9)

\[
\Delta_r G_0 = \frac{I_H}{R} + \frac{a}{R} \ln T + \frac{b}{2R} T + \frac{c}{6R} T^2 + \frac{d}{12R} T^3
\]  

(10)

where \( a = \sum \mu a_\mu, b = \sum \mu b_\mu, c = \sum \mu c_\mu, d = \sum \mu d_\mu \) and the terms containing \( a, b, c, \) and \( d \) are regarded as \( f(T) \). The relation expression is shown in eq 12. Linear fitting of \( [\ln K_e - f(T)] \) against \( 1/T \) was carried out (Figure 9).

\[
\ln K_e - f(T) = I_H - \frac{I_k}{RT}
\]  

(12)

From Figure 9, it can be concluded that

\[
\ln K_e - f(T) = 39.26516 - \frac{188.56765}{T}
\]  

(13)

where \( I_k = 1567.75144 \) and \( I_H = 39.26516 \) J/mol. \( I_k \) and \( I_H \) are substituted into eqs 8−10, and \( \Delta_r H_0, \Delta_r S_0, \) and \( \Delta_r G_0 \) are calculated to be −6.46 kJ/mol, 8.74 J/(mol·K), and −9.06 kJ/mol.
than 0.6, the influence of internal diffusion can be eliminated. The IFBR unit is set at 40 mL/min, the influence of the enthalpy with temperature can be ignored. Two methods is very small, which means that the change in the enthalpy and Gibbs free energy calculated by the methods are negligible, the esterification reaction of the NKC-9 resin in the IFBR could be described by the PH model. The catalytic active site provided by the resin is equivalent to H+.

The molar volume of the solute at the normal boiling point, the molar mass of the solvent, the viscosity of the solvent, and the catalytic active site provided by the resin is equivalent to H+.

**Table 3. Calculated Thermodynamic Results of HAc with IAA (at 298.15 K)**

| Δ_H^0 (kJ/mol) | Δ_H^0 (kJ/mol) | Δ_S^0 (kJ/(mol*K)) | Δ_G^0 (kJ/mol) |
|----------------|----------------|--------------------|----------------|
| constant       | −6.69          | 7.98               | −9.07          |
| changes with temperature | −6.66          | 8.74               | −9.06          |

that there are no significant differences in values. The difference between the two methods is very small, which means that the change in enthalpy with temperature can be ignored.

2.8. Kinetic study. When the liquid circulation flow in the IFBR unit is set at 40 mL/min, the influence of external diffusion can be eliminated. The influence of internal diffusion could be evaluated by the Weisz–Prater criterion (C_{wp}). If C_{wp} is less than 0.6, the influence of internal diffusion on the first-order reaction is negligible.

\[
C_{wp} = \frac{-k_0^2}{C_e D_e} \tag{14}
\]

where \( k \) represents the apparent rate constant of the reaction, \( r_0 \) represents the average particle size of resin pellets, and \( C_e \) and \( D_e \) stand for the concentration of reactants on the surface of the catalyst and the effective diffusion coefficient, respectively. The equation of effective diffusion coefficient \( D_e \) is as follows:\n
\[
D_e = \frac{\varepsilon}{\tau} D_A \tag{15}
\]

\( \varepsilon \) and \( \tau \) stand for the porosity of catalyst particles and the tortuosity factor. The value of \( \varepsilon/\tau \) is 0.50 for the reaction system. \( D_A \) stands for the molecular diffusion coefficient estimated by the Wilke–Chang equation, and its expression is:\n
\[
D_A = 7.4 \times 10^{-5} \left( \frac{\phi M_p}{V_p} \right)^{3/2} T \frac{1}{\mu_b} \tag{16}
\]

where \( \phi \) represents the association factor of the solvent, and the value in the methanol system is 1.0; \( M_p, \mu_b \) and \( V_p \) represent the molar mass of the solvent, the viscosity of the solvent, and the molar volume of the solute at the normal boiling point, respectively, which could be estimated by the Le Bas method. The final calculation results are shown in Table S4. Within the range of experimental temperatures, the influence of internal diffusion can also be ignored.

The pseudo-homogeneous (PH) model, Eley–Rideal (E–R) model and Langmuir–Hinshelwood–Hougen–Watson (LHHW) model are widely used in cation-exchange resin-catalyzed reaction systems. For this reaction, the PH and LHHW models are adopted to simulate the kinetic process. Supposing that the internal and external diffusion effects are negligible, the esterification reaction of the NKC-9 resin in the IFBR could be described by the PH model. The catalytic active site provided by the resin is equivalent to H+.

Without considering the absorption and desorption of acetic acid, isoamyl alcohol, isoamyl acetate, and water on the resin, the kinetic equation of the reaction can be expressed as:

\[
r_{PH} = M_{cat}(k_1a_{HAc}a_{IAA} - k_2a_{IAAC}a_{H, O})
\]

\[
= M_{cat}k_f \left( a_{HAc}a_{IAA} + \frac{1}{K_e}a_{IAAC}a_{H, O} \right) \tag{17}
\]

where \( M_{cat} \) represents the mass concentration of the resin catalyst in the reaction system, \( k_1 \) and \( k_2 \) represent the forward and reverse reaction rate constants, respectively, and \( K_e = k_2/k_1 \) represents the equilibrium constant. The isoamyl alcohol conversion data obtained from the experiment was substituted into the kinetic equation and solved by the fourth-order Runge–Kutta method. The fitting objective function was set as the minimum residual sum of squares between the isoamyl alcohol conversion \( x_{exp} \) and the predicted value \( x_{cal} \) at the corresponding moment in the experiment, as shown in eq 18. The resulting forward and reverse rate constants in line with the PH mechanism at 303.15−343.15 K are shown in Table S5.

\[
SRS = \sum (x_{exp} - x_{cal})^2 \tag{18}
\]

According to the Arrhenius formula, the change of isoamyl acetate esterification rate constant \( k \) with temperature conforms to the following results:

\[
k = k_0 \exp\left( \frac{-E_a}{RT} \right) \tag{19}
\]

\( k_0 \) and \( E_a \) stand for the pre-exponential factor and the activation energy, respectively. And eq 19 can be transformed into

\[
\ln k = \ln k_0 - \frac{E_a}{RT} \tag{20}
\]

The results are listed in Table 4. A comparison between the conversion of isoamyl alcohol predicted based on the PH model and the experimental value is shown in Figure 11. The error between the two is not large, indicating that the PH model is suitable to simulate the kinetics of the esterification reaction process.

Although the PH model simply described the kinetics of the esterification reaction catalyzed by the NKC-9 resin in the IFBR, the absorption and desorption of various substances on the resin surface in the actual reaction were not negligible, which also made the description of the reaction by the PH mechanism inaccurate. Assuming that acetic acid and isoamyl alcohol are first adsorbed on the resin surface and the isoamyl acetate and water generated after esterification are desorbed from the resin surface, the reaction process follows the LHHW mechanism.
and the above reaction process can be divided into the following steps

Acetic acid adsorption:
HAc + S ⇌ HAc-S

Isoamyl alcohol adsorption:
IAA + S ⇌ IAA-S

Surface reaction:
HAc-S + IAA-S ⇌ IAAc-S + H2O-S

Isoamyl acetate desorption:
IAAc-S ⇌ IAAc-S + H2O-S

Water desorption:
H2O-S ⇌ H2O + S

Assuming that the decisive step of the above process is the surface reaction, the kinetic equation describing the esterification reaction process using the LHHW model can be described as

\[
r_{\text{LHHW}} = \frac{M_{\text{cat}}(k_{\text{f}}a_{\text{HAc}}a_{\text{IAA}} - k_{\text{r}}a_{\text{IAAc}}a_{\text{H2O}})}{(1 + K_{\text{HAc}}a_{\text{HAc}} + K_{\text{IAA}}a_{\text{IAA}} + K_{\text{IAAc}}a_{\text{IAAc}} + K_{\text{H2O}}a_{\text{H2O}})^2}
\]

where \(K_{\text{HAc}}, K_{\text{IAA}}, K_{\text{IAAc}}, \text{and } K_{\text{H2O}}\) represent the adsorption equilibrium constants of acetic acid, isoamyl alcohol, isoamyl acetate, and water on the resin surface, respectively, and their relationship with temperature also follows the van’t Hoff equation. After the corresponding fitting treatment, the forward and reverse reactions and \(E_a\) values based on the LHHW mechanism are listed in Table 5. A comparison of the kinetic parameters in this study with previously reported literature values is shown in Table S6.

A comparison between the esterification kinetic results calculated according to the LHHW mechanism and the experimental values is shown in Figure 12. By comparing

Table 4. Kinetic Parameters of the PH Model

| Model       | \(k_0\) (mol·g⁻¹·h⁻¹) | \(E_a\) (kJ·mol⁻¹) |
|-------------|------------------------|-------------------|
| PH model    |                        |                   |
| forward reaction | 2.06 × 10⁸             | 58.6              |
| reverse reaction | 7.89 × 10⁷             | 65.3              |

Table 5. Kinetic Parameters of the LHHW Model

| Model       | \(k_0\) (mol·g⁻¹·h⁻¹) | \(E_a\) (kJ·mol⁻¹) |
|-------------|------------------------|-------------------|
| LHHW model  |                        |                   |
| forward reaction | 6.23 × 10⁹             | 59.5              |
| reverse reaction | 2.38 × 10⁹             | 66.2              |

Table 6. Comparison between PH and LHHW Models

| T (K) | PH    | LHHW |
|-------|-------|------|
| 303.15| 0.92  | 0.54 |
| 313.15| 1.86  | 0.67 |
| 323.15| 0.55  | 0.30 |
| 333.15| 1.29  | 0.08 |
| 343.15| 1.20  | 0.05 |
PH model. In summary, the LHHW mechanism can more accurately describe the synthesis of isoamyl acetate catalyzed by the NKC-9 resin than the PH mechanism.

3. CONCLUSIONS

The esterification reaction between acetic acid and isoamyl alcohol catalyzed by a cation-exchange resin was studied in the designed IFBR system. The parameters of reaction optimization were as follows: NKC-9 as the catalyst; catalyst loading: 20 wt %; volume flow rate: 40 mL/min; initial molar ratio of raw materials: HAc/IAA = 1.2:1; and temperature: 323.15 K. The nonideality of the reaction system was corrected by the UNIFAC group contribution method. The parameters of reaction optimization were as follows: NKC-9 as the catalyst; catalyst loading: 20 wt %; volume flow rate: 40 mL/min; initial molar ratio of raw materials: HAc/IAA = 1.2:1; and temperature: 323.15 K. The nonideality of the reaction system was corrected by the UNIFAC group contribution method; \( \Delta f^0, \Delta S^0, \text{ and } \Delta G^0 \) were \(-6.69 \text{ kJ} \cdot \text{mol}^{-1}, 7.98 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \), and \(-9.07 \text{ kJ} \cdot \text{mol}^{-1} \), respectively, where \( \Delta f^0 \) was the constant value. The PH model and the LHHW model were used to simulate the kinetic process of the reaction. The internal and external diffusion were not the limiting factors as the mass transfer resistances were proven to be negligible; therefore, the LHHW model can better describe the reaction process than the PH model, which may relate to the use of kinetics in the process scale-up.

4. EXPERIMENTS

4.1. Reagents. Acetic acid (AR), isoamyl alcohol (AR), and 1,4-dioxane (AR) were purchased from Alighting Reagent Co. Ltd. Amberlyst 15wet, Amberlyst 35wet, and Amberlyst 39wet were purchased from Tianjin Shuanglian Technology Co. NKC-9 was supplied by Nankai University Factory. The Purolite and the Lanxess Chemical Co supplied CT151, CT275, and Lewatit2620, respectively. All cation-exchange resins were cleaned with deionized water prior to use and then dried to a constant weight in a drying oven.

4.2. Apparatus and Procedures. The reactions were performed in the IFBR device as shown in Scheme 1. The temperature was controlled by the heating medium circulation system. Acetic acid and isoamyl alcohol were added into the preheating tank after the indicated number was stable and mixed evenly. The peristaltic pump was then opened and the time recording was started when the liquid entered the bed. The sample was taken from the preheating tank with a needle tube at regular intervals. At the initial stage of the reaction, samples were taken every 10 min for the first hour and every 1 h thereafter. The sample was diluted with 1,4-dioxane and then analyzed by gas chromatography.

4.3. Gas Chromatographic Analysis. The sample was analyzed using a Shimadzu GC-2014C gas chromatograph with a weak-polarity DM-FAP chromatographic column (30 m × 0.53 mm × 1 \( \mu \)m) and an FID. The nitrogen flow rate was 5 mL/min. The temperatures of the gasification chamber and FID were set at 240 and 260 °C, respectively. The change of column temperature was set as follows: the initial column temperature was 80 °C and maintained for 2 min and then increased to 180 °C at 15 °C/min and kept for 3 min. A single injection was 0.5 \( \mu \)L. The sample composition was analyzed using the area normalization method. The retention time of each component is as follows: 1,4-dioxane, 2.502 min; acetic acid, 5.564 min; isoamyl alcohol, 3.279 min; and isoamyl acetate, 2.755 min.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03116.

- Volume and area parameters of the functional groups (Table S1); interaction parameters of the functional groups \( (a_m/K) \) (Table S2); heat capacity coefficients of each component (Table S3); calculated results of the diffusion coefficient and Weisz–Prater criterion at different temperatures (Table S4); and calculated rate constant values of forward and reverse esterification reactions at different temperatures based on the PH model (Table S5) (PDF)

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Notes

The authors declare no competing financial interest.

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NOMENCLATURE

- \( k_0 \) — pre-exponential factor, \text{mol}^{-1} \cdot \text{L}^{-1} \cdot \text{min}^{-1}
- \( \alpha \) — activity, \text{mol}^{-1}
C_{wp} Weisz–Prater criterion
D_e effective diffusion coefficient, cm^2 s^{-1}
\gamma activity coefficient
D_A infinite dilution molecular diffusivity, cm^2 s^{-1}
E_a activation energy, kJ mol^{-1}
\epsilon particle porosity
\Delta_{l}H^\circ enthalpy, kJ mol^{-1}
\Delta_{S}^0 entropy, J mol^{-1} K^{-1}
\Delta_{G}^\circ Gibbs free energy, kJ mol^{-1}
k reaction rate constant, mol g^{-1} L^{-1} s^{-1}
k_f forward reaction rate constant, mol g^{-1} L^{-1} s^{-1}
k_r reverse reaction rate constant, mol g^{-1} L^{-1} s^{-1}
K_e reaction equilibrium constant
\mu_v viscosity of b, mPa s
M_v molar mass of b, g mol^{-1}
V_a molar volume of a at the boiling point, L mol^{-1}
M_{cat} mass of catalyst per unit volume, g L^{-1}
r_0 radius of resin particle, cm
\varphi association factor
\tau tortuosity factor
R gas constant, J mol^{-1} K^{-1}
wt weight ratio of catalyst/reactants
\chi_{cal} calculated conversion of the reaction
\chi_{exp} experimental conversion of the reaction
x mole fraction
T temperature, K

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