Kinetics of the Esterification Reaction between Pentanoic Acid and Methanol Catalyzed by Noncorrosive Cation Exchange Resin

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Methyl pentanoate, commonly known as methyl valerate, is the methyl ester of pentanoic acid (valeric acid) with a fruity odour. Methyl pentanoate is commonly used in fragrances, beauty care, soap, laundry detergents at levels of 0.1 – 1 %. In its very pure form (purity 99.5 %) it is used as a plasticizer in the manufacture of plastics. In the present investigation, kinetics of esterification of pentanoic acid with methanol catalyzed by heterogeneous catalyst in a batch-type reactor is reported. The effect of reaction conditions such as temperature, molar ratio, catalyst loading, and initial concentration of pentanoic acid and methanol, and the inhibiting effect of water on the kinetics has been studied. The pentanoic acid conversion reached 93 % at 333.15 K at a methanol to pentanoic acid molar ratio of 10:1 with 7 % (g L^{-1}) Amberlyst 15 as catalyst. Mass transfer effects were found to be negligible. Observed reaction rate data was fitted to the regression technique. Estimated Eley-Rideal kinetic model reaction rate constants were fitted to the Arrhenius type equation with activation energy E_A 39.5 kJ mol^{-1} and pre exponential factor k_o 1.8 $\cdot 10^3$ L^2 g^{-1} mol^{-1} h^{-1}.

Key words:
Esterification, ion exchange resin, heterogeneous kinetic, kinetic modelling, Amberlyst 15

Introduction

The extensive demand for cleaner environment is forcing the chemical industry to use less hazardous materials. In this regard, solid catalysts have lately attracted the attention of scientists and researchers around the world.[1–8] By using sufficient amounts of these heterogeneous catalysts, their catalytic activity for ester formation can be equivalent to that of conventional homogeneous catalysts. Solid catalysts have good properties in terms of their esterification efficiency.[9,10] Amongst the wide variety of solid catalysts available, cation ion-exchange resin is widely used in esterification process because it is not corrosive and easy to separate from the reaction mixture.[6,7] Many authors have studied the esterification reactions using ion exchange resins. In spite of many reports on the esterification reactions over ion exchange resins, however, few kinetic studies consider the effect of adsorption, desorption and partitioning phenomenon occurring between the interior and the exterior liquid phases with respect to the resins.

For example, Sanz *et al.*[11] have studied the kinetics of lactic acid esterification reaction with methanol, catalyzed by different acidic resins. These authors have interpreted their results by means of an Eley–Rideal (ER) and a Langmuir–Hinshelwood (LH) model. Ali and Merchant[12] have reported kinetic results related to the esterification between acetic acid and 2-propanol on different resins interpreting the obtained data with various models: pseudo-homogeneous (PH), Eley–Rideal (ER), Langmuir–Hinshelwood (LH). One of the challenges in determining kinetic parameters for the esterification over solid acid catalysts is the proper handling of the water concentration.[13] Yalcinyuva *et al.*[14] demonstrated that the phase partitioning and the swelling phenomena cannot be neglected for an accurate description of an esterification process involving ionic exchange resins. In fact, they have investigated the esterification reaction of myristic acid with isopropyl alcohol catalyzed by Amberlyst 15, and they have shown that the water concentration slows down the conversion, but is found to be lower than the theoretical value calculated on the basis of the measured acid conversion. Lee *et al.*[15] have studied the kinetics of the esterification reaction of acetic acid with methanol, in the presence of Amberlyst 36 as catalyst. According to their study, the magnitude of adsorption strengths follows the order of water > methanol > acetic acid > methyl acetate. Popken *et al.*[16] and Song *et al.*[17] have studied the esterification reaction of acetic acid with methanol also using Amberlyst 15 as catalyst. How-

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ever, the esterification characteristics of nonanoic acid with methanol,[3] acetic acid with n-butanol and isobutanol,[18] lactic acid with isopropanol[19] over Amberlyst 15 has been investigated by our research group in order to gain a full understanding of the relationship between solid acid catalysts and water.

Here we report the esterification of pentanoic acid with methanol over Amberlyst 15 (Heterogeneous Catalyst). It was found that Amberlyst 15 is a better alternate for esterification reaction than acid catalysts which are not ecofriendly. In this article, we determined the rate equations including inhibiting effects applicable to the solid acidic resins. As far as we know, there has been no attempt to investigate the kinetics of pentanoic acid esterification with methanol catalyzed by Amberlyst 15.

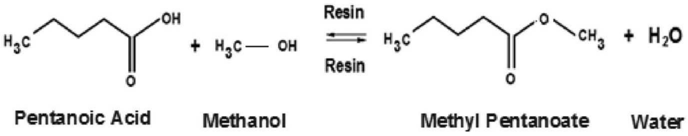
Experimental study

Chemicals and catalysts

Pentanoic acid (purity >99.5), methanol (purity >99), and 1, 4-dioxane were purchased from Merck and used without further purification. Gas chromatography analysis showed their respective purity values to be greater than 99 %. For titration, the alkali used was 0.5 mol L^{-1} NaOH volumetric-standard solution purchased from Aldrich Chemical Co. Amberlyst 15 (wet) was obtained from Rohm and Hass. The catalyst was initially washed four to five times with distilled water and dried at ambient conditions for 4−5 hours. Further, the catalyst was washed by dipping in an 0.1 mol L^{-1} HCl solution for half an hour. This solution was then filtered to separate the catalyst and dried at atmospheric conditions for about 48 h. The characteristics of the catalyst were listed in our previous work.[3]

Apparatus and reaction procedure

The batch experiments were carried out in a 500 mL double jacketed three-necked glass reactor equipped with a reflux condenser in the temperature range of 313 to 333 K. The reaction temperature was maintained using a thermostatic water bath (Julabo F20) within an accuracy of ± 0.1 °C. The reaction mixture was continuously stirred with an overhead stirrer fitted with a motor and a speed regulator. The pentanoic acid and the catalyst were first charged into the reactor through a peephole on the lid and heated to the desired temperature. Thereafter, methanol at the same temperature was fed into the reactor. The time at which the methanol was added was considered as zero time or the starting point of the reaction. Samples of 1 mL were taken every 15 minutes for the first hour, and every 30 minutes for the next 2−6 hours for analysis. The reaction parameters are given in Table 1. All experiments were performed at least three times in order to ensure reproducible results. Below is the scheme of the given reaction:



Analysis

For kinetic measurements, samples were taken periodically, and the amount of pentanoic acid was determined by titration with standard 0.5 mol L^{-1} sodium hydroxide solution using phenolphthalein as an indicator. Parallel tests indicated that the average error of the titration method was less than 2 %. The samples were also analyzed by a gas chromatograph (Nucon 5765) equipped with a fused silica capillary column of 30 m × 0.25 mm I.D. (Inner Diameter of column) × 0.25 μm film thickness, flame ionization detector and a thermal conductivity detector by matching the retention time of the reaction product to the retention time of methyl nonanoate. Nitrogen with a purity of 99.99 % was used as the carrier gas.

Results and discussion

Exclusion of mass transfer effects

For this esterification reaction, fractional conversion of pentanoic acid was found to be independent of external diffusion limitations for stirrer speed of more than 400 rpm. Four runs were carried out at molar ratio of 1 (pentanoic acid) : 10 (Meth-

Table I – *Reaction Parameters*

S.No.	Temp./K	Molar ratio	Catalyst loading	Stirrer speed/rpm	Particle size
1	313 to 333	1:10 (acid to alcohol)	57.6 g L^{-1} (7 % w/v)	500	250–850 μm
2	333	1:10 (acid to alcohol)	32.87 g L^{-1} to 65.80 g L^{-1} (4 % to 8 %)	500	250–850 μm
3	333	1:1 to 1:15 (acid to alcohol)	57.6 g L^{-1} (7 % w/v)	500	250–850 μm
4	333	1:10	57.6 g L^{-1} (7 % w/v)	300–800	250–850 μm
5	333	1:10	57.6 g L^{-1} (7 % w/v)	500	600–850 μm, 250–300 μm

anol), temperature: 333.15 K, catalyst loading: 57.6 g L^{-1} by varying stirrer speeds from 300–800 rpm. Fig. 1 shows that the fractional conversion increases with increase in stirrer speed from 300 to 500 rpm while keeping all other parameters constant, but after 500 rpm there is no significant effect of stirrer speed. Hence an agitation speed of 500 rpm was used for this study in order to rule out the presence of external mass transfer. The effect of particle size was examined by carrying out the reaction using various particle sizes. Fig. 2 shows that fractional conversion is independent of the particle size ranging from 250 – 850 µm. Hence, from the experimental results and comparison with our previous work[3] on Amberlyst 15, internal mass transfer was neglected.

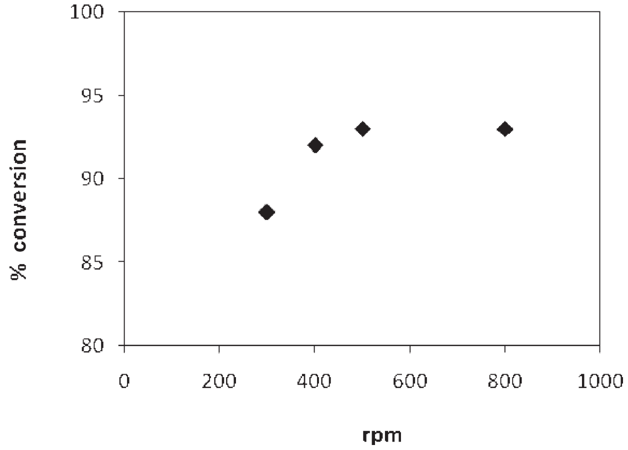


Fig. 1 – *Percentage conversion vs rpm at 333.15 K, 1:10 molar ratio and catalyst loading 57.6 g L^{-1}*

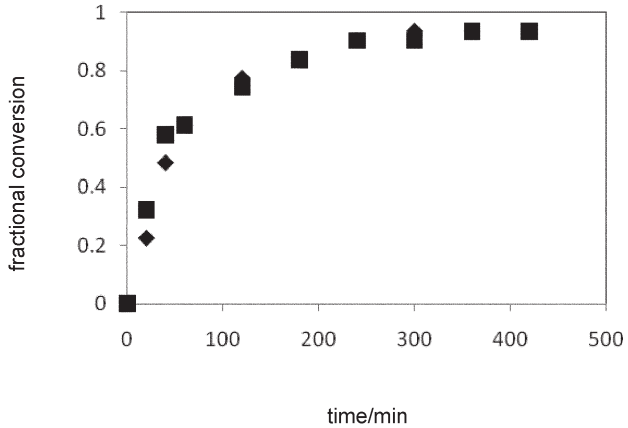


Fig. 2 – *Fractional conversion vs. time (min) for different particle sizes at 333.15 K, 1:10 molar ratio and catalyst loading 57.6 g L^{-1} ♦ 600–850 µm, ■ 250–300 µm*

Effect of catalyst loading

Examined was the effect of varying the catalyst loading from 4 to 8 % (g L^{-1}) on pentanoic acid esterification with methanol at an acid to alcohol molar ratio of 1:10 and temperature 333.15 K. Fig. 3 gives the results for the effect of catalyst loading on conversion of pentanoic acid. It can be seen from Fig. 3 that higher loading of catalyst results in a reduction of the time required to reach reaction equilibrium, and at temperature condition 333.15 K, the use of catalyst loadings greater than 7 % does not appear attractive. All further kinetic studies were therefore conducted at this apparently optimum catalyst loading. Fresh resin was used for each new run.

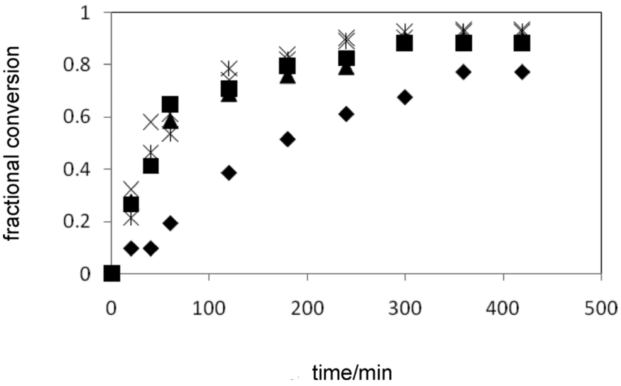


Fig. 3 – *Fractional conversion vs. time for different catalyst loading: ♦ 4 %, ■ 5 %, ▲ 6 %, × 7 %, ✳ 8 %; Molar ratio 1:10, temperature 333.15 K, 500 rpm*

Effect of temperature

The reaction was carried out at various reaction temperatures, ranging from 313.15 to 333.15 K while keeping other parameters constant. The effect of increasing the reaction temperature is shown in Fig. 4 in the temperature region of 313.15 K to 333.15 K, molar ratio of acid to alcohol at 1 : 10, and catalyst loading 7 %. In general, the ester conversion was found to increase with increasing reaction temperature. Increasing the temperature is apparently favorable for the acceleration of the forward reaction.

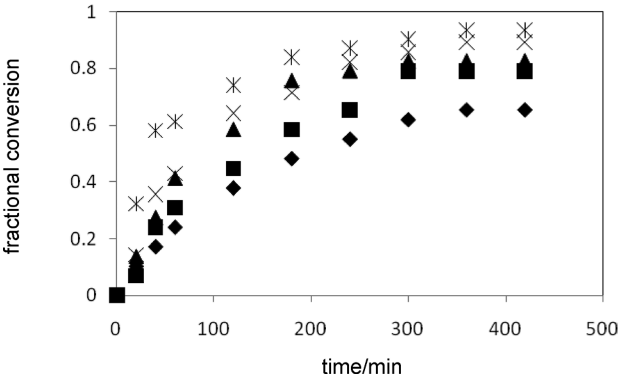


Fig. 4 – *Fractional conversion vs. time (min) for different temperature; ♦ 313.15 K, ■ 318.15 K, ▲ 323.15 K, × 328.15 K, ✳ 333.15 K, Molar ratio 1:10, Catalyst loading 57.6 g L^{-1}, 500 rpm*

Effect of feed molar ratio

Esterification of pentanoic acid with methanol being a reversible reaction is an equilibrium limited chemical reaction and the position of equilibrium controls the amount of ester formed, the use of an excess of methanol drives the equilibrium towards the formation of ester and enhances the forward reaction. The molar ratio of methanol to pentanoic acid was varied from 1 : 1 to 15 : 1 at a temperature 333.15 K, 57.6 g L^{-1} catalyst loading, and stirrer speed of 500 rpm. It was observed that acid conversion increases with the amount of methanol as shown in Fig. 5.

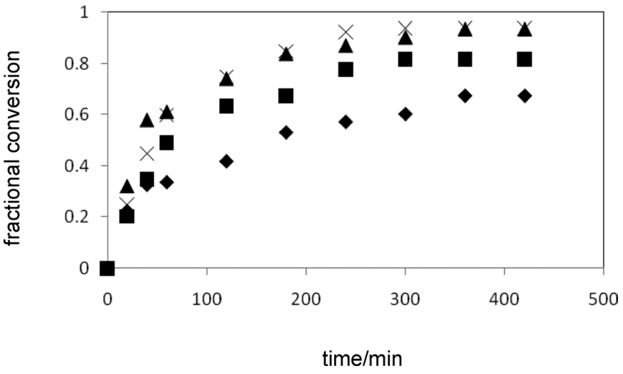


Fig. 5 – *Fractional conversion vs. time (min) for different molar ratio; ◆ 1:1, ■ 1:5, ▲ 1:10, × 1:15, temperature 333.15 K, catalyst loading 57.6 g L^{-1}, 500 rpm*

Mathematical model for esterification kinetics

Initial rate of reaction ($r_{Ao} = \Delta C_{Ao}/\Delta t$) defined up to conversion of 10 % was observed using different concentrations of pentanoic acid, methanol and water. The concentrations were converted to activities according to equation 1 in order to account for the non-ideal behavior of the reaction mixtures.[3] Activity is calculated by eq. 1 given below:

$$a_i = \gamma_i x_i = \gamma_i \frac{C_i}{C_t} \tag{1}$$

where a_i is activity of the components, γ_i is activity coefficient, x_i is mole fraction, C_i (mol L^{-1}) is concentration of reactants, and C_t (mol L^{-1}) is total concentration of the reaction mixture which is kept constant. Activities of the chemical compounds used in this study were calculated using UNIFAC group contribution method.[20–22]

A general kinetic expression for esterification reaction catalyzed by heterogeneous catalysts can be written as:

$$-r_A = \frac{k_f w_{cat}\left(a_A a_B - \dfrac{a_E a_W}{K_e}\right)}{\left(1 + K_A a_A + K_B a_B + K_E a_E + K_W a_W\right)^n} \tag{2}$$

where r_A is the reaction rate, w_{cat} weight of catalyst in terms of the amount of dry catalyst, A, B, E, W are pentanoic acid, Methanol, Methyl pentanoate and Water, respectively. K is the adsorption constant, K_e is equilibrium reaction rate constant, and k_f is the rate constant, where n = 0 for PH model, 1 for ER model and 2 for LHHW model.

As evident from Fig. 6, rather than producing a plateau, the initial reaction rate is a linear function of initial concentration of pentanoic acid, giving evidence that pentanoic acid is not adsorbed over the surface of Amberlyst 15 beads, and at the same time the initial reaction rate increases linearly with methanol concentration, whereas at high methanol concentration, the rate is essentially independent of it. Hence, we can conclude that adsorption effect of methanol is very low at low concentrations of methanol and it almost becomes constant as the concentration is increased further. Whereas, Fig. 6 shows that initial reaction rate is a non-linear function of concentration of water and decreases with increase in concentration of water.[3] This confirms the inhibiting effect of the water concentration as the reaction proceeds. From this analysis, it is concluded that the reaction mechanism can be represented by the Eley-Rideal (ER) model, i.e the reaction occurs between adsorbed molecules of methanol and the molecules of pentanoic acid in the bulk solution. In addition, the water molecules adsorbed by resin have an inhibiting effect on the reaction rate. The adsorption of solvent (dioxane) and ester were reported in the literature to be negligible.[20] So, stoichiometric and corresponding reaction rate expression in the form of Eley-Rideal (ER) model with surface reaction is the rate-determining step, after excluding the adsorption terms of acid and ester reaction, eq. 2 can be written in the ER form;

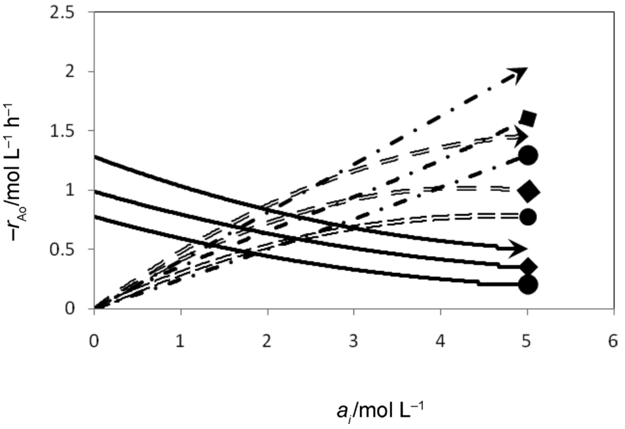


Fig. 6 – *Effect of reactant concentration shown in terms of activity on the initial reaction rate (-r_{Ao}) at three different temperatures, ● 321.15 K, ◆ 326.15 K, → 333.15 K. Catalyst loading 7 % (w/v), 500 rpm; dash-dot line (– • – •) : pentanoic acid, double-dashed line (= = =): methanol, and solid line (—): water.*

$$-r_A = \frac{k_f w_{cat}\left(a_A a_B - \dfrac{a_E a_W}{K_e}\right)}{\left(1 + K_B a_B + K_W a_W\right)} \tag{3}$$

A, B, E, W are pentanoic acid, methanol, methyl pentanoate and water, respectively, and k_f is the forward reaction rate constant in ($L^2\ g^{-1}\ mol^{-1}\ h^{-1}$) is given as $k_i = k_i^o \exp^{\left(\frac{-E_i}{RT}\right)}$, w_{cat} is weight of catalyst in g L^{-1}, K is adsorption constant, and K_e is the esterification reaction equilibrium constant based on activity catalyzed by Amberlyst 15. In eq. (3), activity rather than concentration is used in the rate expression, because it results in improved predictions of the models fitted against the measured kinetic data. Rearranging eq. 3 for the initial reaction rate, with no product present, can be defined as eq. 4:

$$\frac{a_{Ao} a_{Bo}}{-r_{Ao}} = \frac{1}{(k_f w_{cat})} + \frac{K_B}{k_f w_{cat}} a_{Bo} \tag{4}$$

Plot of $\frac{a_{A,o} a_{B,o}}{-r_{Ao}}$ *versus* $a_{B,o}$ results in a straight line with the slope $\left(\frac{K_B}{k_f w_{cat}}\right)$ and intercept $\frac{1}{k_f w_{cat}}$ as shown in Fig. 7. Rearranging eq. 3 to check the inhibiting effect of water, a plot of $\frac{a_{A,o} a_{B,o}}{-r_{Ao}}$ *versus* $a_{W,o}$ results in a straight line with the slope of $\left(\frac{K_W}{k_f w_{cat}}\right)$ and intercept $\frac{1 + K_B a_{B,o}}{k_f w_{cat}}$, as shown in Fig. 8.

From the slopes and intercepts in these figures (7 and 8), the rate constants and adsorption constants k_f, K_B, K_W are obtained and their estimated values at three temperatures are presented in Table 2.

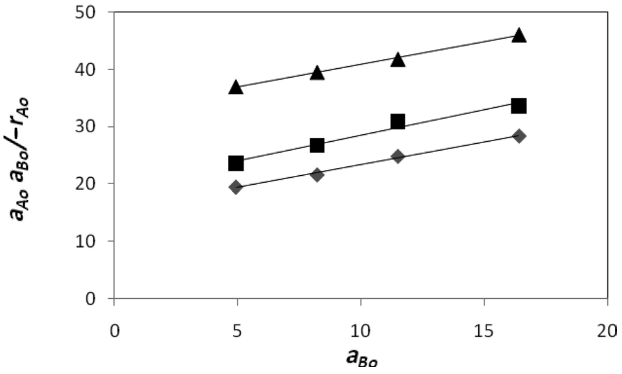


Fig. 7 – $\frac{a_{A.o} \cdot a_{B,o}}{-r_{A,o}}$ versus $a_{B,o}$ *at three different temperatures: ♦ 333.15 K, ■ 326.15 K, ▲321.15 K, catalyst loading 7 % (w/v), 500 rpm*

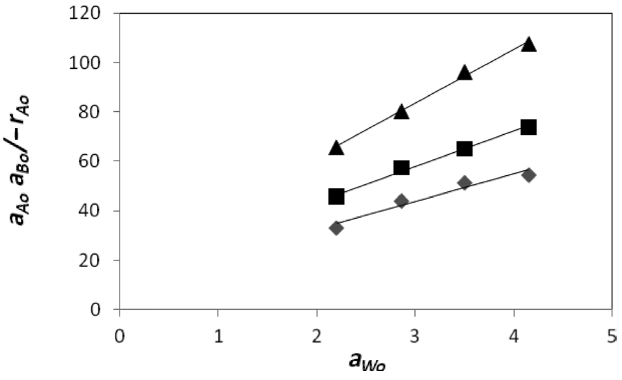


Fig. 8 – $\frac{a_{A,o} a_{B,o}}{-r_{Ao}}$ *versus* $a_{W,o}$ *at three different temperatures: ♦ 333.15 K, ■ 326.15 K, ▲ 321.15 K, catalyst loading 7 % w/v, 500 rpm*

Table 2 – *Kinetics and adsorption parameters*

Temp./K	k_f/$L^2\ mol^{-1}\ g^{-1}\ h^{-1}$	K_B/L mol^{-1}	K_w/L mol^{-1}
321.15	$6.80 \cdot 10^{-4}$	0.15	0.88
326.15	$8.26 \cdot 10^{-4}$	0.13	0.55
333.15	$1.15 \cdot 10^{-3}$	0.08	0.38

Activation energy and rate constants

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

$$k_i = k_i^o \exp^{\left(\frac{-E_i}{RT}\right)} \tag{5}$$

where i = f, B, W, E_i is activation energy, and k_i^o is the frequency factor. From eq. (5), a plot of ln k_f, ln K_B and ln K_W versus $1/T$, gives a straight line with the slope of (E/R) and intercept ln k_i^o, as shown in Fig. 9 versus 1/T. The activation energy was found to be 39.5 kJ mol^{-1} in the presence of Amberlyst 15 ion-exchange resin. The temperature dependency of the rate and adsorption constants can be correlated by the following equations:

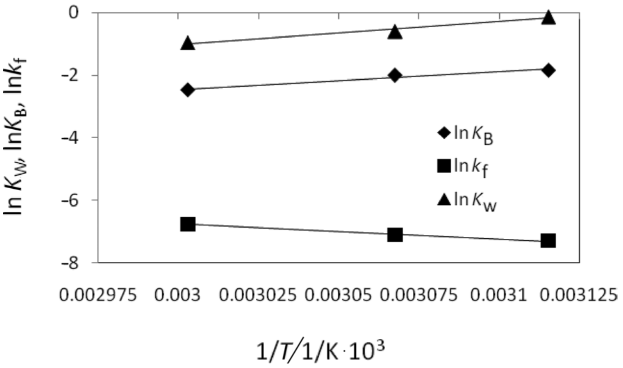


Fig. 9 – *Arrhenius plot of* lnK_B, lnk_f, lnK_W *vs.1/T for catalyst loading 7 % (w/v), 500 rpm*

$$k_f(\mathrm{L^2\,g^{-1}\,mol^{-1}\,h^{-1}}) = \exp\left[7.5 - \frac{4754.2}{T}\right] \qquad (6)$$

$$K_B(\mathrm{L\,mol^{-1}}) = \exp\left[\frac{5556.2}{T} - 19.12\right] \qquad (7)$$

$$K_W(\mathrm{L\,mol^{-1}}) = \exp\left[\frac{7323.7}{T} - 22.98\right] \qquad (8)$$

Model prediction

The observed reaction rate for the esterification of pentanoic acid with methanol was compared with the proposed ER model (eq. 3) using the rate consants described by eqs. 6–8 over the whole range of predicted parameters (given in Table I). Experimental data was calculated by the equation below, where C_A is concentration of acid, t is reaction time, and X is conversion of acid.

$$-r_{A,\mathrm{experimental}} = \frac{\Delta C_A}{\Delta t} = C_{Ao}\frac{\Delta X}{\Delta t} \qquad (9)$$

The parity between the experimental and calculated value is given in Fig. 10. Model eq. 3 represents the data reasonably well within ± 10 %.

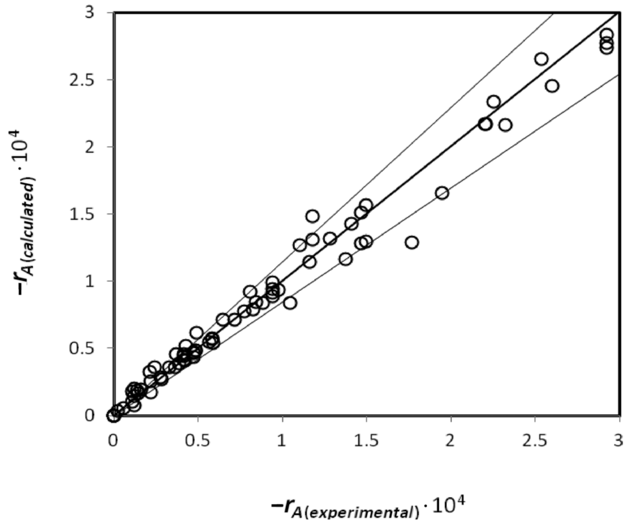


Fig. 10 – *Parity plot (experimental vs. calculated rate) for data in the catalyst range of 4 % (w/v) to 8 % (w/v), molar ratio 1:1 to 1:15, temperature 313.15 K to 333.15 K at 500 rpm*

Conclusion

The reaction kinetics of esterification of pentanoic acid with methanol was studied in a temperature range of 313.15 to 333.15 K, catalyst loading 4 % to 8 %, and molar ratio of acid to alcohol 1:1 to 1:15 at a stirrer speed of ≥ 400 rpm over Amberlyst 15. Experimental findings show that the reaction is kinetically controlled rather than mass transfer effects. Under the conditions studied, the increase in the catalyst loading and molar ratio was found to increase the percent conversion of pentanoic acid. Water has an inhibiting effect on the conversion of acid.

Non-ideal behaviour of the liquid mixture is taken into account and UNIFAC group contribution method was found to predict component activity coefficients reasonably well. On the basis of adsorption study, Eley-Rideal (ER) was developed to interpret the obtained kinetic data. Experimental data fitted the kinetic model well.

Besides proving the adequacy of the tried model, the obtained parity plot for calculated vs. experimental also proves the success of the UNIFAC model in predicting the activity coefficients of the components present in the system. The activation energy, E_A for the forward reaction was found to be 39.5 kJ mol^{-1} for ER model catalyzed by Amberlyst 15.

ACKNOWLEDGEMENT

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Notations

a – Activity
E_A – Activation energy, kJ mol $^{-1}$
k_o – Preexponential factor, L^2 g^{-1} mol^{-1} h^{-1}
K_e – Equilibrium constant
k_f – Forward reaction rate constant, L^2 g^{-1} mol^{-1} h^{-1}
n – Number of experimental data
w_{cat} – Weight of catalyst, g L^{-1}
T – Absolute temperature, K
t – Time
x_i – Molar fraction
γ – Activity coefficient
ln – Natural logarithm (base e)
R – 8.314 J mol^{-1} K^{-1}
ER – Eley Rideal model
UNIFAC – Universal quasichemical functional group activity coefficients
rpm – Revolution per minute

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