

Ion-exchange resin catalysis in the synthesis of isopropyl lactate

G.D. Yadav*, H.B. Kulkarni

Chemical Engineering Division, University Department of Chemical Technology, University of Mumbai, Matunga, Mumbai-400 019, India

Received 7 May 1999; received in revised form 1 October 1999; accepted 25 October 1999

Abstract

Isopropyl lactate is a very important pharmaceutical intermediate. The current practice is to use homogeneous acids as catalysts. These catalysts are hazardous and disposal of liquid acid effluents poses problems. The separation of the liquid catalyst and its reuse is another problem. The current paper deals with the application of heterogeneous catalysts Indion-130, Ambelyst-36, Amberlyst-15, Amberlite-120, Dowex 50W, Filtrol-44, 20% DTPA/K-10 (dodecatungstophosphoric acid supported on K-10 clay) and 20% DTPA/Filtrol-44 (dodecatungstophosphoric acid supported on Filtrol-44 clay). Amongst these Amberlyst-36, Amberlyst-15 and Indion-130 were observed to be most effective. A theoretical kinetic model was developed for evaluation of this slurry reaction. The effects of various parameters on the rate of reaction were evaluated. The reaction was found to be intrinsically kinetically controlled and there were no intraparticle as well as interparticle mass transfer limitations on the rate of reaction. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Heterogeneous catalysis; Esterification; Isopropyl lactate; Ion-exchange resin; Clay; Heteropolyacid; Kinetics

1. Introduction

Organic esters are most frequently used as plasticizers, solvents, perfumery and flavor chemicals. They fall under a very wide category ranging from aliphatic to aromatic with various substitutions and multifunctional groups [1,2].

Esterification is a very widely understood and extensively used reaction, especially in the pharmaceutical, perfumery and flavor industries. Several synthetic routes exist to make esters, but

most of them are not suitable to meet the stringent specifications applied in the perfumery and flavor industry. Yadav and Mehta [2] have reviewed these methods including catalysis. The most acceptable method of making an ester is to react the corresponding acid with an alcohol [3]. The reaction is catalyzed by acids and is reversible. Several methods are available to drive the reaction towards the desired product. One of them is to use an excess amount of alcohol and the other way is to remove the ester formed or the co-product water continuously. In the conventional industrial processes involving homogeneous acids, utilization of cation exchange resin catalysts for low temperature reactions and other heterogeneous catalysts as the

*Corresponding author. Tel.: +91-22-414-5616; fax: +91-22-4145614.

E-mail addresses: gdyadav@yahoo.com, gdy@udct.ernet.in (G.D. Yadav)

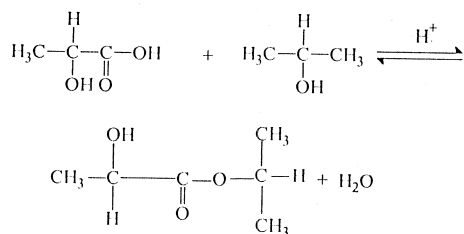
replacement is gaining importance due to their ecofriendly nature [4–7]. These catalysts are non-corrosive and easy to separate from the reaction mixture. They can also be used repeatedly over a prolonged period without any difficulty in handling and storing them.

The emphasis of the current work was to study in detail the kinetics of esterification of lactic acid with isopropanol over cheap and easily available catalysts, ion-exchange resins and clays and clay supported heteropoly acids.

2. Preparation of isopropyl lactate

The reaction of lactic acid (α -hydroxy-propanoic acid) and isopropanol (2-propanol) in the presence of an acid catalyst leads to isopropyl lactate (propanoic acid, 2-hydroxy-1-ethylmethyl-ester) which has stereoisomers [8].

The reaction is rather straightforward and follows the normal esterification mechanism:



3. Experimental

3.1. Chemicals and catalysts

All chemicals and catalysts were procured from firms of repute: Lactic acid (LR, s.d. Fine-Chem Ltd., India), isopropanol (AR, s.d. Fine-Chem Ltd., India), ion-exchange resins (IER) such as Indion-130 (Ion-Exchange Ltd, India), Amberlyst-15, Amberlyst-36, Amberlite IR-120 (Rohm and Hass, USA) and Dowex-50W (Sigma, USA) and clay catalysts, Filtrol-44, K10 montmorillonite (Aldrich Chem. Company Inc., Germany) and DTPA (Dodecatung-

stophosphoric acid) (s.d. Fine-Chem Ltd., India).

3.2. Procedure

Experiments were carried out in a glass reactor of 6.00×10^{-2} m I.D. and 2.50×10^{-4} m³ capacity, provided with a turbine impeller. Reaction was carried out typically by taking 1.6×10^{-4} kmol (1.44×10^{-2} kg) of lactic acid and 1.6×10^{-3} kmol (1.22×10^{-4} m³, 9.6×10^{-2} kg) of isopropanol at a reflux temperature of 85°C at 16.67 rps, by using a suitable solid acid catalyst. The reaction mixture was allowed to reach the desired temperature and the initial/zero time sample was collected. Agitation was then commenced. Samples were withdrawn periodically for analysis. In most of the cases, alcohol was taken in far molar excess over lactic acid to drive the equilibrium away towards the ester formation. It was interesting to note that the reaction mixtures developed the odor of isopropyl lactate as the reaction proceeded. The isolation of the pure product was done by simple distillation and the physical properties such as boiling point, absorbance, λ_{max} , etc. were noted to confirm with those reported in literature.

3.3. Analysis and isolation of product

The reaction product was analyzed by gas chromatography (GC) equipped with flame ionization detector (FID) by matching the retention time of the reaction product to the retention time of isopropyl lactate. Synthetic mixtures were used for qualitative and quantitative analysis of data and the calibration. It was observed that the lactic acid can not be detected on OV-17 column (2×0.003 m) by GC (Model, Chemito 8510), so the calibration was done only with respect to the isopropyl lactate. The conversions lead to both stereoisomers, which were not separated. Other chemical tests were done for ester identification.

For the isolation of the product, the reaction mixture was filtered off and the solid catalyst removed from the reaction mixture for reuse. The reactants, unreacted lactic acid and excess isopropanol were removed from the mixture by simple distillation, for the boiling point of the product is much higher than both lactic acid and isopropanol. Physical properties of the isolated product were observed to be same as that reported in the literature.

4. Theoretical aspects of solid catalyzed liquid phase reactions

The solid acid catalyzed esterification is a typical solid–liquid slurry reaction for which some theoretical work has emanated from this laboratory [9,10]. The theory takes into account the evaluation of the intrinsic kinetics of the reaction. Some other cases are given in Ref. [11].

The esterification reaction involves two organic phase reactants: A (lactic acid) and B (isopropanol) and the desired product E (isopropyl lactate) and W (co-product water) as given below:



At steady state the rate of mass transfer per unit volume of the liquid phase can be given by:

$$R_A, (\text{kmol m}^{-3} \text{ s}^{-1}) = k_{\text{SL-A}} a_p \{ [A_0] - [A_s] \} \quad (2)$$

which is the rate of diffusion of A from bulk liquid phase to the catalyst surface.

$$R_A, (\text{kmol m}^{-3} \text{ s}^{-1}) = k_{\text{SL-B}} a_p \{ [B_0] - [B_s] \} \quad (3)$$

which is the rate of diffusion of B from bulk liquid phase to the catalyst surface.

$$R_A, (\text{kmol m}^{-3} \text{ s}^{-1}) = \frac{\eta k_{\text{R2}} w [A_s] [B_s]}{(1 + K_A [A_s] + K_B [B_s])} \quad (4)$$

which is the rate of surface reaction per unit volume in the presence of intraparticle diffusion.

Eq. (4) is a Langmuir–Hinshelwood–Hougen–Watson type of model. When the adsorption and/or desorption steps are unimportant, Eq. (4), can be replaced by a power-law model. In the current studies, the chemisorption of both A and B was found to be negligible and hence the model reduces to the typical power-law model. This will be explained later.

When external and internal resistances to mass transfer are absent, the following holds:

$$\frac{1}{k_{\text{R2}} w [A_0] [B_0]} > \frac{1}{k_{\text{SL-A}} a_p [A_0]} \quad \text{and} \quad \frac{1}{k_{\text{SL-B}} a_p [B_0]} \quad (5)$$

then the surface reaction is the controlling mechanism and the overall rate of the reaction will be the same as given by the surface reaction, i.e.,

$$R_A = k_{\text{R2}} w [A_0] [B_0] \quad (6)$$

The influence of intraparticle diffusion, reflected in the effectiveness factor (η) can be studied by varying the particle size and also through the reaction temperature. In order to discern the controlling mechanism, it was desirable to study the effect of various parameters on the overall rate of reaction. In the absence of both external and internal resistance to mass transfer, it is possible to determine the intrinsic kinetics. Accordingly, for a pseudo-first order reaction, for which $[B_0] \gg [A_0]$, Eq. (6) becomes:

$$\frac{-d[A_0]}{dt} = k_1 w [A_0] \quad (7)$$

where k_1 is a pseudo-first order rate constant:

$$k_1 = k_{R2}w[B_0] \quad (8)$$

Integrating Eq. (7), the following equation is obtained:

$$-\ln \frac{[A_0]}{[A_0]_i} = k_1 t \quad (9)$$

or

$$-\ln(1 - X_A) = k_1 t \quad (10)$$

where X_A is the fractional conversion of A.

Thus a plot of $-\ln(1 - X_A)$ against time t will give slope which represents k_1 and from which k_{R1} can be determined. The above theory is used for a single liquid phase containing both the reactants, products and the solid catalyst. The water of reaction was miscible in the organic phase in presence of alcohol.

5. Results and discussion

Isopropyl alcohol was always taken in far excess over lactic acid to shift the equilibrium towards the formation of the ester and the preliminary experiments were conducted under otherwise similar conditions of reactant concentration (or mole ratio), catalyst loading, particle size, speed of agitation and temperature except for the type of the catalyst.

5.1. Efficacy of various catalysts

Different solid acid catalysts were used to assess their efficacy in this reaction. The catalysts used were Indion-130, Ambelyst-36, Amberlyst-15, Amberlite-120, Dowex 50W, Filtrol-44, 20% DTPA/K-10, 20% DTPA/Filtrol-44. The method of preparation of clay supported heteropolyacids is given elsewhere [5,6].

In a typical experiment 3.6×10^{-3} kg of solid catalyst along with 1.44×10^{-2} kg lactic acid and 9.6×10^{-2} kg isopropanol were used at a mole ratio of isopropyl alcohol to lactic acid of 10:1 at 85°C and at a speed of agitation 16.67

rps. It was expected to have no influence of external and/or internal resistance to mass transfer so that a comparative study on the basis of intrinsic kinetics could be made. Further, as will be explained later, indeed there was no influence of mass transfer on the rate of reaction of lactic acid with isopropanol. Fig. 1 shows the plot of conversion of lactic acid, the limiting reactant, against time for the various catalysts.

It was found that the cation exchange resins, Amberlyst-36, Amberlyst-15 and Indion-130 showed higher conversions as compared to the other catalysts. Further experiments were conducted with Amberlyst-36 as the catalyst where only one parameter was varied at a time under otherwise similar experimental conditions.

The meq/g dry values for Amberlyst-36, Indion-130, Amberlyst-15 are >5.45, 4.8 and 4.9, respectively. Both Amberlyst-15 and Amberlyst-36 were found to be equally effective. However, the value of meq/g dry for Amberlyst-36 is maximum and also the final conversion by using this catalyst was observed to be maximum. So it was decided to use Amberlyst-36 for further experimentation.

5.2. Effect of speed of agitation

The experiments were carried out at three different speeds 500, 800 and 16.67 rps and it was found that the conversions of lactic acid were unaffected by the speed in the range of 8.33–16.67 rps. (Fig. 2). Therefore, further experiments were conducted at 16.67 rps, to be on the safer side. Since isopropyl alcohol (B) was chosen in far excess, there is a possibility of diffusional resistance for transfer of lactic acid (A) through the liquid film around the catalyst and then inside the pores. According to the model used for this analysis, the liquid phase diffusivity values D_{AB} (lactic acid in isopropanol) and D_{BA} (isopropanol in lactic acid) were required and these values were calculated by using the Wilke–Chang equation [12].

D_{AB} and D_{BA} at 85°C were calculated as

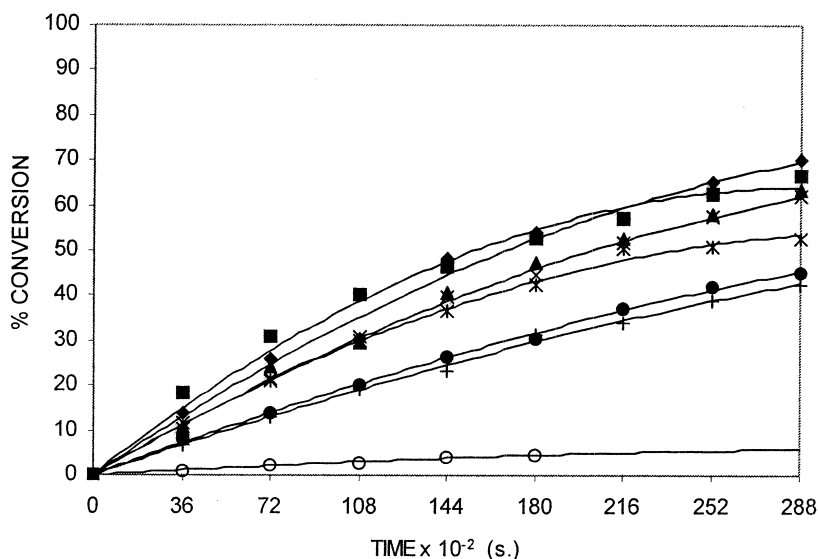


Fig. 1. Effect of different catalysts. Catalyst loading = 27.27 kg/m^3 , temperature = 85°C , reaction volume = $1.32 \times 10^{-4} \text{ m}^3$, lactic acid = $1.6 \times 10^{-4} \text{ kmol}$, speed = 16.67 rps, mole ratio (LA:IPA) = 1:10. ♦, AMB-36; ■, AMB-15; ▲, IND-130; ×, DOWEX; ✱, HPA/K10; ●, HPA/F-44; +, F-44; ○, AMBI-120.

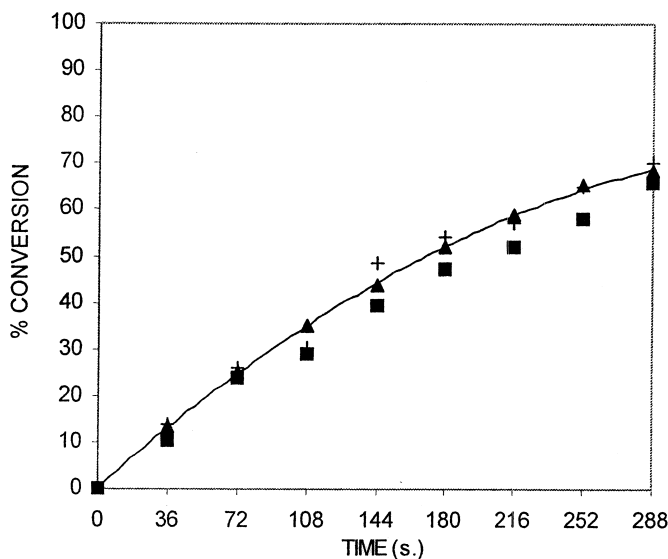


Fig. 2. Effect of speed of agitation. Catalyst loading = 27.27 kg/m^3 , temperature = 85°C , reaction volume = $1.32 \times 10^{-4} \text{ m}^3$, lactic acid = $1.6 \times 10^{-4} \text{ kmol}$, mole ratio (LA:IPA) = 1:10, particle size = $700 \mu\text{m}$. +, 16.67 rps; ■, 8.33 rps; ▲, 13.33 rps.

1.00×10^{-9} and $1.33 \times 10^{-9} \text{ m}^2/\text{s}$, respectively. The effective diffusivity D_{e-AB} was calculated to be $1.00 \times 10^{-10} \text{ m}^2/\text{s}$ for porosity ϵ of 0.3 and tortuosity τ of 3.0.

The values of the solid–liquid mass transfer

coefficients k_{SL-A} and k_{SL-B} were calculated by assuming the Sherwood number, $Sh = k_{SL} dp / D_{AB} = 2$. It should be noted that the actual Sherwood number could be much higher but for orders of magnitude calculations, it is safe to

take the lowest Sherwood number. Thus, k_{SL-A} was found as 2.88×10^{-6} m/s for a particle size of Amberlyst-36 of 700 μm . The particle surface area per unit liquid volume, a_p , was calculated from

$$a_p = \frac{6w}{\rho_p d_p} \quad (11)$$

$$= 117.86 \text{ m}^{-1}$$

Thus,

$$k_{SP-A} a_p [A_0] = 1.76 \times 10^{-3} \text{ kmol m}^{-3} \text{ s}^{-1}$$

and

$$k_{SP-B} a_p [B_0] = 4.90 \times 10^{-4} \text{ kmol m}^{-3} \text{ s}^{-1}.$$

A typical initial rate of reaction was calculated as $4.69 \times 10^{-5} \text{ kmol m}^{-3} \text{ s}^{-1}$. Therefore,

$$\frac{1}{\eta k_{R2} w [A_0] [B_0]} > \frac{1}{k_{SL-A} a_p [A_0]}$$

and $\frac{1}{k_{SL-B} a_p [B_0]}$

i.e., $2.13 \times 10^4 > 5.68 \times 10^2$ and 2.04×10^3 .

The above inequality demonstrates that there is an absence of resistance due the solid–liquid external mass transfer and the rate may be either surface reaction controlled or intra-particle diffusion controlled.

5.3. Effect of intraparticle diffusion

The effect of intraparticle diffusional resistance was studied by taking three different particle size ranges as $0 < S_1 < 90$, $90 < S_2 < 212$, $212 < S_3 < 300$ and $S_4 \approx 700 \mu\text{m}$. The mean particle sizes measured by image analysis were $S_1 = 111$, $S_2 = 279$, $S_3 = 350$ and $S_4 = 700 \mu\text{m}$. The effect of particle size is shown in Fig. 3. For average particle size less than 700 μm , there was no effect of particle size on the conversion of lactic acid. This would suggest that the effectiveness factor for this reaction is almost unity. Thus, there was no intraparticle diffusion and the entire process becomes surface reaction controlled, where the chemisorbed A reacts with chemisorbed B on the interior surface of the particle. The percentage of active sites on the exterior surface of particles is negligible. This has been further confirmed by studying the effect of temperature on the rate of reaction, which gives the energy of activation.

5.4. Effect of catalyst loading

The effect of catalyst loading on the conversion of lactic acid was studied under otherwise similar conditions (Fig. 4). As per Eq. (6), in the absence of mass transfer resistance, the rate

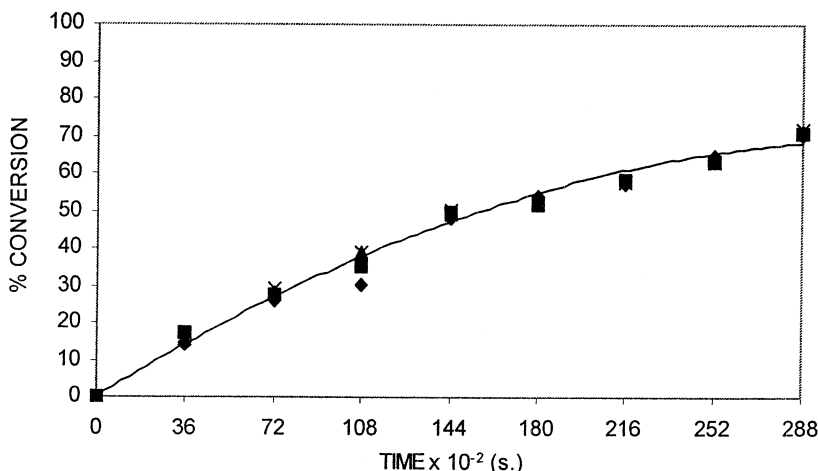


Fig. 3. Effect of particle size. Catalyst loading = 27.27 kg/m³, temperature = 85°C, liquid volume = 1.32×10^{-4} m³, lactic acid = 1.6×10^{-4} kmol, mole ratio (LA:IPA) = 1:10, speed = 16.67 rps, $0 < S_1 < 90$, $90 < S_2 < 212$, $212 < S_3 < 300$ and $S_4 = 700 \mu\text{m}$. ♦, S₁; ■, S₂; ▲, S₃; ×, S₄.

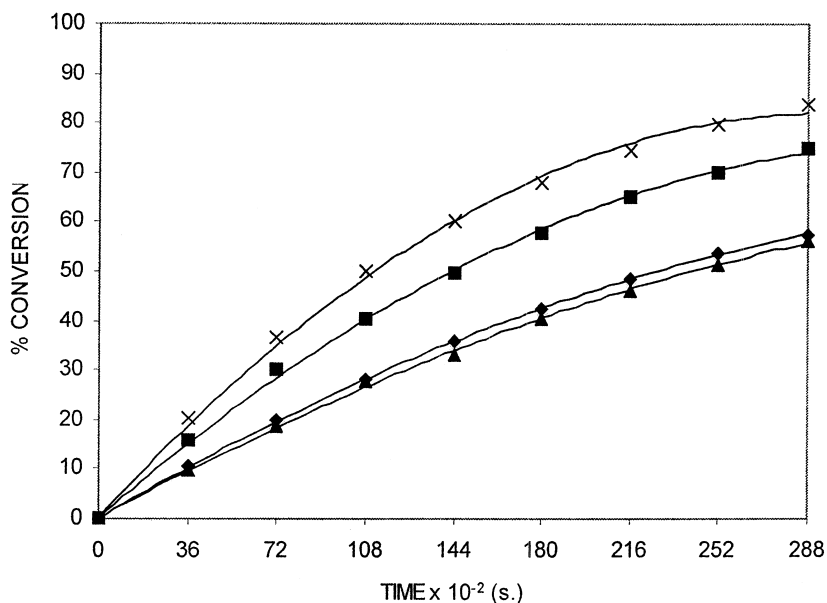


Fig. 4. Effect of catalyst loading. Temperature = 85°C, reaction volume = $1.32 \times 10^{-4} \text{ m}^3$, lactic acid = $1.6 \times 10^{-4} \text{ kmol}$, speed = 16.67 rps, mole ratio (LA:IPA) = 1:10, particle size = 700 μm . ♦, 10.9; ■, 27.27; ▲, 16.36; ×, 38.98.

of reaction is directly proportional to catalyst loading based on the entire liquid phase volume. The catalyst loading was varied from 10.9 to 38.28 kg/m^3 , which corresponds to 10–35%

w/w of the limiting reagent. Thus typical first-order plots were made as per Eq. (10) with w as a parameter (Fig. 5) and the slopes of these lines were calculated as k_1 .

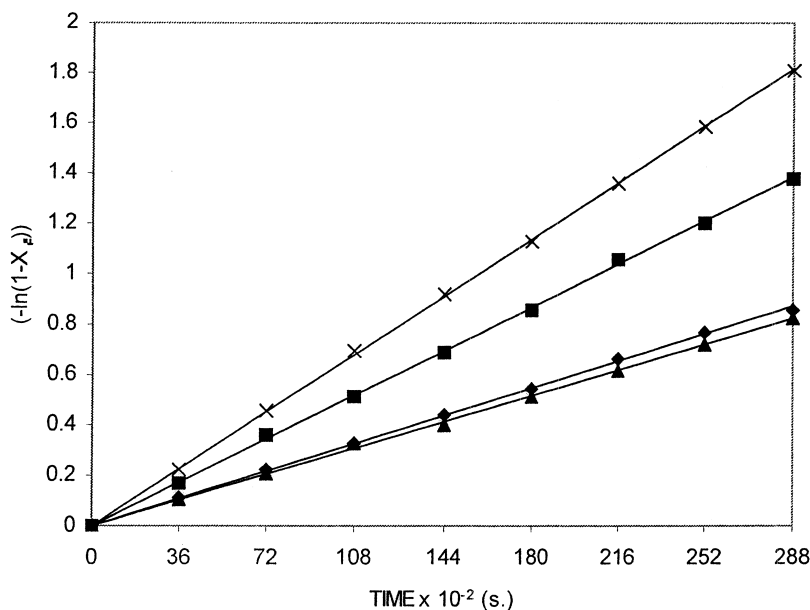


Fig. 5. Effect of catalyst loading. $-\ln(1-X_A)$ vs. time (s). Temperature = 85°C, reaction volume = $1.32 \times 10^{-4} \text{ m}^3$, lactic acid = $1.6 \times 10^{-4} \text{ kmol}$, speed = 16.67 rps, particle size = 700 μm . ♦, 10.9; ■, 27.27; ▲, 16.36; ×, 38.98.

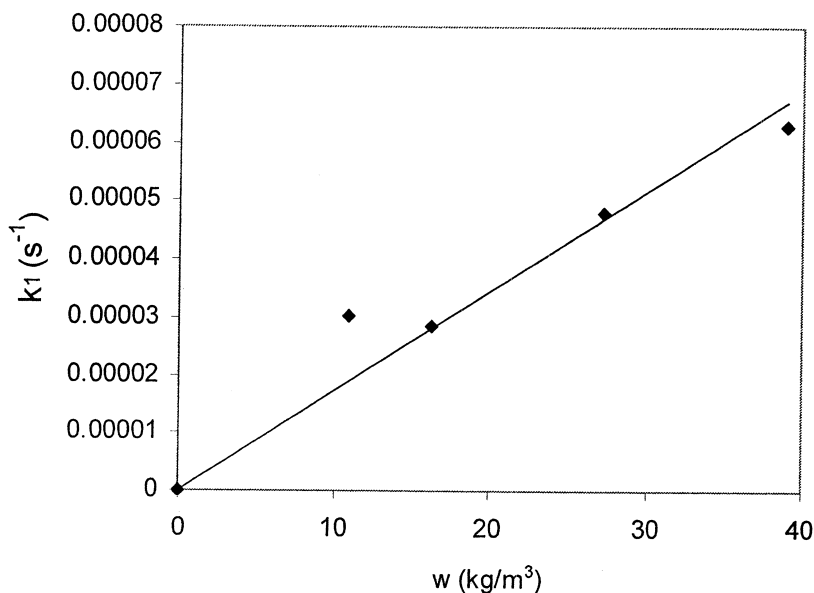


Fig. 6. Effect of catalyst loading, k_1 vs. w . Temperature = 85°C, reaction volume = 1.32×10^{-4} m³, lactic acid = 1.6×10^{-4} kmol, speed = 16.67 rps, mole ratio (LA:IPA) = 1:10, particle size = 700 μ m.

A plot of the pseudo first-order rate constant (k_1) vs. the catalyst loading (w) was made. It is seen that the rate is linearly proportional to w (Fig. 6). Further theoretical analysis was done as is shown:

At steady state,

$$k_{SL-A} a_p \{ [A_0] - [A_S] \} = \eta k_{R1} w [A_S] \quad (12)$$

but

$$a_p = \frac{6w}{\rho_p d_p} \quad \text{and} \quad Sh = \frac{k_{SL-A} d_p}{12D_{AB}} = 2 \quad (13)$$

For $\eta = 1$ (no intra-particle resistance),

$$\frac{[A_0]}{[A_S]} = 1 + \frac{k_{R1} \rho_p d_p^2}{12D_{AB}} \quad (14)$$

When intraparticle diffusion is present, the Thiele modulus is given as:

$$\phi = \frac{d_p}{6} \left[\frac{k_{R1} \rho_p}{D_{e-AB}} \right]^{1/2} \quad \text{and} \quad \eta = 1/\phi. \quad (15)$$

Where,

$$D_{e-AB} = \frac{D_{AB} \epsilon}{\tau} \quad (16)$$

$$\frac{[A_0]}{[A_S]} = 1 + \left[\sqrt{\frac{k_{R1} D_{AB} \epsilon \rho_p}{\tau}} \right] d_p \quad (17)$$

where ϵ = porosity and τ = tortuosity.

Thus, making appropriate substitutions, it is seen that Eq. (12) is valid and not Eq. (17), giving $[A_S] = [A_0]$, i.e., the rate is linearly

Table 1
Effect of mole ratio on the reaction^a

Experiment no.	Lactic acid ($\times 10^4$ kmole)	IPA ($\times 10^3$ kmole)	Mole ratio LA:IPA	Catalyst (g)	Liquid volume ($\times 10^4$ m ³)	Catalyst loading (kg/m ³)
1	1.6	1.60	1:10	3.6	1.32	27.27
2	1.6	3.36	1:21	7.0	2.56	27.27
3	1.6	7.04	1:44	15.0	5.50	27.27

^a Temperature = 85°C, speed of agitation = 16.67 rps.

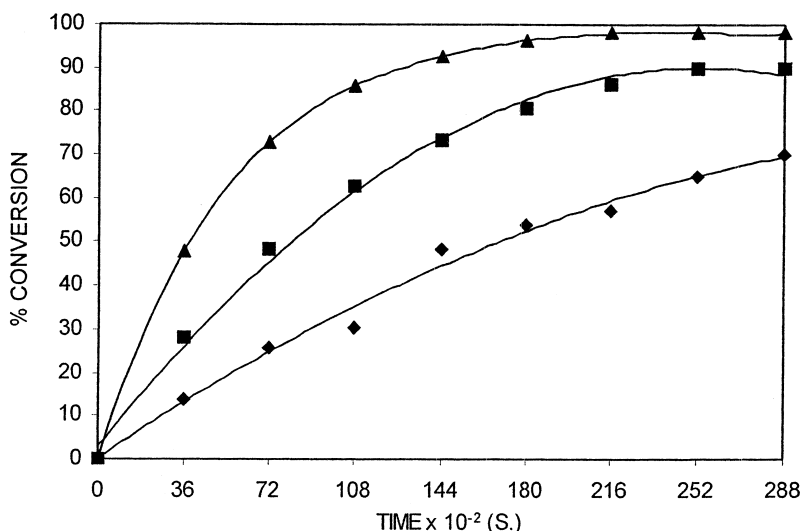


Fig. 7. Effect of mole ratio. Catalyst loading = 27.27 kg/m^3 , temperature = 85°C , lactic acid = $1.6 \times 10^{-4} \text{ kmol}$, speed = 16.67 rps, particle size = $700 \text{ }\mu\text{m}$. ♦, 1.10; ■, 1.21; ▲, 1.44.

proportional to catalyst loading in the absence of any intraparticle diffusion (Fig. 6).

5.5. Effect of mole ratio

Table 1 presents the experimental conditions. The catalyst loading per unit liquid volume was kept constant in all experiments.

Experiments were carried out by taking $1.6 \times 10^{-4} \text{ kmol}$ of lactic acid and the desired quantity of isopropanol with Amberlyst-36 loading of 27.27 kg/m^3 at 85°C . The mole ratio of LA:IPA was changed as 1:10, 1:21 and 1:44.

The concentration of isopropyl alcohol had an influence on the reaction rate and on the conversion. As the mole ratio of lactic acid to isopropanol was increased, the conversion of lactic acid increased due to excess concentration of isopropanol $[B_0]$. This is due to the corresponding increase in the pseudo-first-order constant k_1 (see Eq. (8)). The rate of reaction was linear in the concentration of lactic acid. Beyond 1:44 there was no more effect and the reaction produced almost the same conversions (Fig. 7).

5.6. Kinetics of the reaction

When both external and internal mass transfer resistances are absent, the kinetics of the surface reaction by using the power-law model can be established. In terms of mole ratio and fractional conversion, Eq. (6) can be modified and integrated to the following:

$$\ln \left[\frac{M - X_A}{M(1 - X_A)} \right] = [A_0](M - 1)k_{R2}wt \quad (M \neq 1) \quad (18)$$

Table 2
The rate constants for different catalysts

	$k_1 \times 10^5$ (s^{-1})	$k_{R1} \times 10^6$ ($\text{m}^3/[\text{s kg}]$)	$k_{R2} \times 10^6$ $1/\{[s][\text{kmole/m}^3]$ $[\text{kg/m}^3]\}$
Indion-130	3.48	1.28	0.105
Ambelyst-36	4.14	1.52	0.125
Amberlyst-15	4.00	1.47	0.121
HPA/F-44	2.11	0.77	0.064
HPA/K10	2.92	1.07	0.088
Amberlite-120	2.67	0.098	8.068×10^{-3}
Filtrol-44	1.95	0.714	0.059
Dowex 50W	3.38	1.24	0.102

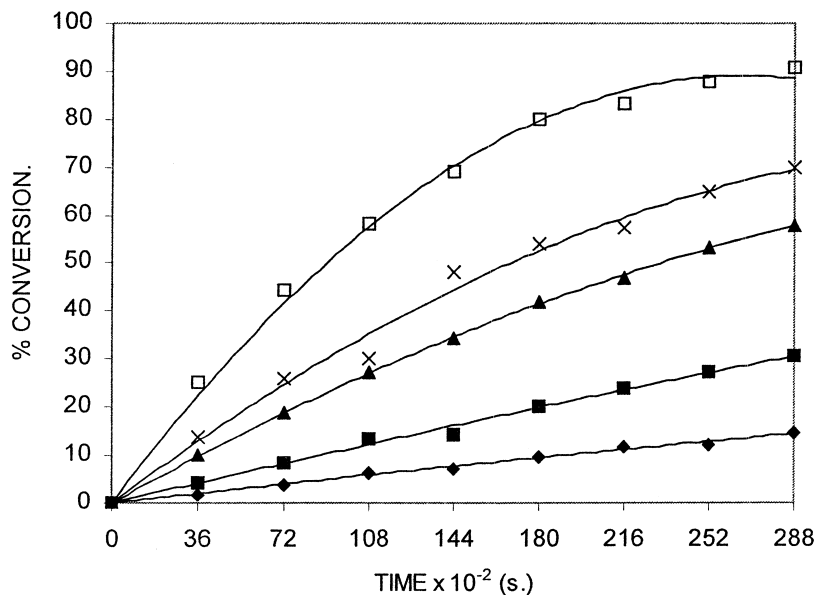


Fig. 8. Effect of temperature. Catalyst loading = 27.27 kg/m³, reaction volume = 1.32 × 10⁻⁴ m³, lactic acid = 1.6 × 10⁻⁴ kmol, speed = 16.67 rps, mole ratio (LA:IPA) = 1:10, particle size = 700 μm. ♦, 60°C; ■, 70°C; ▲, 80°C; ×, 85°C; □, 90°C.

In the present case, M was very high and thus, the above Eq. (18) reduced to Eq. (10). Thus, plots were made of $-\ln(1-X_A)$ vs. t to determine k_1 from which k_{R1} , and hence k_{R2} , were calculated (see Fig. 5, for instance). The data for rate constants for different catalysts are shown in the Table 2.

5.7. Effect of temperature

The effect of temperature on conversion under otherwise similar conditions was studied in the range of 60–90°C (Fig. 8). It is seen that the conversion increases with temperature. The plots of $-\ln(1-X_A)$ vs. time indicate a

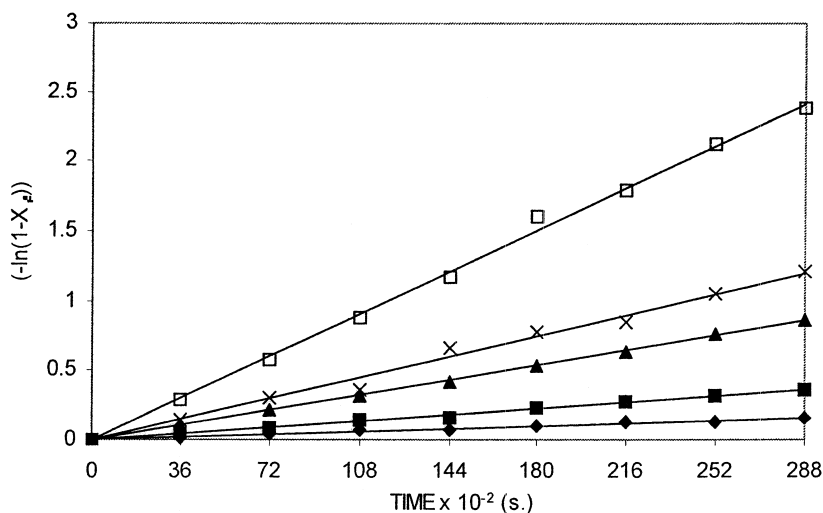


Fig. 9. Effect of temperature. $-\ln(1-X_A)$ vs. time (s). Catalyst loading = 27.27 kg/m³, temperature = 85°C, reaction volume = 1.32 × 10⁻⁴ m³, lactic acid = 1.6 × 10⁻⁴ kmol, speed = 16.67 rps, mole ratio (LA:IPA) = 1:10, particle size = 700 μm. ♦, 60°C; ■, 70°C; ▲, 80°C; ×, 85°C; □, 90°C.

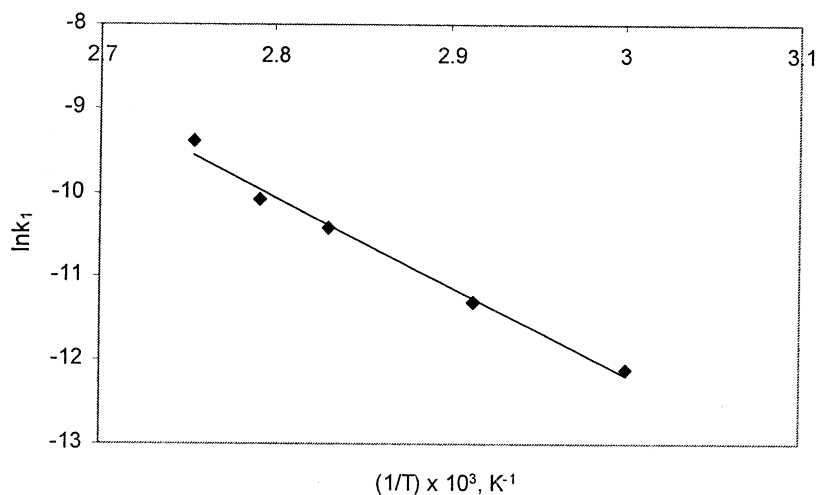


Fig. 10. Effect of temperature. $\ln k$ vs. $1/t$. Catalyst loading = 27.27 kg/m^3 , reaction volume = $1.32 \times 10^{-4} \text{ m}^3$, lactic acid = $1.6 \times 10^{-4} \text{ kmol}$, speed = 16.67 rps, mole ratio (LA:IPA) = 1:10, particle size = $700 \text{ }\mu\text{m}$.

straight-line behavior typical of a pseudo-first order reaction (Fig. 9). The rate constants k_1 at 60, 70, 80, 85 and 90°C were 5.6111×10^{-6} , 1.2138×10^{-5} , 2.9805×10^{-5} , 4.1444×10^{-5} and $8.3611 \times 10^{-5} \text{ s}^{-1}$, respectively. The Arrhenius plot is shown in Fig. 10 to get the activation energy as $21 \times 10^3 \text{ kcal/kmol}$, which

confirms that the reaction is intrinsically kinetically controlled.

5.8. Activity of various catalysts

The activity of the various catalysts is evaluated on the basis of rate constants k_1 that are

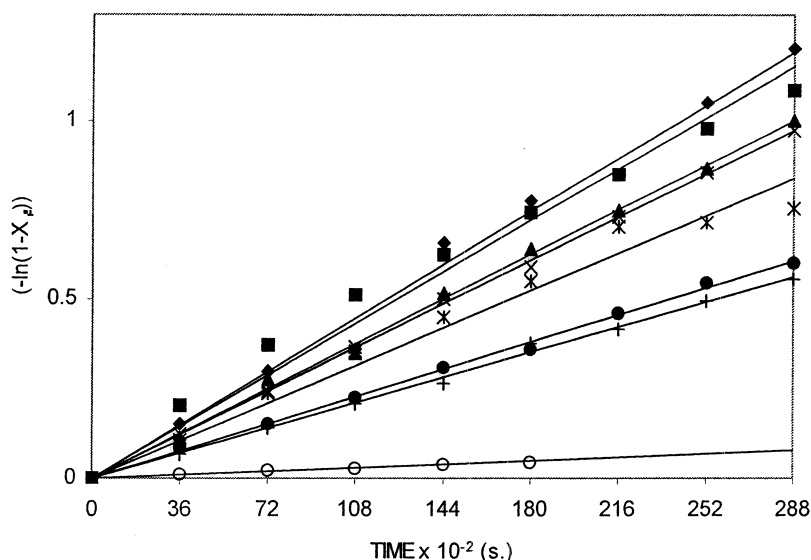


Fig. 11. Effect of different catalysts. $-\ln(1-X_A)$ vs. time (s). Catalyst loading = 27.27 kg/m^3 , temperature = 85°C , reaction volume = $1.32 \times 10^{-4} \text{ m}^3$, lactic acid = $1.6 \times 10^{-4} \text{ kmol}$, speed = 16.67 rps, mole ratio (LA:IPA) = 1:10. ◆, AMB-36; ■, AMB-15; ▲, IND-130; ×, DOWEX; ✕, HPA/K10; ●, HPA/F-44; +, F-44; ○, AMBI-120.

obtained under the kinetically controlled mechanism. Table 2 shows the values of k_1 for various catalysts and Fig. 11 shows the graph of $(-\ln(1-X_A))$ vs. t . The activity of the catalysts are as follows: Amberlyst-36 > Amberlyst-15 > Indion-30 > Dowex-50-W > 20% DTPA/K-10 > 20% DTPA/Filtrol-44 > Filtrol-44 > Amberlite-120. The meq/g dry values for Amberlyst-36, Indion-130, Amberlyst-15 are >5.45, 4.8 and 4.9, respectively. The value of meq/g dry for Amberlyst-36 is maximum and also the final conversion by using this catalyst was observed to be maximum. The ion-exchange resin Amberlite-IR 120 has a tighter pore structure as compared to the others and there is likely to be substantial intraparticle diffusional resistances.

6. Conclusions

The current work has addressed the use of a variety of ion-exchange resin catalysts in the synthesis of isopropyl lactate from lactic acid and isopropyl alcohol. The Amberlyst-36 was found to be the best catalyst. The kinetics of this reaction was studied and the rate was found to be controlled by the surface reaction (intrinsic kinetics) rather than mass transfer effects.

7. Nomenclature

ϵ	Porosity, dimensionless
ρ_p	Particle density, kg/m^3
$[A]$	Concentration of A, kmol/m^3
$[A_0]$	Concentration of A in the bulk, kmol/m^3
$[A_0]_i$	Concentration of A in the bulk at time $t=0$, kmol/m^3
$[A_s]$	Concentration of A at the surface of the catalyst, kmol/m^3
$[B_0]$	Concentration of B in the bulk, kmol/m^3
$[B_s]$	Concentration of B at the surface of the catalyst, kmol/m^3
A	Reactant A, lactic acid

a_p	Surface area per unit volume of the catalyst, m^2/m^3
B	Reactant B, isopropyl alcohol
D_{AB}	Mutual diffusion coefficient of solute A at very low concentrations in the solvent B, m^2/s
D_e	Effective diffusivity, m^2/s
D_{e-AB}	Effective diffusivity, m^2/s
d_p	Diameter of the particle, m
η	Effectiveness factor, dimensionless
k_{R1}	Pseudo first order rate constant, m^3/kmol
k_{R2}	Second order rate constant, $\text{m}^6/\text{kmol}^{-1} \text{kg}^{-1} \text{s}^{-1}$
k_{SL-A}	Solid liquid mass transfer coefficient for species A, m/s
k_{SL-B}	Solid liquid mass transfer coefficient for species B, m/s
M	Mole ratio of $[B_0]$ to $[A_0]$
S_1-S_4	Particle size range, μm
T	Absolute temperature, K
t	time, s
ϵ	Fractional porosity
ϕ	Thiele's modules
τ	Tortuosity, dimensionless
w	Catalyst loading, kg/m^3
X_A	Fractional conversion of A

Acknowledgements

H.B.K. thanks UGC (University Grants Commission) for a JRF. Financial support from Borax Morarji is also acknowledged. Financial support for research activity under the Darbari Seth Professorship Endowment to G.D.Y. is acknowledged.

References

- [1] M.A. Ogliaruso, J.F. Wolfe, *Synthesis of Carboxylic Acids, Esters and Their Derivatives*, John-Wiley, New York, 1991.
- [2] G.D. Yadav, P.H. Mehta, *Ind. Eng. Chem. Res.* 33 (9) (1994) 2198–2208.
- [3] F.A. Carey, *Advanced Organic Chemistry*, 3rd Edition, Plenum Press, New York, 1990.

- [4] T.S. Thorat, V.M. Yadav, G.D. Yadav, *Appl. Catal. A. General* 90 (1992) 73.
- [5] G.D. Yadav, N. Kirthivasan, *J. Chem. Soc. Chem. Commun.* (1995) 203.
- [6] G.D. Yadav, V.V. Bokade, *Appl. Catal. A. General* 147 (1996) 299–323.
- [7] G.D. Yadav, T.S. Thorat, *Ind. Eng. Chem. Res.* 35 (1996) 721–732.
- [8] S.F. Brian, J.H. Antony, G.S. Peter, R.T. Austin, in: *Vogel's Textbook of Practical Organic Chemistry*, 5th Edition, Longman, Oxford University Press, London, 1989, p. 702.
- [9] G.D. Yadav, M.S. Krishnan, *Organic Process Research and Development* 2 (1998) 86–95.
- [10] P.S. Kumbhar, G.D. Yadav, *Chem. Eng. Sci.* 44 (11) (1989) 2535.
- [11] L.K. Doraiswamy, M.M. Sharma, *Heterogeneous Reactions, Analysis, Examples and Reactor Design*, Vol. 2, John Wiley, New York, 1994.
- [12] R.C. Reid, T.K. Prausnitz J.M. Sherwood, *The Properties of Gases and Liquids*, 3rd Edition, McGraw-Hill, New York, 1977.