

Kinetic Study of Esterification Reaction for the Synthesis of Butyl Acetate

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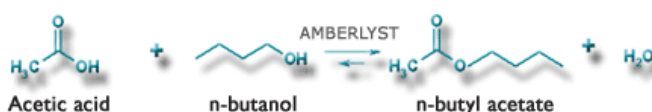
ABSTRACT

The reaction kinetics of the esterification of acetic acid with butanol, catalyzed both homogeneously by the acetic acid, and heterogeneously by Amberlyst 15, have been investigated. The reactions were carried out in a batch reactor at several temperatures between 353.15 and 383.15K and at various starting reactant compositions ranging from stoichiometric regime to the dilute regions. Homogeneous and heterogeneous reactions have been described using the models proposed by P'opken et al. [T. P'opken, L. G'otze, J. Gmehling], Here we have been used Pseudo Homogeneous model to fit the experimental data and found out the activation energies and equilibrium constants for this reaction will be determined experimentally at different temperatures which has been in the range of back experimental data available. The temperature dependency of the constants appearing in the rate expression will also be determined.

Key Words: Esterification, Kinetics, Heterogeneous Catalyst, Butyl Acetate.

Introduction

In order to determine the kinetics of the esterification reaction, few experiments were conducted in a mechanically stirred batch reactor. Extensive reviews on reactions catalyzed by cation exchange resin have appeared in the literature (e.g. Chakrabarti and Sharma, 1993). The use of ion exchange resin as catalyst for esterification reaction has been well studied (e.g. Gelosa et.al., 2003; Mahajani, 2000; Gangadwala et. al., 2003; Teo and Saha, 2004). The kinetics of esterification of acetic acid with n-butanol in the presence of Amberlyst- 15 has also been reported (B. RabindramJermy, A. Pangurangam 2005, 2001). We study the kinetics of this reaction under the conditions of interest. The effect of various parameters like speed of agitation, temperature, mole ratio of reactants and catalyst loading has been investigated. Butyl acetate is an important chemical with an application as versatile solvent. It is used in large quantities as solvent for plastics, liquors, resins, gums and coatings. It is particularly useful as solvent for leather dressing, for extraction and for various applications. It may also be used in photographic industry as a reaction medium for adhesive and in the cosmetic formulations. n-Butanol and acetic acid in the presence of Amberlyst-15 as cation exchange resin catalyst can be represented as follows;



The esterification of BuOH and acetic acid to form butyl acetate (BA), like other esterification reactions, is reversible. The reaction being reversible, the simultaneous removal of product would shift the reaction in forward direction and reduce the load on downstream processing. The reaction proceeds slowly, usually requiring many hours to reach equilibrium. According to Le Chatelier's principle, the yield of ester may be increased by increasing the concentration of either reactant. In this experiment, an excess of the carboxylic acid is used. Since reactions go faster at higher temperatures, the esterification is conducted at the boiling point of the reaction mixture. This is accomplished by refluxing, that is, by boiling the mixture, condensing the vapor in a water-cooled condenser, and returning the liquid to the reaction flask. Reactive distillation can be a suitable option for this system. We study the kinetics of this reaction under the conditions of interest. The effect of various parameters like temperature, mole ratio of reactants and catalyst loading has been investigated.

Experimental:

Chemical and catalysts:

All chemicals and catalysts were procured from firms of repute and used without further purification: Butanol, Acetic acid (S.D. Fine Chemicals, Mumbai India), Amberlyst-15 (Rohm and Hass, USA). The physical properties of these resins are reported in Table 1. The macroporous resin was dried at 75°C for 6 hrs in vacuum drier before use. In all the experiment, the dried catalyst was used.

Reaction Procedure:

Apparatus and Procedure:

The esterification reaction was performed in a glass reactor of 7.5 cm. internal dia. and 9 cm. height with four glass baffles and four bladed disc turbine impeller located at a height of 0.5 cm. from the bottom of the vessel and mechanically agitated with an electric motor. The reactor was immersed in a constant temperature oil bath, the temperature of which was maintained within ± 1 K of the set point. The reactor was equipped with temperature monitoring facility. Fig. shows the Batch Reactor set up. The catalyst was dried at 75 °C under vacuum for 48 hrs before use. The measured quantities of acetic acid and BuOH and catalyst were taken and charged to the reactor separately. Firstly, the quantities of BuOH were taken into reactor and the reactor was dipped in the constant temperature oil bath to reach desired temperature. Side by side acetic acid is heated in other reactor up to same temperature. Once the desired reaction temperature was attained, the catalyst and acetic acid were added to this reactor and this time was considered as zero reaction time. For kinetic measurements, the samples of reaction mixture were removed after specific interval of time and analyzed. The experiments were carried out to study the effect of different parameters such as temperature, catalyst loading, mole ratio of reactants, stirrer speed. The volume of the sample withdrawn from the reactor during a run was negligible compared with the total volume of the system. The total volume of system was around 200 ml.

Table 1: Range of operating conditions:

| Parameter | Range |
|-------------------------------------|---------------------|
| Reaction temperature, K | 343, 353, 363 |
| Agitaitaion speed, rpm | 800, 1000, 1200 |
| Catalyst loading, kg/m ³ | 5, 10, 20 |
| Mole ratio (Butanol:Acetic acid) | 1:1, 1:2, :1:3, 2:1 |

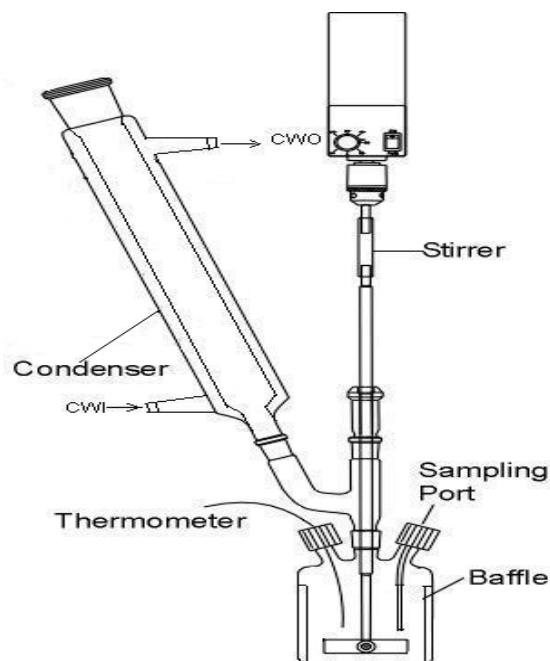


Figure 1: Experimental Set up

Analysis

The analysis of the reactants and products of esterification reaction of acetic acid and butanol was carried out using gas chromatography. Gas chromatograph (GC-911 MakAnalytica India Ltd.) equipped with Thermal Conductivity Detector was used to analyze the samples for water content. A 2 m long packed column Porapack-Q with hydrogen as a carrier gas at a flow rate of 20 ml/min, was used to separate the different components of the reaction mixture using butyl acetate as an internal standard. Injector and detector temperatures were maintained at 220°C and 150°C, respectively. Oven temperature was suitably programmed to get the best resolution and the least time for analysis. Oven temperature was maintained isothermally at 240°C for 4 minutes. The retention times of all the individual components were confirmed by the respective authentic samples. The conditions are listed below:

| | |
|------------------------------|-----------|
| Oven temperature : | 240 °C |
| Injector temperature: | 220 °C |
| Detector temperature (TCD): | 150 °C |
| Carrier gas flow (Hydrogen): | 20 ml/min |

Reaction Kinetics:

Effect of presence of catalyst :

The catalytic activity of the resin was first tested qualitatively through two experiments with different catalytic conditions. In the first one, a non-catalyzed reaction was conducted in a homogeneous liquid phase; in the second, the commercial resin Amberlyst-15 was used. Both the reactions are carried out at 90°C, 1:2 molar ratio of BuOH and acetic acid at 1000 rpm speed of agitator. For the reaction with catalyst 5gm of catalyst dried under vacuum for 8 hrs at 343 K was used. Esterification reaction can takeplace even in the absence of the catalyst due to the weak acidity of acetic acid itself. However, it was observed that the reaction is extremely slow. From Fig.2, it can be seen that the reaction takes place even in the

absence of the catalyst but the rate is very low. After about 3 hrs, when the catalyzed processes have already reached equilibrium, the conversion achieved in the non-catalyzed reaction was 15% while in catalyzed reaction it was 55%. Hence, for all practical the contribution due to self-catalysis was assumed to be negligible.

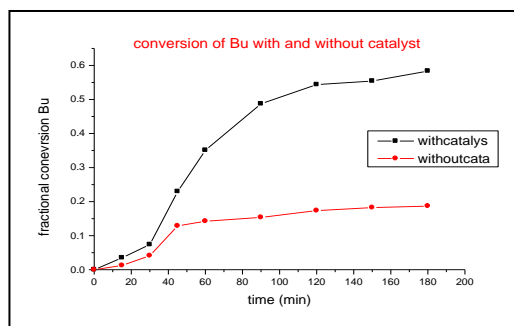


Figure 2: Effect of presence of catalyst: Temperature= 353 K, BuOH: AA mole ratio=1:2, rpm= 1000, catalyst loading= 5 gm/lit

Elimination of mass transfer resistance :

This is typical solid-liquid slurry reaction involving transfer of BuOH and acetic acid from bulk liquid phase to catalyst surface wherein external mass transfer of reactants to surface of the catalyst particle, followed by intra-particle diffusion, adsorption, surface reaction and desorption take place. In this reaction system, there exist two types of mass transfer resistances; one across the solid-liquid interface and the other in the intra-particle region. In order to develop true kinetic model the influence of the external solid-liquid mass transfer resistance and intra-particle diffusion resistance must be ascertained and overcome through the use of proper variable such as speed of agitation, catalyst-particle size.

Effect of speed of agitation:

The speed of agitation was varied to examine the effect of external mass transfer limitations and the role of the intra-particle diffusion, respectively. Experiments were performed at different speeds of agitation over a range 800- 1200 rpm, to examine the effect on external mass resistance.

The experiments were performed at 800,1000 and 1200 rpm speed of agitator at 80°C, 1:2 molar ratio of BuOH and acetic acid and 5 gm/lit catalyst. Fig.3 shows the results obtained over a wide range of speed of agitation (800- 1200 rpm). From the figure, it observed that the conversion obtained is nearly same i.e. 50. It means that the speed of agitation does not have any effect on the rate of reaction or conversion. Hence, all the further runs were conducted at a speed of 1000 rpm.

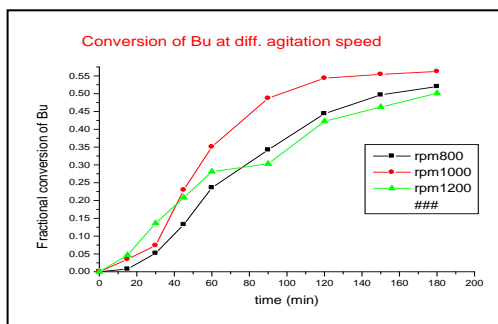


Figure 3: Effect of speed of agitation: Temperature= 353 K, BuOH: AA mole ratio=1:2, catalyst loading= 5gm/lit

Effect of catalyst loading:

In the absence of mass transfer resistance; the rate of reaction is directly proportional to catalyst loading based on the entire volume of the liquid phase. The experiments were conducted with different catalyst loadings i.e. 5 gm, 10 gm, 20 gm at 80°C, 1:2 molar ratio of BuOH and acetic acid and 1000 rpm speed. Fig. 4 shows the effect of catalyst loading on the rate of the reaction. Experiments with different catalyst loadings, under similar conditions, indicated that increase in loading results in an increase in the rate of reaction and fractional conversion because of an increase in number of active sites, which again indicates that mass transfer resistances are absent and the reaction is only controlled by intrinsic kinetics. At higher catalyst loading the rate of mass transfer is excessively high and therefore there is no more increase in the rate.

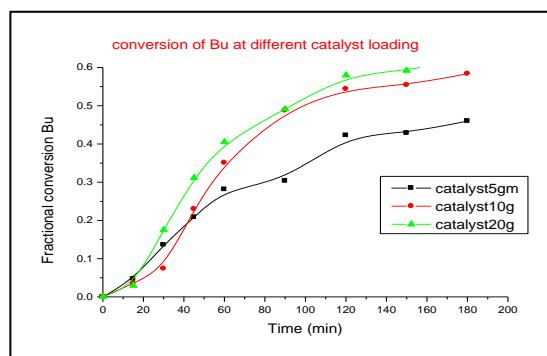


Figure 4: Effect of catalyst loading: Temperature= 353 K, BuOH: AA mole ratio=1:2, rpm=1000

Effect of temperature :

The effect of temperature was studied over a temperature range of 343 K to 363 K. The experiments were carried out at three different temperatures i.e. 343K, 353K and 363K with 1:2 molar ratio of BuOH and acetic acid, 5 gm catalyst, 1000 rpm speed. Results obtained in the Fig.5 indicate that the rate of reaction and conversion are sensitive to a change in temperature. Conversion increases with increase in temperature but equilibrium conversion was found to be insensitive to the changes in reaction temperature indicating that the heat of reaction is not significant.

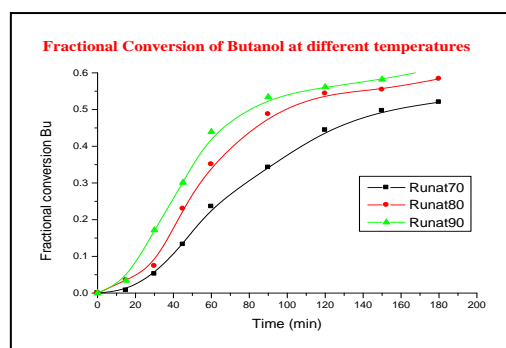


Figure 5: Effect of Temperature: BuOH: AA mole ratio=1:2, rpm=1000, catalyst loading= 5 gm/lit

Effect of mole ratio:

The experiments were conducted at different mole ratios like 1:1, 1:3, 1:2 and 2:1 of BuOH and acetic acid at 80°C, 5gm/lit catalyst, 1000 rpm speed. Results obtained in the Fig.6 shows the effect of mole ratio of alcohol to acetic acid on the reaction kinetics. As expected the rate and equilibrium conversion increase with increase in mole ratio.

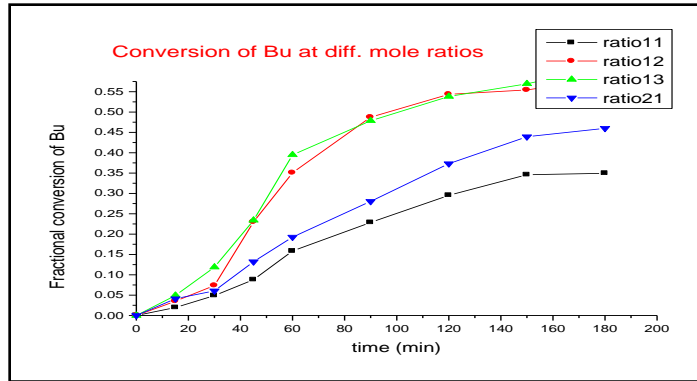
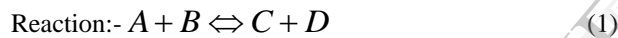


Figure 6: Effect of Mole ratio: rpm=1000,catalyst, loading= 5 gm/lit, Temp=80C

Kinetic model:

The kinetics of liquid phase reactions catalyzed by ion exchange resin is commonly modeled by Pseudo-Homogeneous (PH) model or Langmuir-Hinshelwood (LHW) model in the absence of any intra-particle diffusion limitations (Gangadwala et. al., 2003; Chakrabarty and Sharma, 1993). For Butyl acetate synthesis, it was shown that a pseudo homogeneous model is sufficient for small amounts of water in the reactor. Thus, pseudo homogeneous models were used to describe heterogeneously by ion exchange resin catalyzed esterification reactions. Hence, the pseudo homogeneous model with second order expression was in good agreement with the experimental data.

Esterification reactions are known to be second order reversible reactions. Therefore, for the bimolecular type second order reactions,



With the restrictions that $C_{A0} = C_{B0}$ and $C_{C0} = C_{D0} = 0$, the rate equation can be written as

$$\begin{aligned} -r_B &= -\frac{dC_B}{dt} = C_{B0} \frac{dX_B}{dt} \\ &= k_1 C_A C_B - k_2 C_C C_D = k_1 C_{B0}^2 (1 - X_B)^2 - k_2 (C_{B0} X_B)^2 \end{aligned} \quad (3)$$

where, A,B,C and D refer to acetic acid, n-butanol, butyl acetate and water respectively. k_1 and k_2 are the forward and backward reaction rate constants respectively.

At the equilibrium, $-r_B = 0$. Hence, from the above equations, we find the fractional conversion of B at the equilibrium conditions by

$$K_e = \frac{C_{Ce} C_{De}}{C_{Ae} C_{Be}} = \frac{X_{Be}^2}{(1 - X_{Be})^2} \quad (4)$$

And equilibrium constant given by

$$K_e = \frac{k_1}{k_2} \quad (5)$$

Combining above three equations, in terms of the equilibrium conversion, we obtain

$$\frac{dX_B}{dt} = k_1 C_{B0} \left[(1 - X_B)^2 - \left(\frac{1 - X_{Be}^2}{X_{Be}} \right) X_B^2 \right] \quad (6)$$

With conversions measured in terms of X_{Be} , this may be indicated as a pseudo second order reversible reaction which on integration, gives

$$\ln \left[\frac{X_{Be} - (2X_{Be} - 1)X_B}{X_{Be} - X_B} \right] = 2k_1 \left(\frac{1}{X_{Be}} - 1 \right) C_{B0} t \quad (7)$$

The temperature dependency of rate constants can be expressed by an Arrhenius law relationship,

$$k_1 = k_1^0 \exp\left(\frac{-E_1}{RT}\right) \quad (8)$$

$$k_2 = k_2^0 \exp\left(\frac{-E_2}{RT}\right)$$

This is determined by plotting $\ln k_1$ vs $1/T$

Where k_1^0 , k_2^0 and E_1 , E_2 are the Arrhenius pre-exponential factors and activation energies for forward and backward reactions, respectively. k_e is the equilibrium constant.

Pseudo-homogeneous first order and second order models are generally applicable to highly polar reacting systems (Saha and Streat, 1999). We have used same model to explain our kinetic data available for different temperatures, catalyst loadings and mole ratios.

Kinetic parameters estimation:

Pseudo-homogeneous first order and second order models are generally applicable to highly polar reacting systems (Saha and Streat, 1999). We have used same model to explain our kinetic data available for different temperatures, catalyst loadings and mole ratios.

The equilibrium constant was experimentally determined using amberlyst-15. It was found that the equilibrium constant did not vary strongly with temperature ranging from 343-363 K. The esterification reaction was kinetically controlled since the external mass transfer resistance and the interparticle diffusion resistances were absent. The catalyst used is a macro porous ion exchange resin. In a macro porous resin, the reactants are able to diffuse into the pores without any resistance. Therefore, sorption effects can be neglected and a pseudohomogeneous model should be sufficient. The kinetic behavior of the esterification of acetic acid with n-butanol in the temperature range of 343-363 K and the molar feed ratio of 1:1 was investigated experimentally in a stirred batch reactor using amberlyst-15 catalyst. This reaction was intrinsically kinetically controlled. A pseudo homogeneous kinetic model was employed to fit the experimental data. The experimental data collected at temperatures from 343-363 K were used to plot the left hand side of eq.(7) vs time to get the straight line passing through the origin (figure. 7,8,9). From the slopes of these lines given, the forward reaction rate constant (k_1) was found to be 0.00888, 0.00882, 0.00906 (l/mol.min) at 343 K, 353 K, 363 K respectively. Using these values in Arrhenius eq. (8), $-\ln k$ was plotted against $1/T$ (figure 10,11). The activation energy was obtained as 45.59, 23.90 (kJ/mol). The

temperature dependency of the rate constant was calculated by eq. (8). The parameters estimated by model are given in Table 2.

Table 2: Estimated values of the parameters for the kinetic models

| Parameters | Values |
|-----------------------|-------------------------|
| E_1 (kJ/mol) | 45.59 |
| E_2 (kJ/mol) | 23.90 |
| k_1^0 (lit/mol.min) | 9.0953×10^{-3} |
| k_2^0 (lit/mol.min) | 8.643×10^{-3} |

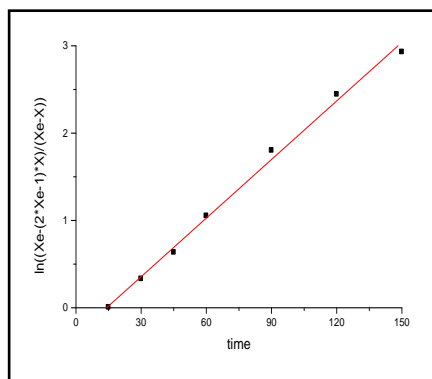


Figure 7: Determination of K at 343 K

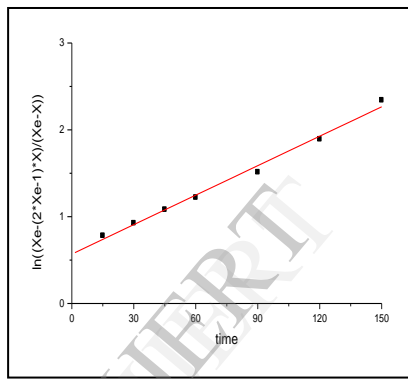


Figure 9: Determination of K at 363 K

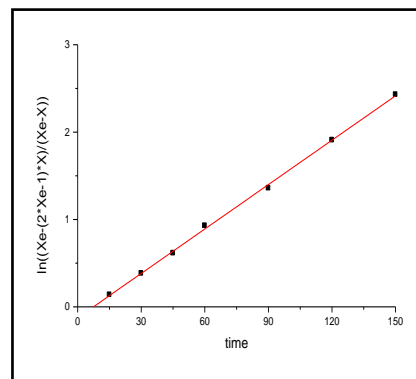


Figure 8: Determination of K at 353 K

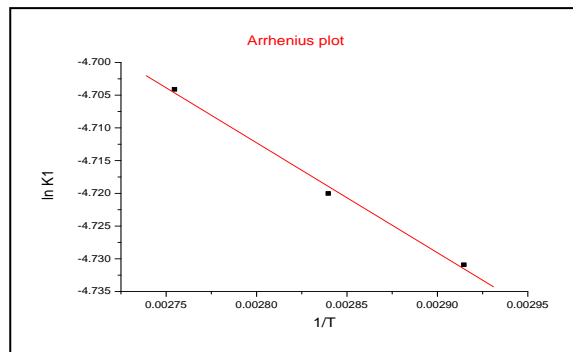


Figure 10: Arrhenius plot for forward reaction

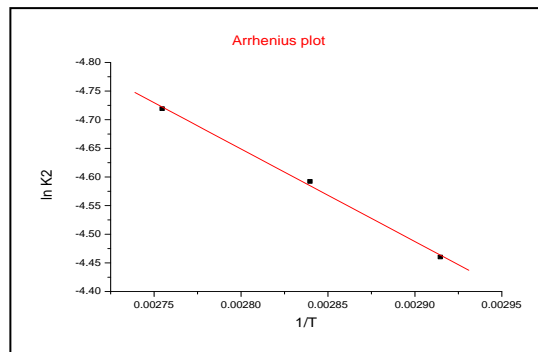


Figure 11: Arrhenius plot for backward reaction

Conclusion

The esterification reaction of acetic acid with butanol was successfully carried out over Amberlyst-15 as cationic exchange resin as a catalyst and in the absence of catalyst also in stirred batch reactor. The effect of temperature, molar ratios, and catalyst loading on the overall rate of reaction as well as concentration-time profiles were investigated. A stirrer speed ≥ 800

rpm was found sufficient for eliminating external diffusion. Internal diffusion was negligible under the employed esterification reaction conditions. The conversion of alcohol increased with increasing temperature and catalyst loading and initial amount of acid. To develop the model, reactions are carried out in the temperature ranging between 308 and 328K and molar feed ratio of 1:1. This reaction was intrinsically controlled. A pseudo homogenous kinetic model was employed to fit the experimental data. The activation energies for catalysed forward and backward reactions were evaluated as 45.59KJ/mol and 23.90KJ/mol.

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