Adsorption and Kinetic Parameters for Synthesis of Methyl Nonanoate over Heterogeneous Catalysts

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ABSTRACT: Methyl nonanoate was synthesized in a batch reactor by esterification of nonanoic acid with methanol catalyzed by the cation exchange resins, Dowex 50WX2, Amberlyst 35, and Amberlyst 15. The effect of various parameters such as speed of agitation, catalyst loading, molar ratio, and reaction temperature on degree of conversion has been reported. The conversion of nonanoic acid to methyl nonanoate was found to increase with an increase in temperature in the range of 303.15—333.15 K and the increase was appreciable with an excess use of methanol in the reaction mixture. Nonideality of the liquid phase was taken into account by using activities instead of concentration. The activity coefficients were calculated using the UNIFAC group contribution method. The possible mechanism of reaction was mathematically treated using theories of the Eley—Rideal model based on inhibition by water and methanol on the Amberlyst 15. The reaction rate constants and the adsorption coefficients for methanol and water were determined from the experimental data established at three different temperatures for the effect of initial concentration of acid and alcohol. The kinetics reported in this study was obtained under conditions free of both external and internal mass transfer resistance. Activation energy and pre-exponential factor of the reaction were found to be 47.6 kJ mol⁻¹ and 3.2 × 10⁴ L² g⁻¹ moP₁ h⁻¹, respectively.

1. INTRODUCTION

Esterification of carboxylic acids with alcohols represents well-known liquid-phase reactions of considerable industrial interest due to the importance of organic ester products. Esterification reactions can proceed with or without a catalyst but in the absence of a catalyst, the reaction is, however, extremely slow, since its rate depends on the auto-protolysis of the carboxylic acid. Therefore, esterification is carried out in the presence of an acid catalyst, which acts as a proton donor to the carboxylic acid. For this reason, both homogeneous and heterogeneous catalysts have been used to accelerate the reaction rate. While the mineral acids can be given as the example of the homogeneous catalyst, a cation-exchange resin in the acid form can serve as a heterogeneous catalyst. Despite a strong catalytic effect, the use of homogeneous catalysts such as sulfuric acid suffers from drawbacks, such as the existence of side reactions, equipment corrosion, and having to deal with acid-containing waste. The replacement of homogeneous catalysts by heterogeneous catalysts is gaining importance because heterogeneous catalysts have good physical and chemical properties, show no corrosion, and have high selectivity and thermal stability. Many heterogeneous catalysts reported in literature for the esterification reaction includes ion exchange resins, H-ZSM-5, niobic acids, heteropolyacids, and zeolites-T membrane. The effects of many ion exchange resins were investigated in esterification reactions. For example, the esterification of acrylonitrile acid with propylene glycol was investigated in the presence of Amberlyst 15. Miller et al. studied the kinetics of mixed succinic acid/acetate with Amberlyst 70 ion-exchange resin as catalyst and investigated batch isothermal reactions at different ethanol/acid molar ratios (1:1—27:1), temperatures (343—393 K) and catalyst loadings (1.0—9.3 wt % of solution). Meanwhile, the research on the esterification of acetic acid with methyl alcohol over heterogeneous catalyst, Amberlyst 36, has been reported, where it was concluded that the magnitude of adsorption strengths follows the order of water > methanol > acetic acid > methyl acetate and that the ER and the LHHW model determine the kinetic parameters equally well. The investigation of the kinetics for the esterification reaction on the basis of experimental data obtained in the batch reactor has been widely reported in the literature.

Despite many reports on the esterification with heterogeneous catalysts, however, a few kinetic studies consider the effect of adsorption, desorption, reaction, and diffusion in the heterogeneous system, unlike homogeneous catalytic system. Therefore, the reaction mechanisms and rate expressions are more complex than those in the case of the homogeneous system. Typical and widely used kinetic models in heterogeneous catalytic systems are the pseudo-homogeneous (PH) model, Langmuir—Hinshelwood (LH) model, and Eley—Rideal (ER) model. The PH model is similar to the power law model for homogeneous reactions where adsorption and desorption of all components are negligible. The LH model represents the rate-determining step being the reaction of both the reactants (e.g., acid and alcohol in the esterification reaction) adsorbed on the catalyst surface, whereas the ER model indicates that the rate-determining step is the reaction between one reactant adsorbed on the catalyst surface and its counterpart reactant in the bulk region. Sane et al. carried out the kinetic study for the esterification of lactic acid with methanol over Amberlyst 1S, where the kinetic behavior of heterogeneous 

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esterification and the correlation of experimental data with the PH, LH, and ER models were investigated. The behavior of liquid mixtures in the liquid phase reactions may deviate markedly from that of the ideal solution. The activity coefficients were used in the model to account for the nonideal mixing behavior of the bulk liquid phase, and the activity coefficients were predicted using the UNIFAC group contribution method. Nonanoic acid can be esterified with alcohols such as methanol, ethanol, and propanol. A systematic reaction scheme for esterification of nonanoic acid with methanol is given in Scheme 1.

The ester of nonanoic acid with methanol, namely, methyl nonanoate finds wide industrial application. It is used as plasticizers and lubricating oils. It is used in modifying alkyd resins to prevent discolor and to keep flexibility and resistance to aging since saturated nonanoic acid will not be oxidized. It is known that C₉=O, straight and saturated chain fatty acids esters are capable of removing the waxy cuticle of the broadleaf or weed, causing the tissue death. Methyl nonanoate is used as an active ingredient of environment friendly herbicides and as a chemical intermediate for synthetic flavours, cosmetics, pharmaceuticals and corrosion inhibitors. The present work are listed in Table 1.

### Table 1. Physicochemical Characteristics of Catalysts

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>Matrix Type</th>
<th>Ionic Form</th>
<th>Total Exchange Capacity (meq/mL (wet))</th>
<th>Cross-Linkage (% DVB)</th>
<th>Max. Operating Temp. (K)</th>
<th>Surface Area (m²/g)</th>
<th>Particle Size (mm)</th>
<th>Total Pore Vol (mL/g)</th>
<th>Average Pore Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dowex 50 Wx2</td>
<td>Styrene</td>
<td>H⁺</td>
<td>0.6</td>
<td>78</td>
<td>413</td>
<td>6.940</td>
<td>0.4</td>
<td>1.0</td>
<td>1.48 x 10⁻²</td>
</tr>
<tr>
<td>Amberlyst 15</td>
<td>Styrene</td>
<td>H⁺</td>
<td>1.9</td>
<td>20</td>
<td>393</td>
<td>45</td>
<td>0.600-0.850</td>
<td>0.60</td>
<td>300</td>
</tr>
<tr>
<td>Amberlyst 35</td>
<td>DVB</td>
<td>H⁺</td>
<td>1.9</td>
<td>20</td>
<td>423</td>
<td>45</td>
<td>0.700-0.950</td>
<td>0.55</td>
<td>300</td>
</tr>
</tbody>
</table>

*Note: Figures are approximate, and vary somewhat with manufacturers.

2. EXPERIMENTAL SECTION

2.1. Materials. Nonanoic acid (purity >99.5%), methanol (purity >99), and 1,4-dioxane were purchased from Merck and used without further purification. The purity of all chemicals was checked by gas chromatography. Heterogeneous catalysts Amberlyst 15 (wet) and Amberlyst 35 (wet) were obtained from Rohm and Hass, and Dowex 50Wx2 was obtained from Dow Ltd. The catalyst was initially washed with distilled water for five times and was dried at ambient conditions for 4–5 h. Further the catalyst was washed by dipping in 0.1 N hydrochloric acid solutions 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 catalysts used in the present work are listed in Table 1.

2.2. Apparatus and 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 303 to 333 K. The reaction temperature was maintained using a thermostatic water bath (Julabo F20). The temperature was maintained 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 nonanoic acid and the catalyst were first charged into the reactor through a peephole on the lid and heated to the desired temperature. Then 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 min for the first hour, and 30 min for the next 2–6 h for analysis. The reaction parameters are given in Table 2. All experiments were performed at least three times in order to ensure reproducible results. Experimental setup is shown in Figure I.

2.3. Analysis. For kinetic measurements, samples were taken periodically, and the amount of nonanoic acid was determined by titration with a standard sodium hydroxide solution of normality 0.5 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. 30 m x 0.25
3. RESULT AND DISCUSSION

A parametric study was carried out to establish the optimum parameters for this reaction. The parameters included: type of catalysts, molar ratio of nonanoic acid to methanol, catalyst loading and reaction temperature. The presence or absence of mass transfer effect was established by carrying out experiments at different rpm and different particle size of the catalyst.

3.1. Comparison of Homogeneous and Heterogeneous Catalysts. Batch experiments on homogeneous (sulfuric acid) and heterogeneous (Amberlyst 15, Amberlyst 35, Dowex 50WX2) catalysts were conducted for the esterification of nonanoic acid with methanol at 333 K temperature, for 9% catalyst loading and 1:10 (acid/alcohol) molar ratio. The observed conversion for each catalyst is shown in Figure 2.

From Figure 2 it is observed that Amberlyst 15 and Dowex 50 WX2 yield nearly same conversion of nonanoic acid at a reaction time of 360 min in comparison to Amberlyst 35. Keeping in view the higher cost of Dowex 50WX2 in comparison to Amberlyst 15, in all subsequent experiments Amberlyst 15 was used as a catalyst.

3.2. Effect of External Mass Transfer. To determine the optimum agitation speed, four runs were carried out at stirrer speed of 300, 500, 600, and 800 rpm using acid to alcohol molar ratio of 1:10, temperature of 333.15 K, Amberlyst 15 as catalyst with catalyst loading of 8%, for each run. As shown in Figure 3 there was a slight increase in maximum percentage conversion for each run when the stirrer speed was increased from 300 to 500 rpm but above 500 rpm the differences in maximum percentage conversion for each run can be considered to be negligible. This indicates the absence of external mass transfer limitations above 500 rpm. Therefore, all experiments were conducted at 500 rpm so as to neglect the effect of external mass transfer and to avoid the breakage of catalyst at higher rpm.

3.3. Influence of Internal Mass Transfer. To access the activation sites inside the catalyst particle, the reactants have to

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Table 2. Reaction Parameters

<table>
<thead>
<tr>
<th>sample no.</th>
<th>temperature (K)</th>
<th>molar ratio</th>
<th>catalyst loading</th>
<th>RPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>303 to 333</td>
<td>1:10 (acid to alcohol)</td>
<td>65.87 g/L (8% w/v)</td>
<td>500</td>
</tr>
<tr>
<td>2</td>
<td>333</td>
<td>1:10 (acid to alcohol)</td>
<td>32.93 g/L to 81.20 g/L (4% to 11%)</td>
<td>500</td>
</tr>
<tr>
<td>3</td>
<td>333</td>
<td>1:1 to 1:20 (acid to alcohol)</td>
<td>65.87 g/L (8% w/v)</td>
<td>500</td>
</tr>
</tbody>
</table>

mm i.d. × 0.25 mm 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.

Figure 1. Experimental setup.

Figure 2. Fractional conversion vs time for different catalysts: (O) Amberlyst 15, (B) Dowex 50WX2, (A) Amberlyst 35, (×) without catalyst, (●) H2SO4. Catalyst loading for all reactions, 9%; RPM, 500; molar ratio, 1:10; temperature, 333.15 K.

Figure 3. Fractional conversion vs time for different catalysts: (O) Amberlyst 15, (B) Dowex 50WX2, (A) Amberlyst 35, (×) without catalyst, (●) H2SO4. Catalyst loading for all reactions, 9%; RPM, 500; molar ratio, 1:10; temperature, 333.15 K.
3.4. Effect of Catalyst Loading. Experiments were carried out at 4% (32.93 g/L) to 11% (81.20 g/L) (weight of the catalyst/total volume of the mixture) at a temperature 333.15 K, molar ratio 1:10 (acid/alcohol) and stirrer speed of 500 rpm. The conversion of nonanoic acid as a function of time with different catalyst loadings is shown in Figure 5. As it can be seen from this Figure, with increasing catalyst loading the conversion of nonanoic acid increases due to the increase in the total number of available active catalytic sites for the reaction. Figure 6 shows the percent conversion of nonanoic acid to methyl nonanoate increases almost constant as the catalyst loading is increased after 8% (65.87 g/L). The optimum catalyst loading was taken as 8% (65.87 g/L).

3.5. Effect of Temperature. To investigate the effect of temperature on the esterification rate constant, the reactions were carried out in the temperature range of 303.15 to 333.15 K while keeping the molar ratio of acid to alcohol at 1:10 and catalyst loading of 8% (w/v). The ester conversion was found to increase with an increase in reaction temperature. Increasing the temperature is apparently favorable for the acceleration of the forward reaction. The observed value of fractional conversion at 360 min is about four times higher for the experiments at 333.15 K than the one for experiments at 303.15 K as shown in Figure 7.

3.6. Effect of Feed Molar Ratio. Esterification of nonanoic acid with methanol is an equilibrium limited chemical reaction and the position of equilibrium controls the amount of ester formed: the esterification reaction is generally slowed down by the reversible reaction so use of an excess of methanol drives the reaction in the forward direction. The molar ratio of methanol to nonanoic acid was varied from 1:1 to 20:1 at a reaction temperature 333.15 K.

Figure 3. Plot of percentage maximum conversion for each run up to 360 min vs RPM (revolutions per minute) at 333.15 K, 1:10 molar ratio, and catalyst loading of 8% (w/v).

Figure 4. Fractional conversion vs time (min) for different particle sizes at 333.15 K, 1:10 molar ratio, and catalyst loading of 8% (w/v), (□) 600–850 μm, (♦) 250–300 μm.

Figure 5. Fractional conversion vs time for different catalyst loading: (♦) 4%, (—) 5%, (A) 6%, (X) 7%, (■) 8%, (•) 9%, (+) 10%; molar ratio, 1:10; temperature, 333.15 K; RPM, 500.

Figure 6. Plot of percentage maximum conversion obtained for each catalyst loading up to 360 min vs catalyst amount: molar ratio, 1:10; temperature, 333.15 K; RPM, 500.
4. KINETIC MODELING

The esterification reaction catalyzed by heterogeneous catalysts can be described using different kinetic models such as PH, LHHW, and ER, etc. based on different approaches. Although the PH model does not take into account the adsorption effect of species in the reactant medium, the LHHW and ER models both include the adsorption effects of species in the reactant medium. The basic assumption of the LHHW model is that all reactants are adsorbed on the catalyst surface. The ER model assumes that the reaction takes place between adsorbed and nonadsorbed reactants. A general kinetic expression for all the three models is written as

$$-rac{dc}{dt} = k_{\text{app}} (C_A C_B) \left( \frac{K_m C_m}{(C_m + K_m C_m)^n} \right) \left( 1 + K_a C_a + K_b C_b + K_c C_c + K_d C_d \right)^{n-1}$$

where $r$ is the reaction rate in terms of concentration of $i$ component, $A$, $B$, $E$, and $W$ are nonanoic acid, methanol, methyl nonanoate, and water, respectively. $K$ is the adsorption constant and $K_i$ is equilibrium reaction rate constant; $k_i$ is the rate constant and $w_i$ is the weight of catalyst in g/L, with $n = 0$ for the PH model, 1 for the ER model, and 2 for the LHHW model.

Reactions over heterogeneous catalysts are more complex than a normal elementary reaction mechanism and are not so easily reducible to a simple pseudohomogeneous model. Hence when modeling the reaction for a liquid system where the mixture is nonideal, the correction must be made to the concentration to indicate the departure from the ideal case. The nonideality spawns from differences in interactions between the molecules, as well as size and shape of differences in the molecules participating in the liquid mixture. Nonideality of the mixture needs to be approximated in the rate equation. Generally the rate eq 3 is then written in the form activity of each component ($a_i = y_i x_i = y_i (C_i/C_i)^e$; $a_i$ is activity of each component, $y_i$ is activity coefficient, $x_i$ is mole fraction of each component, $C_i$ is concentration of each component, and $c_i$ is total concentration of reaction mixture which is kept constant. First the concentration needs to be written in terms of activity. Hence eq 3 becomes:

$$-rac{dc}{dt} = k_{\text{app}} (a_A a_B) \left( a_A a_B / K_m a_m \right) \left( 1 + K_a a_a + K_b a_b + K_c a_c + K_d a_d \right)^{n-1}$$

where $k_i = (k_i C_i^e) / (y_i x_i)$ is a forward reaction rate constant. Activities of the chemical compounds used in this study were calculated using the UNIFAC group contribution method (Table 3). The UNIFAC group contribution method allows the prediction of liquid phase activity coefficients $y$ as a function of temperature and composition. The activity coefficient is expressed as the sum of a combinatorial part (C) and a residual part (R). The values can be derived from the quantities that have been tabulated by Fredenslund. The relative van der Waals volume ($r_i$) and surface area ($q_i$) values of molecule $i$ can be calculated from the known van der Waals properties $R_i$ and $Q_i$ of the structural groups $k$.

### Table 3. UNIFAC Activity Coefficients Parameters for a System

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration, C (mol/L)</th>
<th>Activity Coefficient, $y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonanoic acid</td>
<td>1.72</td>
<td>1.01</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.64</td>
<td>1.26</td>
</tr>
<tr>
<td>Methyl nonanoate</td>
<td>0</td>
<td>0.82</td>
</tr>
<tr>
<td>Water</td>
<td>0</td>
<td>3.52</td>
</tr>
</tbody>
</table>

Experiments were carried out in the presence of Amberlyst 15 catalyst at three different temperature 321, 326, and 333 K using 1,4-dioxane as solvent. Influence of external or internal diffusion was neglected on the basis of studies on mass transfer in sections 3.2 and 3.3. An initial rate of reaction ($r_{\text{初}}$) defined up to conversion of 10% was observed using different concentrations of nonanoic acid, methanol, and water. The concentrations were expressed in terms of activities so as to account the nonideal behavior of the reaction mixtures. As seen in Figure 10, that initial
reaction rate is a linear function of initial activity of acid. Figure 11, shows that the initial reaction rate, increases with increasing alcohol activity whereas at high alcohol activity, the rate is essentially independent of the alcohol activity, hence we can conclude that the initial reaction rate is a nonlinear function of initial activity of methanol. Figure 12 shows that the initial rate is a nonlinear function of activity of water and decreases with an increase in the activity of water, hence confirming the inhibiting effect of the water concentration as the reaction proceeds. From Figures 10 to 12 we conclude that the adsorption effect of nonanoic acid can be neglected as it is a linear function of activity, but a significant adsorption effect of methanol and water is present. The adsorption of solvent (dioxane) and ester were reported to be negligible in the literature. This analysis demonstrates the Eley–Rideal model based on these hypotheses:

(i) All the active sites of the resin are occupied and, in particular, the major part of them is occupied by the methanol in a protonated form. This hypothesis is justified by the high methanol molar excess used in most of the experimental runs (molar ratio of methanol/nonanoic acid, >10:1) by considering that, initially, water is not present in the reacting medium. Methanol will be preferably adsorbed with respect to acid. (ii) All the components (acid, water, and methyl ester) undergo a protonic exchange equilibrium with the protonated methanol adsorbed onto the active sites. (iii) The reactive event occurs through an Eley–Rideal mechanism between a protonated acid and the methanol coming from the liquid phase absorbed inside the resin particles. The stoichiometry and corresponding reaction rate expression is in the form of the Eley–Rideal model with the surface reaction as the rate determining step; after excluding the adsorption effects of nonanoic acid and methyl nonanoate. The initial reaction rate, with no product present, can be defined as

\[ \frac{-r_{Ao}}{1 + \frac{1}{k_f \hat{K}}} = \frac{k_f \hat{K} \hat{K}_{ao} (a_{Ao} - (a_{Wo}/K_c))}{1 + K_p a_p + K_w a_w} \]  

(5)

where \( k_f \) is the forward reaction rate constant in mol L/(g min) and is given as \( k_f = k_f^0 \exp \left(-E_f/(RT)\right) \), \( a_p \) is the weight of catalyst in g/L and \( K_c \) is the esterification reaction equilibrium constant based on activity catalyzed by Amberlyst 15. In eq 5, activity rather than concentration is used in the rate expression, because it results in improvement in the predictions of the models fitted against the measured kinetic data. Using eq 5, the initial reaction rate, with no product present, can be defined as

\[ \frac{-r_{Ao}}{1 + \frac{1}{k_f \hat{K}}} = \frac{k_f \hat{K} \hat{K}_{ao} (a_{Ao} - (a_{Wo}/K_c))}{1 + K_p a_p + K_w a_w} \]  

(6)

Rearranging eq 6 as

\[ \frac{a_{Ao} \hat{K}_{ao}}{a_{Wo} \hat{K}_{ao}} - \frac{1}{k_f} \frac{a_{Ao} \hat{K}_{ao}}{a_{Wo} \hat{K}_{ao}} = \frac{1}{k_f \hat{K}} \frac{a_{Wo} \hat{K}_{ao}}{a_{Wo} \hat{K}_{ao}} \]  

(7)

A plot of \( (a_{Ao} \hat{K}_{ao})/\Delta r_{Ao} \) versus \( a_{Wo} \) results in a straight line with the slope \( K_c/(k_f \hat{K}) \) and intercept \( 1/(k_f \hat{K}) \) as shown in Figure 13.

To evaluate the inhibiting effect of activity of water, eq S, with no ester being present initially, can be written as

\[ \frac{-r_{Wo}}{1 + \frac{1}{k_f \hat{K}}} = \frac{k_f \hat{K} \hat{K}_{wo} (a_{Wo} - (a_{Wo}/K_c))}{1 + K_p a_p + K_w a_w} \]  

(8)

from which the following equation can be obtained:

\[ \frac{a_{Wo} \hat{K}_{wo}}{a_{Wo} \hat{K}_{wo}} - \frac{1}{k_f} \frac{a_{Wo} \hat{K}_{wo}}{a_{Wo} \hat{K}_{wo}} = \frac{1}{k_f \hat{K}} \frac{a_{Wo} \hat{K}_{wo}}{a_{Wo} \hat{K}_{wo}} \]  

(9)

Figure 10. Initial rate of reaction (—rAo) vs activity of acid (aAo) at three different temperatures: (0) 333 K, (■) 326 K, (△) 321 K; catalyst loading, 8% (w/v); RPM, 500.

Figure 11. Initial rate of reaction (—rAo) vs activity of alcohol (aBo) at three different temperatures: (♦) 333 K, (■) 326 K, (△) 321 K, catalyst loading, 8% (w/v); RPM, 500.

Figure 12. Initial rate of reaction (—rAo) vs activity of water (aWo) at three different temperatures: (♦) 333 K, (■) 326 K, (△) 321 K; molar ratio, 1:10 acid/alcohol; catalyst loading, 8% (w/v); RPM, 500.

Figure 13. (a_{Ao} \hat{K}_{ao})/\Delta r_{Ao} versus a_{Wo} at three different temperatures: (♦) 333 K, (■) 326 K, (△) 321 K; catalyst loading, 8% (w/v); RPM, 500.
A plot of \((a_o - a_w)/r_o - a_w/a_o\) as shown in Figure 14.

Figure 14. \((a_o - a_w)/r_o - a_w/a_o\) for alcohol at different temperatures: (♦) 333 K, (■) 326 K, (▲) 321 K; catalyst loading, 8% w/v; RPM, 500.

From Figures 13 and 14 the slopes and intercepts of the linear equation were obtained and the corresponding rate constant and adsorption parameters were calculated by the method of averages (Alime et al.), the values of which are tabulated in Table 4.

<table>
<thead>
<tr>
<th>temp (K)</th>
<th>(k_f) (L^2/(mol g h))</th>
<th>(K_w) (L/mol)</th>
<th>(K_{acw}) (L/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>321</td>
<td>5.4 \times 10^{-4}</td>
<td>0.53</td>
<td>2.68</td>
</tr>
<tr>
<td>326</td>
<td>6.9 \times 10^{-4}</td>
<td>0.40</td>
<td>1.90</td>
</tr>
<tr>
<td>333</td>
<td>1.02 \times 10^{-3}</td>
<td>0.25</td>
<td>1.18</td>
</tr>
</tbody>
</table>

4.2. Temperature Dependency. The effect of temperature on the rate of reaction was studied by conducting the reactions at different temperatures from 321 to 333 K under the conditions of catalyst loading of 8% (w/v) and RPM of 500. The temperature dependency of the rate constant is expressed by the Arrhenius law:

\[
k_i = k_i^0 \exp\left[-\frac{E}{RT}\right]
\]  

Where \(i = f, b,\) and \(W, E,\) is activation energy, and \(k_i^0\) is the frequency factor. From eq 10, a plot of \(\ln k_f,\) \(\ln K_w,\) and \(\ln K_{acw}\) versus \(1/T,\) gives a straight line with the slope of \((E/RT),\) as shown in Figures 15 and 16. The activation energy was found to be 47.5 kJ/mol in the presence of Amberlyst 15 ion-exchange resin. By applying the Arrhenius equation to the values of slope and intercepts of graphs 15 and 16 the temperature dependency of the constants can be correlated by the following equations:

\[
\ln k_f = -10.861 - 33.77
\]  

4.4. Reaction Enthalpy, Entropy, and Free Energy. If a constant reaction enthalpy is assumed within the operating temperature range, the reaction enthalpy \(\Delta H,\) and entropy \(\Delta S,\)
can be estimated by setting the experimental value of eq 15 in to eq 16:

\[
\ln K = \left( \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \right)
\]

The reaction enthalpy \(\Delta H\) and reaction entropy \(\Delta S\) are found to be 90 J mol\(^{-1}\) and 280.805 J K\(^{-1}\) mol\(^{-1}\), respectively. Furthermore, the liquid phase reaction free energy change can be calculated to be \(\Delta G = \Delta H - T \Delta S = -93418.18\) J mol\(^{-1}\).

4.5. Model Prediction. The observed reaction rate for the esterification of nonanoic acid with methanol was compared with the proposed Eley—Rideal model (eq 5) using the rate constants described by eqs 11–13 over the whole range of predicted parameters (given in Table 2) and experimental data was calculated by this equation

\[
\gamma_{\text{experimental}} = C_1 \Delta \gamma / \Delta t
\]

The parity between the experimental and calculated value is given in Figure 18. The model eq 5 represents the data reasonably well within ±15%.

**5. CONCLUSION**

For the esterification of nonanoic acid with methanol, cation exchange resins as catalysts were investigated. The catalytic activity of three heterogeneous catalysts, Amberlyst 15, Amberlyst 35, and Dowex50WX2, was tested at temperatures of 333.15 K, catalyst loading of 9% (w/v), and 1:10 molar ratio (acid/alcohol). Amberlyst 15 was found to be the most cost-effective catalyst in this study. A stirrer speed of 500 rpm was found to be effective in eliminating external diffusion limitations. Hence, the effect of catalyst loading, temperature, and acid to alcohol molar ratio on reaction kinetics was determined at 500 rpm. At 500 rpm, internal diffusion limitations were assessed by the Weiss Prater criterion and found to be absent. For all the reactions, increasing the acid to alcohol molar ratio increases conversions of the acid, and this enhancement in kinetics is more pronounced when the molar ratio is raised from 1 to 10 than when it is raised from 1 to 1.

**ACKNOWLEDGMENTS**

We gratefully acknowledge the financial support received from UGC (Government of India) vide Project No. F.No.37-295/2009 (S.R.).

**NOTATIONS**

- **E** = activation energy (kJ mol\(^{-1}\))
- **s** = number of structural groups of kind \(k\) in a molecule of component \(i\)
- **c** = concentration
- **C** = activity coefficient
- **\(\gamma\)** = activity coefficient
- **\(K\)** = reaction order
- **\(K_e\)** = equilibrium constant
- **\(k_f\)** = forward reaction rate constant, (mol L\(^{-1}\) g\(^{-1}\) min\(^{-1}\))
- **\(k_a\)** = preexponential factor (mol L\(^{-1}\) g\(^{-1}\) min\(^{-1}\))
- **\(W\)** = water
- **\(W_i\)** = weight of catalyst, g L\(^{-1}\)
- **\(R\)** = gas constant
- **\(R\)** = gas constant
- **\(RMP\)** = revolutions per minute
- **\(UNIFAC\)** = universal quasichemical functional group activity coefficients

**REFERENCES**
