

Kinetics of esterification of propionic acid with n-amyl alcohol in the presence of cation exchange resins

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Abstract—Esterifications of n-amyl alcohol with propionic acid catalyzed by macroporous (Amberlyst-15) and micro-porous (Dowex 50 W and Amberlite IR-120) polymeric ion-exchange resins were carried out between 333–348 K. When these catalysts were used as commercially available, Amberlyst-15 was observed to be the most effective catalyst with respect to rate constants, but after drying it became the less effective one. The reaction rate increased with increase in catalyst concentration and reaction temperature. Stirrer speed and different mesh sizes had virtually no effect on the rate under the experimental conditions. The effect of divinylbenzene content was examined for the microporous resin Dowex 50 W, and the results showed that the propionic acid conversion decreased as the divinylbenzene content was increased. The rate data were correlated with a second-order homogeneous reaction model. The apparent activation energies, reaction enthalpies and entropy values were calculated for each catalyst. Reaction monitoring is simple and fast by volumetric method and the reproducibility of this method was the order of $\pm 2.54\%$.

Key words: Esterification, Ion-exchange Resin, Heterogeneous Catalysis, Kinetics, Propionic Acid, n-Amyl Alcohol

INTRODUCTION

Esters of carboxylic acids have practical importance, since millions of tons of polyesters are produced via the reaction of dicarboxylic acids with diols and a wide variety of mono- and di-esters are used in the production of fine and speciality chemicals such as pharmaceuticals, pesticides and fragrances [Weisermel and Arpe, 1993]. The esterification reaction is a liquid-phase process, where the limiting conversion of the reactants is determined by equilibrium. Typically, esterification reactions are very slow, requiring several days to attain equilibrium in the absence of catalyst [Lilja et al., 2002]. To accelerate the reaction rate, catalysts are always employed in a liquid-phase esterification. Despite a strong catalytic effect, the use of a homogeneous catalyst like sulphuric acid and p-toluene sulfonic acid suffers several drawbacks such as the existence of more side reactions, equipment corrosion, and the need to deal with the waste containing acid. Under this situation the use of solid acid catalysts has received great attention in past years. While there exist many solid acid catalysts, ion-exchange resins are the most commonly used and have been proven to be effective in liquid-phase esterification [Liu and Tan, 2001]. Typical resin catalysts are sulfonic acids fixed to polymer carriers, such as polystyrene cross-linked with divinylbenzene (DVB) [Lilja et al., 2002]. Heterogeneous catalysts like cationic exchange resins have proven to be beneficial from both catalysis and engineering points of view. Their potential of offering equally good performance in both polar and non-polar reaction media at low concentration of reactants has made them attractive candidates for many acid catalyzed reactions [Mahajani, 2000].

Research in catalysis by ion-exchange resins is undoubtedly interesting, not only from a purely physicochemical point of view but also

in terms of the advantages of these types of catalysts over the conventional ones. Ion-exchange resins increase the product yield, keep their activity a long time, and do not pollute [Kırbaşlar et al., 2001]. But the complication in heterogeneous catalysis compared with homogeneous conditions arises from the complex nature of the heterogeneous processes including diffusion, adsorption, desorption as well as several surface reaction steps. Since the heterogeneous process, different from homogeneous catalysis, proceeds on the surface, knowledge of the structure of the surface of a catalyst affects the catalysis phenomena. The reaction, as a rule, proceeds on the phase interface, i.e., on the surface of the solid- the catalyst [Gerasimov et al., 1974].

The rate of a resin-catalyzed reaction will be a function of (1) the acidity and (2) the accessibility of the active sites, i.e., $r=f$ (acidity, accessibility) where $\text{acidity}=f$ (type and numbers of acid groups, divinylbenzene content, reaction medium) and $\text{accessibility}=f$ (divinylbenzene content, particle size, porosity, reaction medium, diffusivity) [Chakrabarti and Sharma, 1993]. Chakrabarti and Sharma pointed out that most resin-catalyzed reactions can be classified either as quasi-homogeneous or as quasi-heterogeneous. The idealized homogeneous state requires complete swelling of the resin and total dissociation of the polymer-bound- SO_3H group. They concluded that in all cases which have so far been studied, and in which limitations due to slow diffusion process can be ruled out, the kinetic order of the chemical reaction in the particles was found to be the same as in homogeneous catalysis by a dissolved electrolyte. This is strong evidence in support of the view that the reaction mechanism is essentially the same in both cases [Xu and Chuang, 1996].

The preliminary mathematical modelling of the observed esterification kinetics was based on second order kinetics which principally could be applied to both homogeneous and heterogeneous catalyst. The sulfonic acid groups ($-\text{SO}_3$) on a heterogeneous catalyst or H^+ in a homogeneous catalyst (e.g. H_2SO_4 , HCl) initiate the esterification reaction by donating a proton to the carboxylic acid

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molecule.

Styrene copolymerized with a small amount of divinylbenzene at a low monomer dilution results in gel-type copolymers, which are characterized by a swollen state porosity. The pore size only depends on the proportion of divinylbenzene because of the restricted swelling of polymer structure by cross-linking. Therefore, the gel-type resins are completely ineffective as ion-exchangers or catalysts in non-polar media. If the gel beads are dry, the polymer matrix collapses and the polymer chains will be as close as atomic forces allow. In this condition, unless a reactant is capable of swelling the matrix, the collapsed gel beads exhibit almost no catalytic activity because only the sites on the bead's surface are accessible to the reactants. Macroporous copolymers, by contrast, contain significant non-gel porosity in addition to the gel one. The permanent porosity involves channels between agglomerates of minute spherical gel particles. Due to their pore structure macroporous resins are quite effective in non-swelling solvents [Coutinho and Souza, 2004].

In the present work, the applicability of both macroporous and gel resins has been examined for the esterification of propionic acid and n-amyl alcohol. The reasons for choosing this esterification reaction are that, n-pentyl propionate is used in food additives, cleaning fluids, fragrance solvents and printing inks; it is a slow evaporating solvent and its linear structure contributes to effective viscosity reduction.



Important variables such as catalyst concentration, mole ratio of reactants, reaction temperature, stirrer speed, mesh size, divinylbenzene content affecting the rate of the reaction were studied. And also, the emphasis of the current work was to determine the activity orders of different ion-exchange resins catalyzing the esterification reaction before and after being dried and to calculate the kinetic and the thermodynamic parameters for each catalyst.

EXPERIMENTAL

1. Chemicals

Propionic acid and n-amyl alcohol were purchased from Merck A.G. Propionic acid 99% (w/w) and n-amyl alcohol of 99% (w/w) were used as supplied.

2. Catalysts

The ion-exchange resins used as catalysts (Amberlyst-15, Dowex

50 W and Amberlite IR-120) were purchased from Fluka-Sigma AG. Their typical physical properties are reported in Table 1. At first, all these resins were used without any prior treatment in their commercial forms. And then, as the water contents of these resins are very different, drying them became necessary to compare the rate constants of the model reaction catalyzed by the different resins having equal water contents. For this reason, these catalysts were dried at 353 K, since drying at higher temperature involves the risk of losing sulfonic acid sites in the form of SO_3 , because of desulfurization of the polystyrene matrix of the catalyst [Hart et al., 2002].

3. Operation Procedure

The experimental assembly consisted of a 0.25 dm³ reactor fitted with a reflux condenser to prevent any loss of products. The reaction mixture was magnetically stirred at 700 rpm. The reaction vessel was kept in a stirred constant temperature bath where the temperature could be controlled within an accuracy of ± 0.1 K by a controller. Experiments were carried out at various molar ratios of propionic acid and n-amyl alcohol in the temperature range of 333, 338, 343 and 348 K ± 0.1 K by using different concentrations of catalyst (for Amberlyst-15) changing from 1.0% to 40.0% (by mass, catalyst/propionic acid).

In a typical experiment 10% (by mass) catalyst concentration of all resins was used at a molar ratio of propionic acid to n-amyl alcohol of 1 : 1 at 333 K and at a speed of agitation 700 rpm. The most widely employed and supposedly faster production technique for esters involves the reaction of acid and alcohols in the presence of acid catalyst. Use of solvents is not always convenient and is expensive on an industrial scale [Park et al., 1999]. For this purpose, we did not prefer to use solvent since propionic acid and amyl alcohol can dissolve within each other.

Propionic acid and polymeric catalyst were charged into the reaction vessel in a predetermined ratio. After the desired temperature was reached, n-amyl alcohol, at the same temperature, was drained into the reactor. This moment was considered as the beginning of the reaction and the liquid samples withdrawn from the reactor at regular intervals were analyzed by volumetric method.

4. Analysis

In this method, propionic acid in the reaction mixture was analyzed by titration with standard sodium hydroxide solution with phenolphthalein as an indicator. For this purpose an automatic titrator (DIGITRATE) was used to analyze the samples with the average standard deviations of ± 0.05 .

Table 1. Some physical and chemical properties of ion-exchange resins used as catalysts for the model reaction

Properties	Amberlyst-15	Dowex 50 W \times 2-4-8	Amberlite IR-120
Functional group	Sulphonic acid	Sulphonic acid	Sulphonic acid
Type	Macroreticular	Gel(microporous)	Gel type
Mesh size	20-50	20-50	16-45
Mean particle size (μm)	560	570	525
Thermal stability (°C)	120	150	120
*Water content (%)	2.00	78.44-66.41-44.81	53.50
*Capacity (meq/gram)	4.9003	4.7717-4.5502-4.3509	4.3289
* \pm standard error	0.1026	0.1255	0.1096

*The values determined experimentally (others are taken from the literature).

RESULT AND DISCUSSION

1. Effect of Agitation

The external mass transfer resistance to the reaction process can be affected by stirrer speed. A high degree of agitation was maintained in order to eliminate the liquid film resistance. It was found that a stirrer speed of about 500 rpm was enough to keep all the catalyst particles in suspension and that the stirrer speed did not affect the rate of the reaction above this speed. Hence, in the range of stirrer speeds employed the reaction rate was not affected by the liquid film resistance. Fig. 1 shows that the conversion rate of propionic acid is independent of stirrer speed. This indicates that the external mass transfer resistance is not a rate-controlling step. In the subsequent tests, a stirrer speed of 700 rpm was used to ensure that the measured reaction rate was free from external diffusion.

2. Effect of Mesh Size and Divinylbenzene Content

To investigate the internal diffusion effects on the reaction of Eq. (1), after being dried at 353 K Dowex 50 W \times 4 resins having different mesh sizes (50-100 mesh, 100-200 mesh and 200-400 mesh)

were used as catalysts in the model reaction. Fig. 2 shows the effects of different mesh sizes on the conversion of propionic acid. Yadav and Mehta [1994], concluded that the intraparticle diffusional resistance was absent for these catalysts and that theoretical analysis showed that internal resistance exists for particle sizes larger than 0.6 mm. For this reason, ion-exchange resins having small particles (500-570 μ m) have been chosen as catalysts on the esterification reactions, and as seen from Fig. 2, the effect of internal diffusion on reaction rate is not significant.

Organic ion exchangers have several specific properties as catalysts, one of which is the effect of the amount of cross-linking agent in the macromolecule of polymer on their physical, chemical and catalytic properties. Some authors found that catalytic activities of microporous ion exchangers decrease with the increasing of cross-linking degree, while those of macroporous ion-exchangers increase due to their increasing surface areas [Rodriguez and Setinek, 1975]. The effect of divinylbenzene content on the rate of reaction was studied by conducting the reactions with Dowex 50 W resins having 2%, 4% and 8% DVB contents under otherwise similar conditions. These resins having different DVB contents were dried at 353

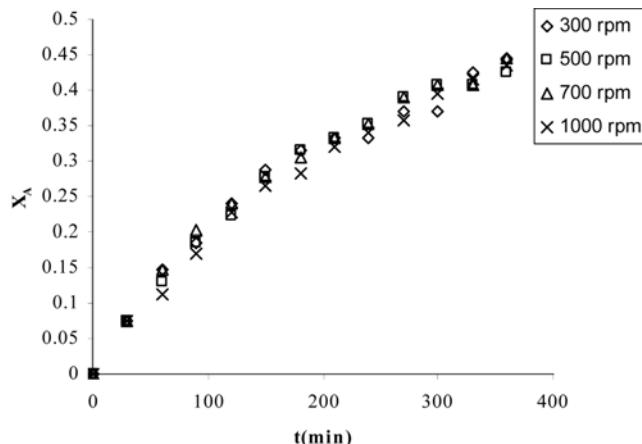


Fig. 1. Experimental data obtained at different stirrer speeds for a molar ratio of n-amyl alcohol to propionic acid of 1:1 at 333 K using 5.0% (w/w) Amberlyst-15 as the catalyst.

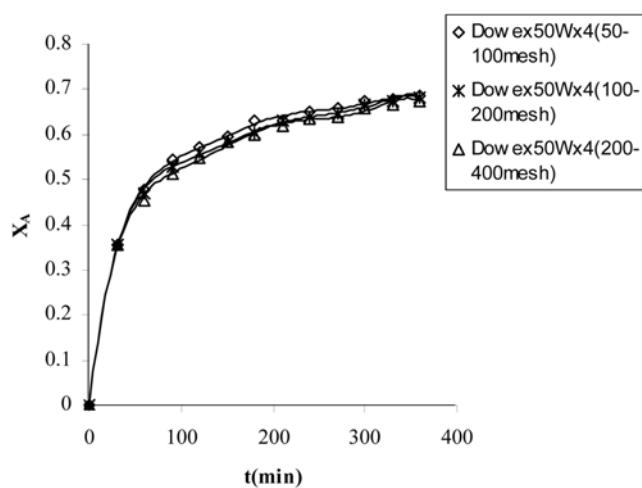


Fig. 2. Effect of resin mesh sizes on propionic acid conversion.

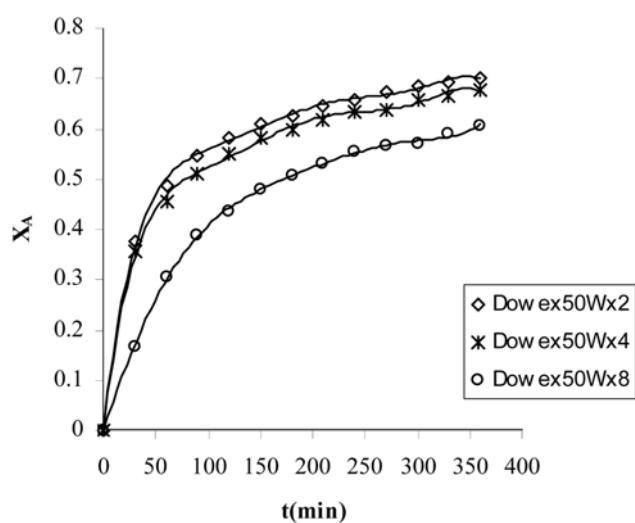


Fig. 3. Effect of % divinylbenzene content on propionic acid conversion.

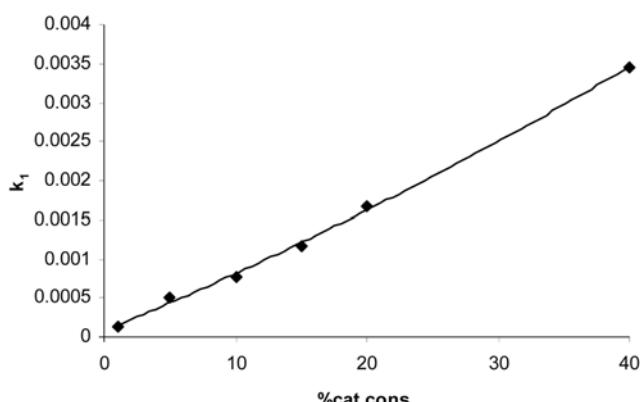


Fig. 4. Effect of various amounts of catalyst (Amberlyst-15) used on the rate of the model reaction at 333 K (M=1/1).

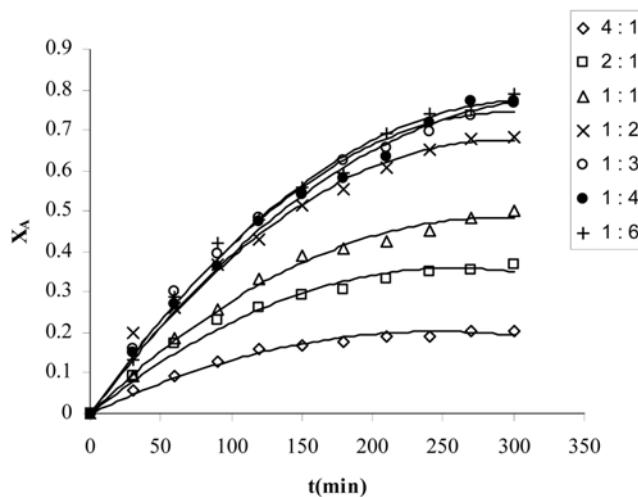


Fig. 5. Esterification of propionic acid with n-amyl alcohol at 333 K on Amberlyst-15 at varying molar ratios between propionic acid and n-amyl alcohol; 4:1, 2:1, 1:1, 1:2, 1:3, 1:4 and 1:6.

K until the mass remained constant (about 2 days). The effect of %DVB content is shown in Fig. 3. As the %DVB contents increased, the propionic acid conversion was found to decrease not-linearly due to their different water contents.

3. Effect of Catalyst Loading

The catalyst loading was varied from 1.0% (by mass) to 40% (by mass) on the basis of the amount of propionic acid at constant temperature, 333 K. Fig. 4 shows the effect of catalyst loading on the rate of esterification reaction. The rate of reaction is directly proportional to the catalyst loading because the surface area and hence the total number of active sites increase linearly with it, and so do the reaction rate constants.

4. Effect of Mole Ratio

The mole ratio of propionic acid to the n-amyl alcohol was varied from 4:1 to 1:6 to assess its effect on the rate of reaction with a catalyst loading of 10% w/w based on the propionic acid, at constant temperature 333 K (Fig. 5). The concentration of n-amyl alcohol had an influence on the reaction rate and the conversion. It was observed that as the mole ratio of the n-amyl alcohol to propionic acid was increased from (4:1) to (1:3), the conversion increased substantially. There was no further increase in conversion when mole ratio was increased (1:3) to (1:6). This suggests that n-amyl alcohol or the product is strongly adsorbed and there is a competitive adsorption of propionic acid with n-amyl alcohol or the product. Adsorption of propionic acid is essential to generate carbocations for the reaction to proceed. Adsorption of n-amyl alcohol is reduced and many sites are occupied by propionic acid.

5. Effect of Temperature

The effect of temperature on the rate of reaction was studied by conducting the reactions at 333, 338, 343 and 348 K under otherwise similar conditions. The propionic acid conversion was found to increase with temperature (see Fig. 6) for all catalysts.

6. Effect of Different Catalysts on Reaction Rate

The limitation of the gel resins was largely overcome, around 1960, with the advent of the "macroporous" ion-exchange resins. As the catalyst used is a macroporous ion-exchange resin, a homo-

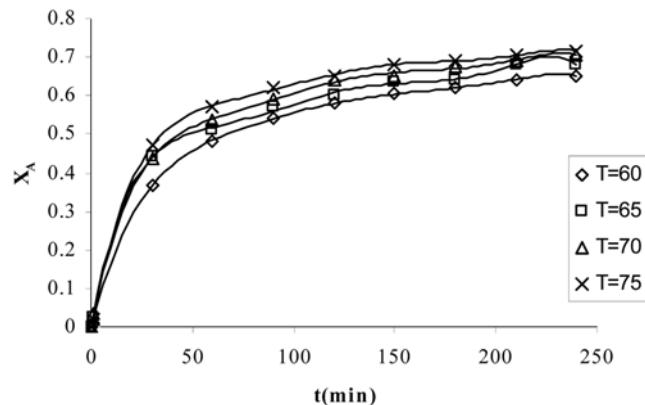


Fig. 6. Effect of temperature on conversion of propionic acid (M = 1/1), Dowex 50 W \times 2 catalyst loading based on propionic acid; 10% (by mass).

Table 2. According to Eq. (4), the calculated rate constants of the model reaction carried out with different types of catalysts before and after being dried in the same conditions by volumetric method

Catalyst type	$k_1 (\times 10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{min}^{-1})$	
	Before being dried	After being dried
Amberlyst-15	7.78	8.05
Dowex 50 W \times 2	5.38	21.50
Amberlite IR-120	3.56	9.13

geneous reaction could be assumed. This is because, in a macroporous resin, the pores are so large that the reactants are able to diffuse into the pores and the products to diffuse out without any resistance [Roy and Bhatia, 1987]. The concentrations of the reactants in the bulk and inside the pores were almost the same and thus led to a homogeneous reaction in the liquid phase. The protons responsible for catalyzing the reaction were available in the liquid phase to enable the reaction to proceed [Kırbaşlar et al., 2001].

In the present study, at first these three different catalysts were employed without any prior treatment under similar conditions of reaction temperature (333 K), catalyst loading of 10% w/w (catalyst/propionic acid), mole ratio (1:1) and stirrer speed 700 rpm. The activities of these catalysts were evaluated on the basis of rate constants k_1 that are obtained under the kinetically controlled mechanism. Table 2 shows the calculated rate constants according to Eq. (4) before and after being dried. The catalysts' activities were in the following order under otherwise similar conditions for the two different cases: in the first case, Amberlyst-15 $>$ Dowex 50 W $>$ Amberlite IR-120. In the second case, Dowex 50 W $>$ Amberlite IR-120 $>$ Amberlyst-15. In the first case, in spite of their very close ion-exchange capacities Amberlyst-15 showed maximum conversion since it had bigger pores and more surface areas [Yadav and Bhagat, 2005]. In contrast, the ion-exchange resin Amberlite IR-120 had a tighter pore structure as compared to the others and there was likely to be substantial intraparticle diffusional resistance. Therefore, in the second case the activity order changed because of their different water contents.

7. Kinetic Model

The rate of model reaction (1) by using the homogeneous model

can be written as

$$-\frac{dC_{PA}}{dt} = k_1 C_{PA} C_{AA} - k_2 C_{AP} C_W \quad (2)$$

For a mol ratio of $M = C_{PA,0}/C_{AA,0} = 1$ and initial concentrations of n-amyl propionate and water, $C_{AP} = C_{water} = 0$; Eq. (2) can be written to give the following equation in terms of the fractional conversion of the propionic acid.

$$\frac{dX_{PA}}{dt} = k_1 (1 - X_{PA})^2 - k_2 (X_{PA})^2 \quad (3)$$

For a mole ratio of $M = C_{PA,0}/C_{AA,0} = 1$ Eq. (3) can be integrated to give the following equation [Levenspiel, 1972]:

$$\ln \frac{X_{PA,e} - (2X_{PA,e} - 1)X_{PA}}{X_{PA,e} - X_{PA}} = 2k_1 \left(\frac{1}{X_{PA,e}} - 1 \right) C_{PA,0} t \quad (4)$$

where X_{PA} , fractional conversion of propionic acid,

$$X_{PA} = \frac{C_{PA,0} - C_{PA}}{C_{PA,0}} \quad (5)$$

Thus, a plot was made of the left-hand side versus time for Eq. (4) to determine the slope of the line from which the values of k_1 were calculated. Kinetic plots for the reactions between n-amyl alcohol and propionic acid are shown in Fig. 7. The values of k_1 for the catalysts loading 1%, 5% and 10% (by mass) mol ratio $M = 1/1$ and temperature 333 K were found to be $1.25 \times 10^{-4} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$, $5.04 \times 10^{-4} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ and $7.78 \times 10^{-4} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$, respectively. Fig. 7 shows the suitability of this model for the representation of the rate data. The data fall on straight lines for different catalyst loading, confirming the applicability of the model for this reaction.

$$\ln k_1 = \ln A - \frac{E_A}{R} \left(\frac{1}{T} \right) \quad (6)$$

From Eq. (6), Arrhenius plots ($\ln k_1$ versus $1/T$) were made as shown in Fig. 8, to find out the activation energies (E_A) and pre-exponential

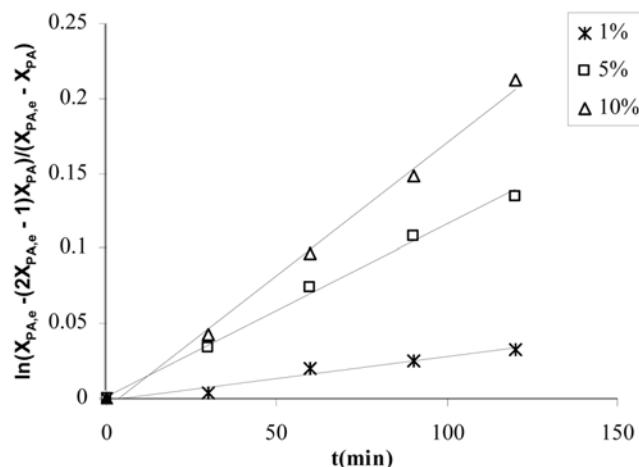


Fig. 7. Suitability of homogeneous model assuming second order reaction, kinetic plots for the reaction between n-amyl alcohol and propionic acid at 333 K ($M = 1/1$), catalyst loading based on propionic acid; 1%, 5% and 10% (by mass), respectively.

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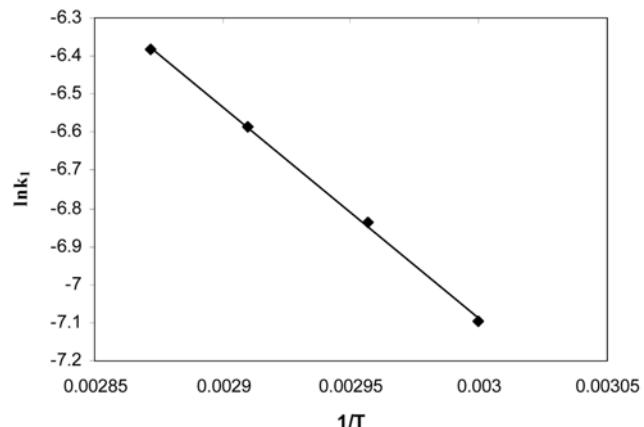


Fig. 8. Arrhenius Plot: mole ratio, n-amyl alcohol:propionic acid (1 : 1); catalyst, Amberlyst-15; catalyst loading, 10% (w/w) based on propionic acid; speed of agitation, 700 rpm.

Table 3. According to the Arrhenius plots, the calculated activation energies and pre-exponential factors of the model reaction carried out with different types of catalysts and the suitability of the Arrhenius plot to the linear regression model

Catalyst type	E_A (kJ/mol)	A ($\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$)	R^2
Amberlyst-15	45.956	13322.370	0.9991
Dowex 50 W×2	27.376	42.161	0.9914
Amberlite IR-120	38.875	1150.901	0.9813

tial factors (A). These values are represented in Table 3.

8. Calculation of Experimental Equilibrium Constant

The apparent equilibrium constant of the reaction can be found from the equilibrium conversions determined experimentally by using Eq. (7),

$$K_{eq} = \frac{C_{AP,e} C_{water,e}}{C_{PA,e} C_{AA,e}} = \frac{X_{PA,e}^2}{(1 - X_{PA,e})(M - X_{PA,e})} \quad (7)$$

For the molar ratio of propionic acid to n-amyl alcohol, $M = 1/1$, the equilibrium conversions of propionic acid were determined at different temperatures, 333, 338, 343 and 348 K for each catalyst and then,

$$\ln K_{eq} = \left(\frac{-\Delta G_r^0}{RT} \right) = - \frac{\Delta H_r^0}{RT} + \frac{\Delta S_r^0}{R} \quad (8)$$

from Eq. (8) [Hause, 1997], the values of the heat of reaction (ΔH_r^0) and entropy (ΔS_r^0) of this reaction were estimated and they are displayed in Table 4.

Table 4. According to Eq. (8), the calculated heat of reaction and the entropy of the reaction carried out with different types of catalysts and the suitability of the Eq. (8) to the linear regression model

Catalyst type	ΔH_r^0 (kJ/mol)	ΔS_r^0 (kJ/mol·K)	R^2
Amberlyst-15	-11.726	-0.036	0.9977
Dowex 50 W×2	-6.436	-0.008	0.9974
Amberlite IR-120	-9.804	-0.027	0.9980

CONCLUSIONS

The resins catalyzing the esterification reaction showed an absence of external mass transfer resistance and internal diffusional effect. The values of the kinetic constants of the model reaction studied at different agitation speed and obtained with differently mesh sized ion exchangers are not discussed, since they were influenced by experimental errors of kinetic experiments.

The acid catalytic activity of sulfonated polystyrene ion-exchange resins shows a pronounced dependence on the degree to which the polymer is sulfonated. When the resins are used as anhydrous catalysts this increased acid strength is a direct result of structural features such as the degree of di-substitution, the presence of sulfone bridges and interactions between neighbouring groups [Yadav and Kulkarni, 2000].

The gel and macroporous resins have very different activity orders before and after being dried until the mass remained constant. As the concentration of sulfonic acid in the internal gel solution increases, stronger acid sites and higher specific catalytic activities are generated. A similar trend of increasing acid strengths has been observed in anhydrous resins, but this has been explained in terms of structural features such as di-substitution of sulfonic acid groups on styrene units, giving rise to intrinsically stronger acid sites.

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NOMENCLATURE

C	: concentration of components in the bulk liquid phase [mol·dm ⁻³]
E _A	: activation energy [kJ·mol ⁻¹]
ΔH _r ⁰	: heat of reaction [kJ·mol ⁻¹]
ΔS _r ⁰	: reaction entropy [kJ·mol ⁻¹ ·K ⁻¹]
PA	: propionic acid
A	: pre-exponential factor [dm ³ ·mol ⁻¹ ·min ⁻¹]
k _f	: second-order rate constant for forward reaction [dm ³ ·mol ⁻¹ ·min ⁻¹]
K _{eq}	: equilibrium constant
M	: mol ratio of propionic acid to n-amyl alcohol
AP	: amyl propionate
AA	: n-amyl alcohol
R	: gas constant [J·mol ⁻¹ ·K ⁻¹]
T	: temperature [K]
t	: time [min]
X _{PA}	: fractional conversion of propionic acid

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