Synthesis of isobutyl propionate using Amberlyst 15 as a catalyst
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Synthesis of isobutyl propionate using Amberlyst 15 as a catalyst

A. Alime Izci,[a] B. Halit L. Hosgun,[a]

[a]*Department of Chemical Engineering, University of Eskisehir Osmangazi, 26480 Eskisehir, Turkey.*

Abstract

In this study, the adsorption equilibrium constants of adsorbed species and the kinetic parameters of the reaction of isobutanol with propionic acid were investigated. Experiments were carried out in a stirred batch reactor using dioxan as a solvent. The reaction has been catalyzed heterogeneously by an acidic ion-exchange resin (Amberlyst 15). The chemical equilibrium composition was measured at temperature ranges of 318-348 K and kinetic information was also obtained at the same temperature intervals at various starting compositions of the reactants and products. For this reaction, the mechanism was found to follow the Eley-Rideal theory in which an adsorbed and protonated propionic acid molecule reacted with an isobutanol molecule in the bulk. The rate limiting step is the surface reaction. Using experimental data and reaction equilibrium equations, the esterification reaction concentration based equilibrium constants were calculated at the same temperature ranges. The activation energy of the esterification reaction was found to be 42.5 kJ/mol. The heat of adsorption for isobutanol and water was also calculated as -36.9 kJ/mol and -48.7 kJ/mol, respectively.

Keywords: Esterification, Heterogenous Catalyst, Isobutyl propionate, Kinetics

1. Introduction

Esterification reactions are one of the industrially important reactions. Esters, product of these reactions, widely used in chemical industry such as solvents of paints, adhesives, plasticizers, flavours and fragrances, pesticide and emulsifiers. In order to start the esterification reaction, a proton transfer from acid catalyst to the alcohol and forms an alkyloxonium ion. Acid is protonated on its carbonyl oxygen. Nucleophilic addition of a molecule of the alcohol to carbonyl carbon of acid forms an intermediate product. This intermediate product is protonated on one of its hydroxyl oxygens. Intermediate product loses a water molecule and proton to give an ester (1-7).

Esterification reaction can be realized in the absence of catalysts, it is extremely slow, because of autoprotolysis of the carboxylic acid. Catalyst such as mineral acid, p-toluen sulphonic acid and ion exchange resins are always used in liquid phase esterification reactions to raise the product yield (8-10). Although homogeneous catalysts have high catalytic activity, using the heterogeneous solid

catalysts can eliminate many of the disadvantages involved with use of homogeneous catalysts: generation of side products, posing environmental and corrosion problems and separation of the pure product from the homogeneous catalyst (11-15).

Several works have reported the kinetics of the esterification reaction in the presence of ion exchange resin. Yu et al, 2004 studied esterification of acetic acid with methanol using Amberlyst 15 as a catalyst. Authors obtained the adsorption equilibrium constants, dispersion coefficients, and kinetic parameters and suggested a mathematical model for a quasi-homogeneous kinetics (16). Huang and Sundmacher, 2007 investigated the reaction between acetic acid and n-propanol catalyzed by Amberlyst 15. They reported that pseudo-homogeneous, Rideal-Eley and Langmuir-Hinshelwood-Hougen-Watson kinetic models were developed to evaluate the obtained kinetic data (17). Gangadwala et al. 2003 studied the esterification of acetic acid with n-butanol in the presence of Amberlyst-15. They have investigated the influence of various parameters and proposed the rate equation model. Authors also investigate the kinetics for the side-reaction etherification (18). Synthesis of n-butyl acetate has also studied by Blagow et al. 2006. In this study, three ion-exchange resin catalysts (Purolite CT 269, Amberlyst 46, and Amberlyst 48) were compared (19). Lee et al. 2000 choose the Dowex 50 Wx8 as a catalyst in their esterification reaction between acetic acid and amyl alcohol. They showed the kinetic data were correlated with the quasi-homogeneous, Langmuir-Hinshelwood, Eley-Rideal, and modified Langmuir-Hinshelwood models (20). Ali et al. 2007 also use Dowex 50 Wx8 as a catalyst the reaction of propionic acid with 1-propanol. Several kinetic models were tested to correlate the kinetic data by the authors (21). Liu and Tan, 2001 were takes place the esterification of propionic acid with n-butanol catalyzed by Amberlyst 15, Amberlyst 35, Amberlyst 39 and HZSM-5 pellets. Rideal-Eley theory was found the possible mechanism to kinetic data obtained from the reaction catalyzed by Amberlyst 35 (22).

Esterification of propionic acid with isobutanol over Amberlyst 15 catalyst has never been reported before. The catalytic esterification reaction of propionic acid and isobutanol to form isobutyl propionate and water is given by

Isobutanol (IB) + Propionic Acid (PA) ↔Isobutyl Priopionate (IBP) + Water (W) (1)
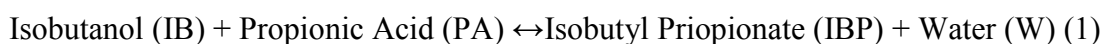
The objective of this study is to develop a kinetic model and rate expression which describes an esterification reaction of propionic acid and isobutanol over Amberlyst 15.

2. Experimental Section

2.1. Chemicals

Propionic acid and isobutanol were obtained from Merck AG. Propionic acid of 99%, isobutanol of 98.5% purity was used as obtained. The reactions were carried out in the solution of dioxan of 99.8% purity (Carlo Erba).

2.2. Catalyst

The acidic ion exchange resin (Amberlyst 15 of Rohm and Haas Co.) was obtained from Sigma AG. Amberlyst 15 was washed with methanol and distilled water, then vacuum-dried at 348 K the over night. The properties of catalysts were given in Table 1.

Table 1. Properties of Amberlyst 15

Matrix Type	Styrene-DVB
Operating pH	0-14
Ionic Form	H^+
Total Exchange Capacity	
a)mEq/g(dry)	a)4.7
b)mEq/ml(wet)	b)1.7
Temperature Stability (K)	393
Crosslinkage (% DVB)	20-25
Particle Size	600-850 μm

2.3. Apparatus and Procedure

The experiments were conducted in a two-necked glass reactor of 400 mL capacity. This reactor was equipped with an outer circulating heating jacket to maintain constant temperature inside the reactor and a reflux condenser to prevent the vaporization of reaction mixture. The temperature of the mixture was kept constant within ± 0.1 K by circulating water from a water bath (Julabo MC6). The reaction mixture was magnetically stirred at 1000 rpm. In a typical run, catalyst, isobutanol and solvent (dioxan) were charged into the reactor and heated to desired temperature. Propionic acid, at the same temperature, was poured finally and this time was taken as zero time for a run. Samples were taken periodically.

2.4. Analytical Methods

Samples were taken periodically and analysed by a gas chromatograph (HP 6890) equipped with a flame ionisation detector (N_2 as the carrier gas; DB-WAX 30 m × 0.53 mm column; split 10:1). GC analysis confirmed that no by-products were formed. Water contents of samples were analyzed by Karl Fischer method (Schott TA05 Plus).

3. Results

In a heterogeneous catalytic reaction, there are seven steps (23): mass transfer (from bulk to catalyst external surface), diffusion (from external surface to internal surface of catalyst), adsorption, surface reaction, desorption, diffusion, mass transfer (from the external surface to bulk). The slowest step determines the overall rate of reaction. A typically mechanism involve an adsorption step, a surface reaction step and a desorption step. Before we proposed a mechanism, we have to determine which reactants adsorbed on the catalyst surface. For this purpose, we conducted several experiments. Initial reaction rates obtained from these experiments were plotted versus the initial concentrations of reactants. Initial reaction rates can be calculated as follows:

$$-r_{A0} = \frac{\Delta C}{\Delta t} \tag{2}$$

Effects of initial concentration of propionic acid, isobutyl alcohol, water, and isobutyl propionate on the initial reaction rate are illustrated in Fig. 1-4, respectively.
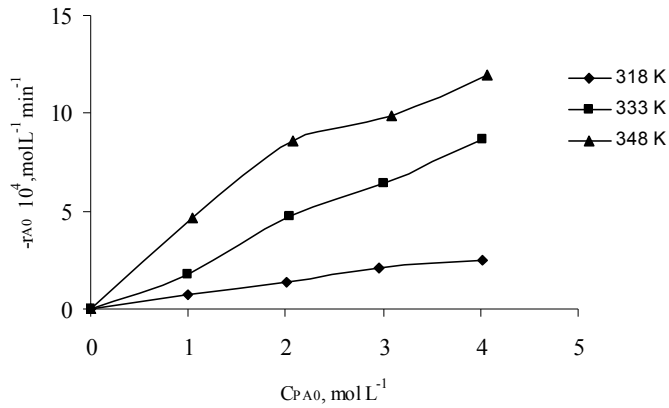
Fig. 1 Effect of initial concentration of propionic acid (1000 rpm,, $m_{cat} = 4$ g).

As seen in Fig. 1, the initial reaction rates increases linearly with the increasing of initial propionic acid concentrations. Fig. 2 is similar to Langmuir isotherm. Increasing of initial concentrations of alcohol after definite concentrations, initial reaction rate almost stabilized.
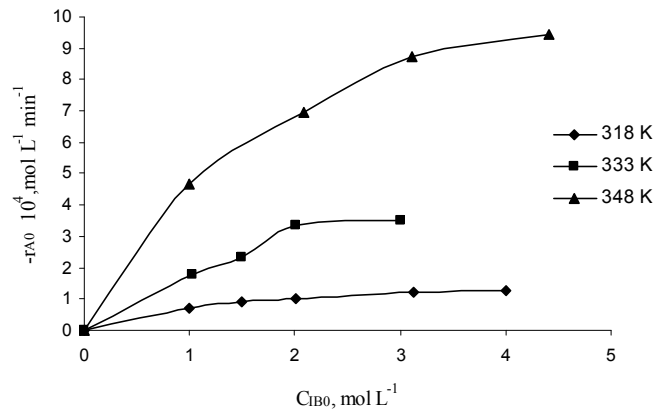

Fig. 2 Effect of initial concentration of isobutyl alcohol (1000 rpm,, $m_{cat} = 4$ g).
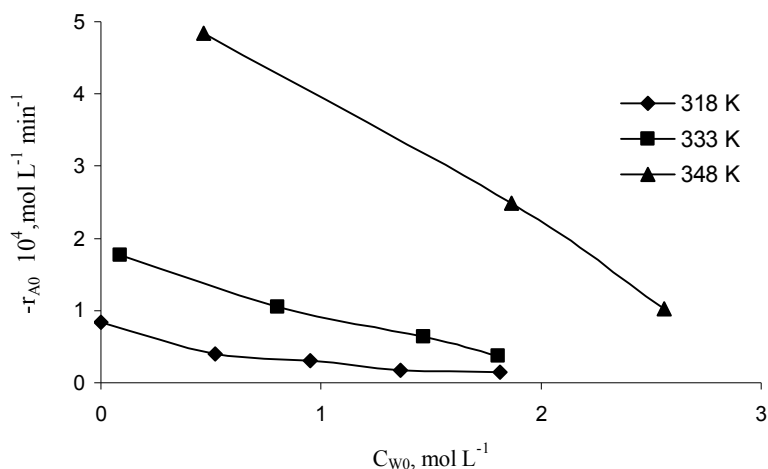
Fig. 3 Effect of initial concentration of water (1000 rpm,, $m_{cat} = 4$ g).

It is clearly show that inhibiting effect of water in Fig. 3. Initial reaction rate decreased to adding of water. Fig. 4 shows that initial reaction rates independence of isobutyl propionate concentrations. There is no inhibiting effect of ester molecules.
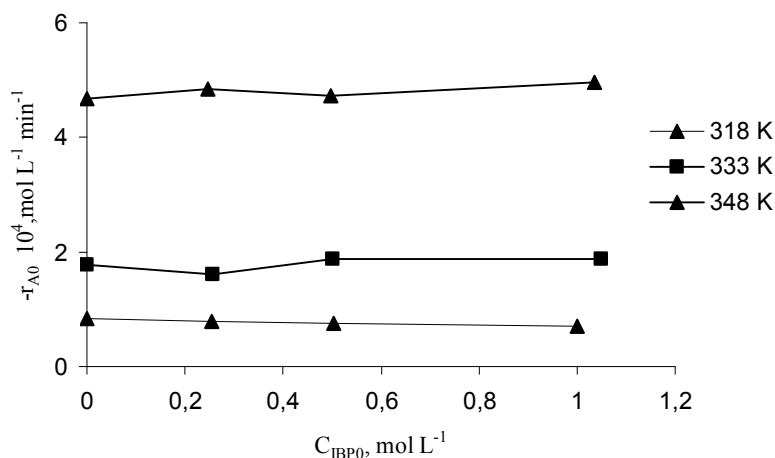

Fig. 4 Effect of initial concentration of isobutyl propionate (1000 rpm,, $m_{cat} = 4$ g).

According to these conclusions, while water and isobutyl alcohol were adsorbed on the catalyst surface, propionic acid and isobutyl propionate were not adsorbed. Reaction occurred between adsorbed alcohol molecules and acid molecules in the bulk at the catalyst surface (Eley-Rideal). The mechanism related to esterification reaction between propionic acid and isobutyl alcohol can be written:

$$IB + S \leftrightarrow IB.S \tag{3}$$
$$IB.S + PA \leftrightarrow IBP + W.S \tag{4}$$
$$W.S \leftrightarrow W + S \tag{5}$$

where S represents to vacant sites of catalyst surface. Fig 1-4 also display that reaction is very sensitive to temperature. Therefore, assuming the surface reaction control was done. The overall rate of reaction taking into account of all assumptions can be given by

$$-r = \frac{k_f \dfrac{m}{V}(C_{PA}C_{IB} - \dfrac{C_{IBP}C_W}{K_e})}{1 + K_{IB}C_{IB} + K_W C_W} \qquad (6)$$

where k_f is the forward reaction rate constant, K_e is the overall reaction equilibrium constant, K_{IB} and K_W are the adsorption equilibrium constant, m is the amount of dry catalyst and V is the volume of reaction mixture. In order to calculate the rate constant and equilibrium constants, Eq. 6 was rearranged. The procedure of determination of these constants was described in detail a previously work (11, 24). Applying the Arrhenius equation to the values obtained from experiments, the temperature dependency of the constants was found to be:

$k_f = \exp(5.706 - 5361/T)$ $L^2 (\text{g- dry resin})^{-1}.\text{mol}^{-1}.\text{min}^{-1}$ (7)
$K_B = \exp(3496/T - 11.455)$ $L.\text{mol}^{-1}$ (8)
$K_W = \exp(4000/T - 11.065)$ $L.\text{mol}^{-1}$ (9)

The activation energy of the esterification reaction was found to be 42.5 kJ/mol. The heat of adsorption for isobutanol and water was also calculated as -36.9 kJ/mol and -48.7 kJ/mol, respectively.

4. Conclusions

The kinetic behavior has been investigated experimentally for the synthesis of isobutyl propionate using Amberlyst 15 as a catalyst. The experimental data were obtained in a batch reactor within the temperature range 318–348 K. The reaction has been found to takes place between an adsorbed alcohol molecule and a molecule of acid in the bulk phase (Eley–Rideal model). It is also observed that water has inhibiting effect of reaction. Temperature dependency of the kinetic constants (k_f, K_{IB} and K_W) has found to applying Arrhenius equation. The activation energy of the esterification reaction was found to be 42.5 kJ/mol. The heat of adsorption for isobutanol and water was also calculated as -36.9 kJ/mol and -48.7 kJ/mol, respectively.

5. Acknowledgment

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