

Liquid-phase esterification of acetic acid with isobutanol catalyzed by ion-exchange resins

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Abstract

Esterification of carboxylic acids with alcohols represents well-known liquid-phase reactions of considerable industrial interest due to the importance of organic ester products. These ester products include environmentally friendly solvents, flavors, pharmaceuticals, plasticizers, and cosmetics.

In this study, the esterification kinetics of acetic acid with isobutanol in 1,4-dioxan as a solvent without adding a catalyst and catalyzed by ion-exchange resins are carried out using a batch reactor. The effect of catalyst type, stirrer speed, the effects of reaction temperature and catalyst loading on the initial reaction rate, the effect of speed of agitation and the conversion of acetic acid versus time were investigated. The kinetics of heterogeneous catalyzed esterification of acetic acid with isobutanol was correlated by a kinetic model based on pseudo-homogeneous catalysis. The strong acidic cation exchange resins were used as solid catalysts, Dowex 50 Wx2, Amberlite IR-120, respectively. As a result, it was found that the weight-based activity of the heterogeneous catalysts increases in the following order: Dowex 50 Wx2 > Amberlite IR-120 and these catalysts were effectively for the synthesis of isobutyl acetate under these experimental conditions.

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Keywords: Esterification; Ion exchange resin; Heterogeneous catalysis; Dowex 50 Wx2; Amberlite IR-120

1. Introduction

Esterification of carboxylic acids with alcohols in the presence of acid catalysts has been the subject of investigation by many research workers [1–8].

Conversions for esterification reactions have long been known to be limited by a slow reaction rate and the existence of reversible reactions. For this reason, both homogeneous and heterogeneous catalysts have been used to accelerate the reaction rate.

While the mineral acids can be given as the example of the homogenous catalyst, a cation-exchange resin in the acid form can serve as a heterogeneous catalyst [7,9–13]. Catalysts are always employed in a liquid phase esterification. Despite a strong catalytic effect, the use of homogeneous catalyst, e.g., sulfuric acid, suffers from drawbacks, such as the existence of side reactions, equipment corrosion. In many reactions ion exchangers have been found to offer better selectivity towards the desired product(s) compared to homogeneous catalysts [6,14–16]. The use of ion-exchange resins as solid catalysts have many advantages over homogeneous acid catalysts. They can be separated from liquid reaction mixture

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by filtration or decantation and have high selectivity [10–12,17].

The ester of isobutanol, namely, isobutyl acetate, finds wide industrial applications. Butyl acetates are used primarily as solvents in the lacquer and enamel industries. It is used in coatings, where its solvent capacity and its low relative volatility make it useful for adjustment of evaporation rate and viscosity. It is particularly useful as a solvent or thinner for acrylic polymers, vinyl resins, as reaction medium for adhesives, as solvent for leather dressings, and a process solvent in various applications and in cosmetic formulations [7,18,19].

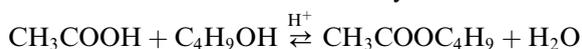
Zang and co-workers have studied kinetics of esterification of lactic acid with ethanol over different kinds of cation exchange resins. They investigated the order of catalytic activity of resins. They concluded that the order of catalytic activity is as follows; D002 < D001 < Amberlyst-15 < NKC < 002 [5].

In the synthesis of isopropyl lactate, Yadav and Kulkarni have reported the application of heterogeneous catalysts such as Indion-130, Amberlyst-36, Amberlyst-15, Amberlite-120, Dowex 50 W, Filtrol-44, 20% DTPA/K-10 and 20% DTPA/Filtrol-44. According to this paper, Indion-130, Amberlyst-36 and Amberlyst-15 were found to be effective in catalyzing the reaction [20].

Gel type Dowex 50Wx8 as a solid catalyst was used to study the effects of the particle size, the amounts of catalyst on the esterification reaction by Sharma et al. They found that the internal mass-transfer resistance could be neglected and the conversion could be enhanced in a smaller particle size of the resin [21].

Mazzotti and co-workers carried out a quasi-homogeneous kinetics model for the esterification of acetic acid to ethyl acetate in presence of Amberlyst 15 ion exchange resin catalyst. They assumed that the reaction occurs only in the polymer phase, and that the bulk liquid and polymer phases are in constant equilibrium conditions [22].

In the present study, the esterification of acetic acid with isobutanol, without adding a catalyst and heterogeneously catalyzed, were carried out, and this reaction can be shown by:



The effects of reaction temperature and catalyst type, stirrer speed, and catalyst loading on the initial reaction rate were investigated. Experimental reaction rates were correlated by pseudo-homogeneous

model for the esterification reaction system catalyzed by Dowex 50 Wx2 ion exchange resin. A comparison of two acid ion-exchange resins was made for synthesis of isobutyl acetate.

2. Experimental section

2.1. Chemicals

Acetic acid and isobutanol were purchased from Merck with a claimed purity of 99.8% and 98.5%, respectively. The reactions were realized in the solution of dioxan of 99.8% purity (Carlo Erba).

2.2. Catalysts

Ion exchange resins which were used in this study were purchased from Rohm and Haas Co. and Dow Chemical Co. These are cross-linked three-dimensional structures of polymeric material obtained by sulfonation of a copolymer of polystyrene and divinyl benzene. These resins are heat-sensitive and lose activity above temperatures given in Table 1. The specific surface area (BET), average pore diameter and total pore volume were determined on a Quantochrome Autosab 1-C instrument. Surface area and pore size distribution analysis for all samples was carried out by the N₂ adsorption/desorption method at 353 K. For the determination of BET surface area the value of p/p_0 in the range $0.01 < p/p_0 < 0.15$ was used. The catalysts were first pre-treated. Dowex 50 Wx2 was dried under vacuum at 348 K over night after washing with deionized water to eliminate poisoning or fouling. On the other hand, Amberlite IR-120 was dried at 363 K over 48 h to remove moisture completely after being washed with methanol and then deionized water. The properties of the catalysts used at the present work are listed in Table 1. Then these resins were stored under air-tight conditions before use.

2.3. Apparatus and procedure

Esterification of acetic acid with isobutyl alcohol was carried out in thermostatic stirrer batch reactor of 150 mL capacity. A reflux condenser was placed on top of the reactor in order to prevent the escape of volatile compounds. The total liquid volume in the experiments was 100 mL. Experiments were performed with a feed mole ratio (acetic acid to isobutyl alcohol) at a temperature of 318–348 K, 5 g dry

Table 1
Physical and chemical properties of ion exchange resins

Physical property	Dowex 50 Wx2	Amberlite IR 120
Matrix type	Styrene-DVB	Styrene-DVB
Operating pH	0–14	0–14
Ionic form	H ⁺	H ⁺
Total exchange capacity		
(a) meq/g (dry)	4.8	4.4
(b) meq/ml (wet)	0.6	1.9
Moisture (%)	~78	44–48
Crosslinkage (% DVB)	2	8
Max. operating temperature (K)	423	393
Particle size (μm)	80–150	300–840
Surface area (m ² g ⁻¹)	6.940	1.532
Total pore volume (cm ³ /g)	1.48 × 10 ⁻²	1.10 × 10 ⁻²
Average pore diameter (Å)	85.34	288.5

resin L⁻¹ catalyst loading, and a stirrer speed of 500 rpm.

Ion exchange resin and 1,4-dioxan of known amount were charged into stirring batch reactor and also, in predetermined amount of isobutyl alcohol added into the reactor. After reaching desired temperature, acetic acid was drained in the reactor. This was considered as the starting time of the reaction. In experiments relating to the “catalyst loading” and “speed of agitation”, 3 samples were withdrawn. On the other hand, in time-conversion experiments about 10 samples were withdrawn each has a volume of 1 mL for GC analysis. Therefore, the concentration change due to the volume change can be neglected.

2.4. Analysis

All samples were analyzed by gas chromatography (Agilent 6890 instrument with FID; N₂ as the carrier gas; DB-WAX 30 m × 0.53 mm column; split 10:1). The injector and detector were kept at 523 K. The oven temperature was controlled from 363.15 to 473.15 K. Initial column temperature was 313 K for 5 min. Temperature was increased from 313 K to 463 K by 10 K/min and maintained at 463 K for 1 min. *m*-Xylene is used as an internal standard for quantitative analysis of samples.

Water contents of samples were analyzed by Karl Fischer method (Schott TA05 Plus).

3. Results and discussion

The esterification reaction of acetic acid with isobutanol was studied in a batch reactor in the pres-

ence of acidic ion exchange resin catalysts, Dowex 50 Wx2 and Amberlite IR-120 and without adding a catalyst. A pseudo-homogeneous reaction model has been used to describe the esterification reaction catalyzed by Dowex 50 Wx2 ion-exchange resin because Dowex 50 Wx2 resin has higher activity than Amberlite IR-120 resin. The effects of temperature, catalyst loading, catalyst type and the speed of agitation were studied.

3.1. Catalyst performance

In Fig. 1, a comparison of the behavior of the Dowex 50 Wx2 and Amberlite IR-120 catalysts as catalyst is shown. Catalysts were used to assess their efficacy in the esterification reaction of acetic acid with isobutanol. Dowex 50 Wx2 and Amberlite IR-120 were shown to be effective catalysts as to without adding resins in order to synthesize isobutyl acetate. The catalytic activity of Dowex 50 Wx2 has higher activity than Amberlite IR-120. It is an expected result due to Dowex 50 Wx2 has higher total exchange capacity, surface area and pore volume than Amberlite IR-120.

3.2. Effect of temperature

In esterification reaction, the investigation on the effect of temperature is very important because this

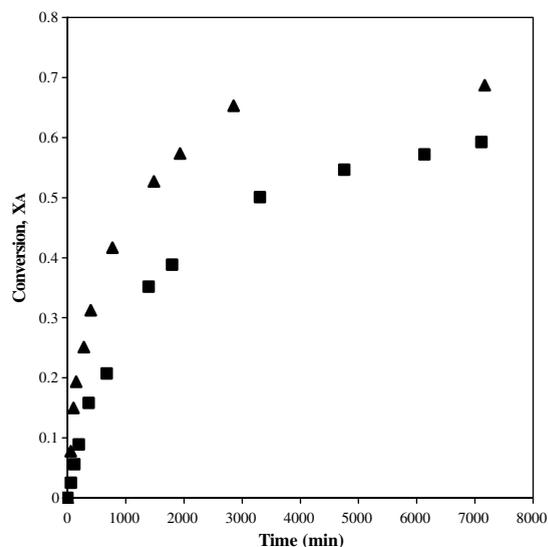


Fig. 1. Effect of different resins on the conversion of acetic acid. Resin loading = 5 g dry resin/L, mole ratio (acetic acid/isobutanol) = 1:1, $T = 333$ K, speed = 500 rpm, ▲, Dowex 50 Wx2; ■, Amberlite IR-120.

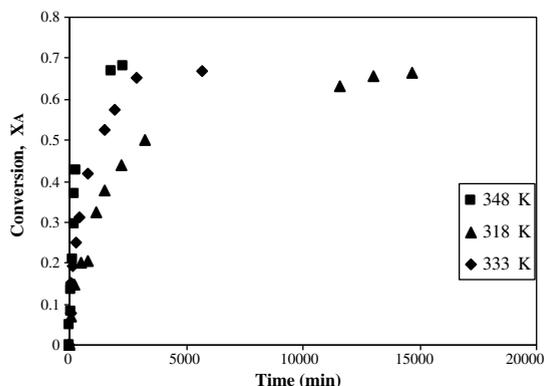


Fig. 2. Effect of temperature on conversion of acetic acid. Resin loading = 5 g dry resin/L, mole ratio (acetic acid/isobutanol) = 1:1, speed = 500 rpm, Resin: Dowex 50 Wx2.

information is useful in calculating the activation energy. In order to investigate the effect of temperature, esterification reactions were carried out in the temperature region 318–348 K while keeping the acid: alcohol molar ratio at 1:1 and the catalyst weight at 5 g dry resin L⁻¹ (Fig. 2). With an increase in reaction temperature, the initial reaction rate or the conversion of the acetic acid was found to increase substantially. It shows that the higher temperature yields the greater conversion of acetic acid at a fixed contact time.

3.3. Effect of catalyst loading

The effect of catalyst loading on the conversion of acetic acid or the initial reaction rates and is represented in Fig. 3. Catalyst loading was varied from 0.5 g to 1.5 g at a temperature of 333 K, feed mole ratio of 1:1, and stirrer speed of 500 rpm. It was seen that the conversion of acetic acid increased with an increase in the catalyst loading. Thus, the time required to reach the reaction equilibrium was reduced owing to the increase in the total number of acid sites available. But the catalyst loading does not have any effect on the equilibrium conversion.

3.4. Elimination of mass transfer resistance

The effect of the speed of agitation on the initial reaction rate and conversion was carried out at four different speeds 400, 500, 600, 700 rpm to examine the influence of an external mass transfer effect and the results obtained were shown in the Figs. 4 and 5. It is clear that there was very little effect of speed of agitation in the range 400–700 rpm on

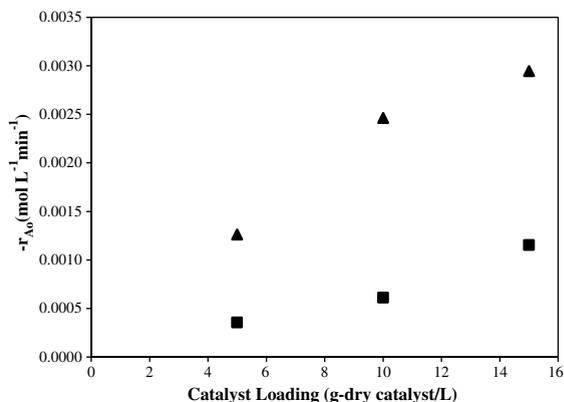


Fig. 3. Effect of resin loading on the initial reaction rate. Mole ratio (acetic acid/isobutanol) = 1:1, $T = 333$ K, speed = 500 rpm, ▲, Dowex 50 Wx2; ■, Amberlite IR-120.

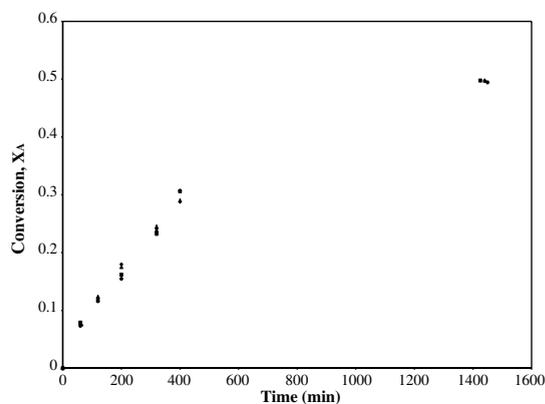


Fig. 4. Effect of speed of agitation on the conversion of acetic acid. Resin type: Dowex 50 Wx2, mole ratio (acetic acid/isobutanol) = 1:1, $T = 333$ K, Resin loading = 5 g dry resin/L; ●, 400 rpm; ■, 500 rpm; ▲, 600 rpm; ◆, 700 rpm.

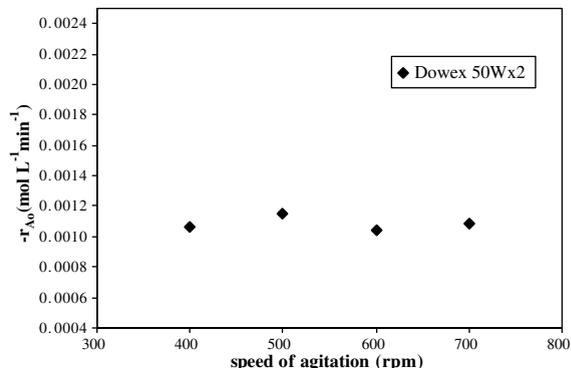


Fig. 5. Effect of speed of agitation on the initial reaction rate. Resin type: Dowex 50 Wx2, Resin loading = 5 g dry resin/L, $T = 333$ K, mole ratio (acetic acid/isobutanol) = 1:1.

the overall initial rate of the reaction. This implies that there was no resistance to mass transfer of acid to the external surface of the catalyst. Previous studies pointed out that if not the viscosity of the reactant mixture is very high or the speed of agitation is very low, the external diffusion does not generally control the overall rate in the ion exchange resin [23–25]. Therefore, all experiments were conducted at 500 rpm.

It was also reported from previous studies that intraparticle diffusion resistances of the reactant in the ion exchange resin are not important [2,4]. Hence, all experiments were conducted with the ion exchange resin that was supplied by manufacturer (Rohm and Haas Co. and Dow Chemical Co.) without any size screening.

3.5. Kinetic model

A pseudo-homogeneous model can be effectively applied to correlate the kinetic data of the liquid–solid catalytic reaction. The esterification reactions are known to be reversible reactions of second-order [13,15,26,27]. The general reaction rate expression can then be written as

$$-r_A = -\frac{dC_A}{dt} = k_1 \left(C_A \cdot C_B - \frac{C_E \cdot C_W}{K} \right) \quad (1)$$

where subscripts *A*, *B*, *E* and *W* refer to acid, alcohol, ester and water, respectively, k_1 is forward reaction rate constant, K is the equilibrium constant of the reaction.

Eq. (1) can be integrated to give the following equation while keeping the acid: alcohol molar ratio at 1:1, the catalyst weight at 5 g dry resin L⁻¹ and without catalyst.

$$\ln \left(\frac{X_{Ac} - (2X_{Ac} - 1)X_A}{X_{Ac} - X_A} \right) = 2k_1 \left(\frac{1}{X_{Ac}} - 1 \right) C_{A0}t \quad (2)$$

where X_A , fractional conversion of reactant A; X_{Ac} , fraction of the equilibrium conversion of reactant A which was found to be independent of temperature ranging from 318 to 348 K, is about 0.667.

Plotting of left-hand-side of Eq. (2) versus time, a straight line with the slope of $2k_1 \left(\frac{1}{X_{Ac}} - 1 \right) C_{A0}$ is obtained for the bimolecular type second order reactions [28]. These lines were presented in Fig. 6 (in the presence of Dowex 50 Wx2) and in Fig. 7 (without adding a catalyst). The values of k_1 in

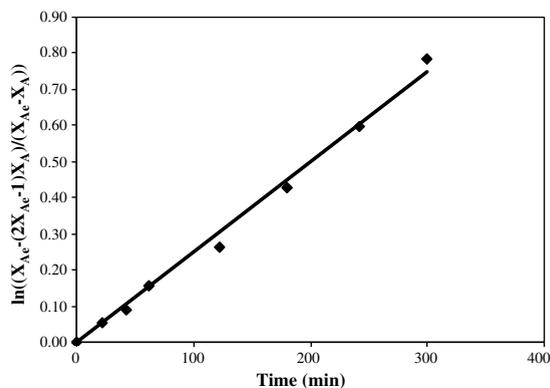


Fig. 6. LHS of Eq. (2) versus time at 348 K. Resin type: Dowex 50 Wx2, mole ratio (acetic acid/isobutanol) = 1:1, speed = 500 rpm, Resin loading = 5 g dry resin/L.

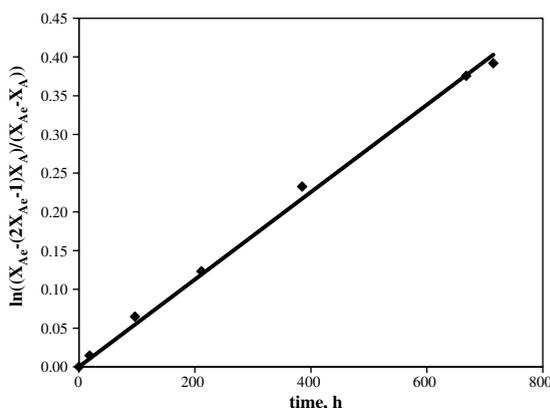


Fig. 7. LHS of Eq. (2) versus time at 348 K. Resin type: without resin, mole ratio (acetic acid/isobutanol) = 1:1, speed = 500 rpm.

Table 2

The values of k_1 for different temperatures

T (K)	k_1 ($1 \text{ mol}^{-1} \text{ min}^{-1}$) $\times 10^3$
318	0.24
333	1.00
348	3.07

the presence of Dowex 50 Wx2 for different temperatures are given in Table 2.

The temperature dependency of the rate constant is expressed by the Arrhenius law:

$$k_1 = k_1^0 \exp \left(\frac{-E_A}{RT} \right) \quad (3)$$

where E_A , activation energy; k_1^0 , frequency factor.

From Eq. (3), A plot of $-\ln k_1$ versus $1/T$, at constant acid and alcohol concentrations, gives a straight line with the slope of (E_A/R) as shown in

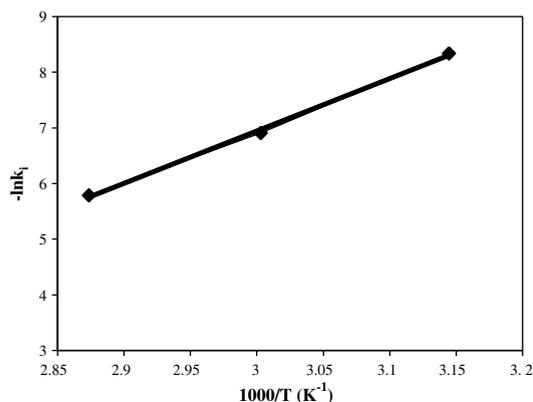


Fig. 8. Arrhenius plot of the rate constants.

Fig. 8. The activation energy was found to be $1.745 \text{ kJ mol}^{-1}$ in the presence of Dowex 50 Wx2 ion exchange resin. This value was obtained as 59.3 kJ mol^{-1} in the absence of resin. In other words, in the absence of catalyst, the reaction proceeds quite slowly.

3.6. Calculation of experimental equilibrium constant

The apparent equilibrium constant of the esterification reaction can be obtained from the equilibrium conversion determined experimentally and using Eq. (4),

$$K = \frac{C_{\text{Ee}}C_{\text{We}}}{C_{\text{Ac}}C_{\text{Be}}} = \frac{X_{\text{Ac}}^2}{(1 - X_{\text{Ac}})^2} \quad (4)$$

The equilibrium constant, being independent of temperature ranging from 318 to 348 K, was determined to be 4 for mole ratio $M = 1/1$.

4. Conclusions

Solid acid catalysis is very effective from the point of view of activity and reusability compared with homogeneous catalysts [29]. In this study two solid catalysts, Dowex 50 Wx2 and Amberlite IR-120 were used to examine their reactivity towards the synthesis of isobutyl acetate via the esterification of acetic acid and isobutanol. Comparison of these catalysts shows that catalytic activity of Dowex 50 Wx2 has higher activity than Amberlite IR-120. It is an expected result due to Dowex 50 Wx2 has higher total exchange capacity, surface area and pore volume than Amberlite IR-120. Therefore, the kinetic study for the synthesis of isobutyl acetate was carried out in the presence of Dowex 50 Wx2

ion exchange resin, at reactants mole ratio of 1:1 and in temperatures ranging 318–348 K. It was observed that initial reaction rate increases with the increasing of reaction temperature and catalyst loading. It was also found that the speed of agitation has no effect on the reaction rate. It was proposed that catalyst size has no effect on the reaction rate [2,4,21]. In this study a single size of catalyst was used. It was shown that pseudo-homogeneous model can be effectively applied to correlate the kinetic data of the liquid–solid catalytic reaction. The activation energy was found to be 1.745 kJ/mol in the presence of Dowex 50 Wx2 ion exchange resin. Whereas this value is 59.3 kJ/mol in the absence of resin. It means that Dowex 50 Wx2 ion exchange resin has very high activity in the synthesis of isobutyl acetate.

As for the equilibrium conversion, which is independent between temperatures 318–348 K, was found to be about 0.667 and equilibrium constant was calculated to be 4. The kinetic equation developed in this study can be used in the design of the reactive distillation process for purification of acetic acid.

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