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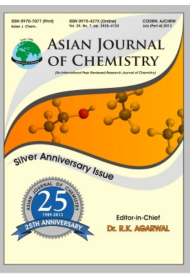

Kinetics of the Esterification of Acetic Acid with *n*-Octanol Catalyzed by Amberlyst 15

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Esterification kinetics of acetic acid with *n*-octanol were studied in presence of the Amberlyst 15 as catalysts. The effect of various parameters such as agitation speed, particle size, temperature, catalyst loading, initial reactants molar ratio and catalyst reusability was investigated. A pseudo-homogeneous kinetic model was applied to correlate the experimental data in the temperature range from 333.15 to 363.15 K. The estimated kinetic parameters made the calculated results in excellent agreement with the experimental results, indicating that the pseudo-homogeneous model could give a good representation of the esterification kinetics using cation exchange resins as catalysts.

Key Words: Esterification, Octyl acetate, Kinetic model, Cation exchange resins.

INTRODUCTION

Octyl acetate is an industrially important chemical with applications as food flavor and solvent. It is used in large quantities as food additive with fruity, orange-like and jasmine-like odor. It may also be used in the coating industry as a solvent for resins and paints. Octyl acetate can be synthesized by esterification of acetic acid with *n*-octanol using a suitable acid catalyst. The overall reaction can be expressed as

$$C_8H_{17}OH + CH_3COOH \xrightarrow{H^+} C_{10}H_{20}O_2 + H_2O$$

The conventional industrial production of octyl acetate has been performed using homogeneous acid catalysts (*e.g.*, H_2SO_4), which gave rise to some problems such as corrosion of equipment, pollution of environment and tedious isolation of catalyst and product. To overcome drawbacks of homogeneous acid catalysts, a number of solid heterogeneous catalysts such as zeolites[1], sulphates[2], heteropoly acid[3] and cation exchange resins have been studied. Among them, cation exchange resins were received increasing attention because of their excellent performance of easy separation, no pollution environment and good thermal stability. Studies on esterification reaction of carboxylic acids with alcohols using cation exchange resins as catalysts have been extensively carried out by many researchers[4-11].

Studies on the esterification of acetic acid with *n*-octanol to produce octyl acetate using strong acid cation exchange resins as catalysts have not been reported in the literature so far. However, a number of similar studies on the esterification reaction of acetic acid with other alcohols have been reported using cation exchange resins. For example, Gangadwala *et al.*[12] studied the esterification of acetic acid with *n*-butanol in the presence of Amberlyst 15 and determined the intrinsic reaction kinetics. Steinigeweg and Gmehling[13] also studied the synthesis of *n*-butyl acetate using cation exchange resins and presented the pseudo-homogeneous kinetic model. Studies on kinetics of esterification of acetic acid with amyl alcohol have been carried out in the presence of Amberlyst 36 and Dowex 50Wx8-100 as catalysts[14,15]. In addition, the other work related to the esterification of acetic acid with other alcohols was carried out using strong acid cation exchange resins[16-20], such as esterification of acetic acid with *n*-propanol[16], esterification of acetic acid with ethylene glycol to ethylene glycol monoacetate and ethylene glycol[17], esterification of dilute acetic acid with *n*-hexanol[18].

According to the above studies, cation exchange resins showed the high catalytic activity in the esterification reaction. At present no information is available in literature describing the kinetics of acetic acid esterification with *n*-octanol to octyl acetate using cation exchange resins as catalysts. Thus, the kinetics of the esterification of acetic acid with *n*-octanol was carried out using Amberlyst 15 as catalysts in this work. The effect of various operating parameters such as agitation speed, particle size, temperature, catalyst loading, initial reactants molar ratio and catalyst reusability was studied in detail. A pseudo-homogeneous kinetic model was used for the correlation of the experimental data and corresponding kinetic parameters were estimated.

EXPERIMENTAL

Acetic acid (purity ≥ 99.8 %) and *n*-octanol (purity ≥ 99.8 %) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. (China). Octyl acetate (purity ≥ 99 %) was supplied from Westingarea Technology (China) Co., Limited. The commercial cation exchange resin Amberlyst 15 from Rohm and Haas Company. Its appearance was opaque beads with the particle size of 0.600-0.850 mm, surface area of 53 m^2/g and average pore diameter of 30 nm. The concentration of active sites was 4.7 eq/kg and temperature stability was 393 K.

The esterification reactions were carried out in a 250 mL glass stirred tank reactor equipped with an online measuring devices of agitation speed and temperatures. The temperature was controlled within ± 0.1 K with a constant temperature water bath. In a typical run, acetic acid (0.5 mol) and *n*-octanol (0.50 mol) were charged into the reactor. When the desired temperature was achieved, the catalyst (Amberlyst 15 cation exchange resins) was then added into the reactor and the agitation speed was adjusted to be 500 rpm. The corresponding time was considered as the zero reaction time for the run. Samples were taken out at specific time intervals and immediately transferred to an ice bath in order to ensure that no further reaction took place.

Analysis: The amount of unreacted acetic acid in the reaction mixture was determined by titration using 0.1 M standard sodium hydroxide solution with phenolphthalein as an indicator. The results of sample analysis have been checked frequently by gas chromatography (Shimadzu GC-17A) equipped with a hydrogen flame ionization detector (FID) to ensure that there is no byproducts formation in the sample. A capillary column DB-17 (30 m × 0.544 mm × 1.0 μm) was used for the separation of the components and nitrogen was used as a carrier gas. The temperature of the inlet and the detector were set to be 573 K.

RESULTS AND DISCUSSION

Effect of mass transfer resistances: The esterification reactions were performed at 400, 500 and 600 rpm under the same reaction conditions of 363.15 K temperature, acid to alcohol molar ratio of 1 and catalyst loading of 10 % (w/w, of acetic acid). The results were shown in Fig. 1. As seen in Fig. 1, the conversion rate increased with the increase of the agitation speed from 400-500 rpm and kept unchanged for the agitation speed up to 600 rpm. It indicated that the external mass transfer resistance could be neglected when the agitation speed was over 500 rpm. Therefore, all subsequent experiments were carried out at constant agitation speed of 500 rpm.

The effect of particle size of resins on the esterification reaction was examined using different particle sizes in the range of 0.40-0.85 mm under constant reaction conditions of 363.15 K, acid to alcohol molar ratio of 1 and catalyst loading of 10 % (w/w, of acetic acid). The results were shown in Fig. 2. As seen in Fig. 2, the reaction rate was almost independent of particle size. It indicated that the influence of particle size in the above range on the conversion of acetic acid was negligible, implying that the reaction was not controlled by internal mass transfer.

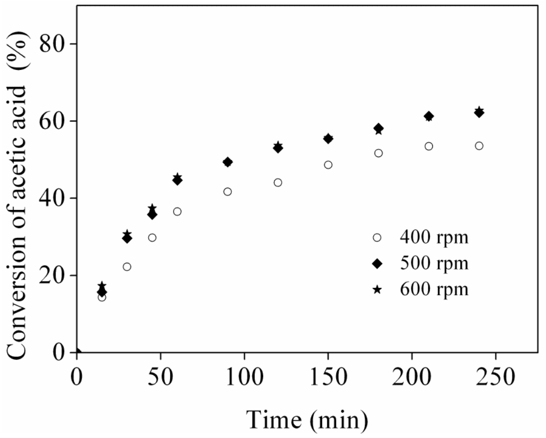

Fig. 1. Effect of the agitation speed on conversion at 363.15 K, catalyst loading of 10 % and acid to alcohol molar ratio is 1

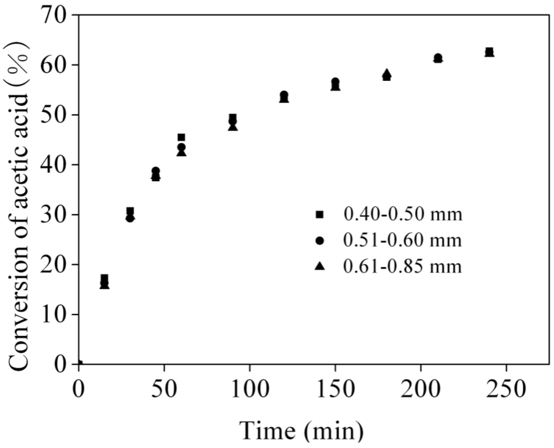

Fig. 2. Effect of the particle size on the conversion at 363.15 K, catalyst loading of 10 % and acid to alcohol molar ratio is 1

The above results indicated that the influences of external and internal mass transfer could be neglected, implying that the kinetics of the esterification reaction of acetic acid with *n*-octanol was the intrinsic kinetics. These results were in good consistency with the literature reports of esterification reactions catalyzed by the Amberlyst series resins[12,14,20].

Effect of temperature: The effect of temperature in the range from 333.15 to 363.15 K on the reaction rate was investigated under the constant reaction conditions of catalyst loading of 10 % (w/w, of acetic acid) and acid to alcohol molar ratio of 1. As seen in Fig. 3, the conversion of acetic acid increased with the increase of reaction temperature. It was due to that the increase of temperature brought more successful collisions. These successful collisions had sufficient energy (activation energy) to break the bonds and form products and thus resulted in higher conversion of acetic acid, which agreed with esterification studies reported in the literatures[8,20].

Effect of catalyst loading: The effect of catalyst loading varying from 3-10 % (w/w, of acetic acid) was tested under the same reaction conditions and the results were shown in Fig. 4. It can be observed that the conversion of acetic acid increased with the increase of catalyst loading. It was due to that the increase of catalyst loading corresponded to more available active sites for the esterification reaction, resulting in higher reaction rate.

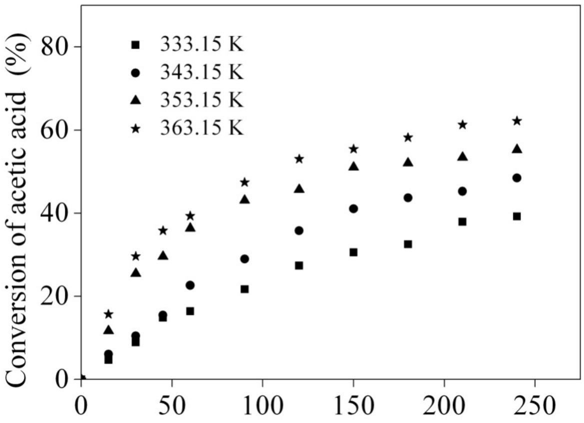

Fig. 3. Effect of temperature on the conversion at catalyst loading of 10 % and acid to alcohol molar ratio is 1

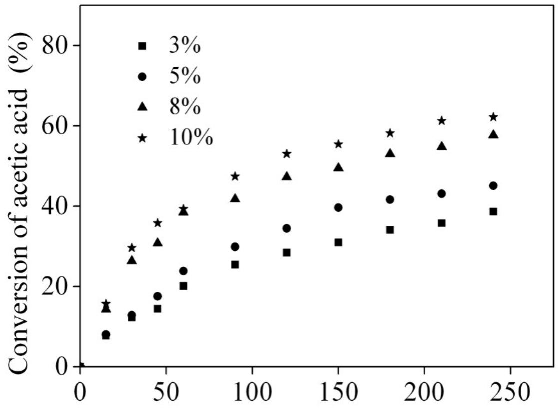

Fig. 4. Effect of catalyst loading on the conversion at 363.15 K and acid to alcohol molar ratio is 1

The initial reaction rate was shown to be a linear function of the catalyst loading. The initial reaction rate was calculated using the eqn. 2 at the starting point of reaction (t = 0). A plot of the initial reaction rate *vs.* catalyst loading was shown in Fig. 5. It was seen that the initial reaction rate increased with the increase of the catalyst loading. There was linear relationship between the initial reaction rate and the catalyst loading since the available active sites for this reaction was proportional to the catalyst loading. The mathematical expression relating the initial reaction rate to the catalyst loading can be derived from Fig. 5 as follows:

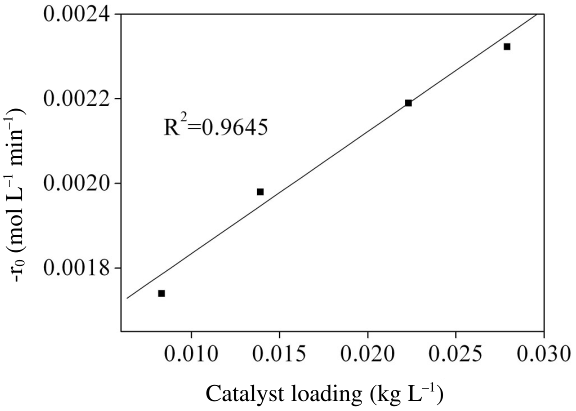

Fig. 5. Effect of catalyst loading on the initial reaction rate at 363.15 K and acid to alcohol molar ratio is 1

$$-r_0 = 0.00155 + 0.0289C_{cat} \qquad (1)$$

where C_{cat} was the catalyst loading, kg L^{-1}. This equation was valid only at 363.15 K and acid to alcohol molar ratio of 1 at which the experiments were carried out.

Effect of initial reactants molar ratio: The effect of different initial reactant molar ratio of acetic acid to *n*-octanol from 3:1 to 1:3 was carried out at 363.15 K and loading catalyst of 10 % (w/w, of acetic acid) (Fig. 6). As seen in Fig. 6, the conversion of acetic acid increased with decreasing the acid to alcohol molar ratio from 3:1 to 1:2. It may be ascribed that the reaction equilibrium moved forwards the product side with the increasing concentration of reactant *n*-octanol. However, when the amount of alcohol was further increased (acid:alcohol = 1:3), no remarkable increase was observed fir the conversion of acetic acid. It may be due to the fact that acetic acid was diluted by increasing alcohol contents, which prevented acetic acid from adsorbing on the catalyst acid sites.

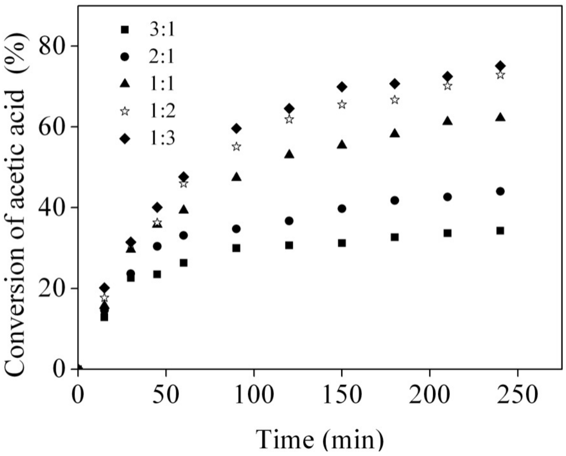

Fig. 6. Effect of initial reactants molar ratio on the conversion at 363.15 K and catalyst loading of 10 %

Effect of catalyst reusability: The reusability of Amberlyst 15 cation exhange resins was tested under the same conditions (temperature of 363.15 K, molar ratio of acetic acid to *n*-octanol of 1:1, catalyst loading of 10 % (w/w, of acetic acid), reaction time of 3 h). Before each experiment, the catalyst was separated by filtration. The catalyst was washed with ethanol several times and was then dried at 353.15 K under vacuum. The results were shown in Table-1. After eight times of reaction no obvious decrease in activity of catalyst was observed. The results indicated that Amberlyst 15 cation exchange resins possessed good mechanical performance and chemical stability in the esterification reaction of acetic acid with *n*-octanol.

Kinetic model: A pseudo-homogeneous model was used to describe esterification reactions using cation exchange resins as catalyst[5,11,12,17]. The kinetic equation of the esterification of acetic acid with *n*-octanol using Amberlyst 15 cation exchanger resins as catalysts can be established under the conditions of negligible external and internal mass transfer limitation. Esterification reactions were known to be reversible reactions of second order. Therefore, the overall rate equation for the reaction can be written as

$$-r = M_{cat}(k_1C_AC_B - k_{-1}C_DC_E)$$

TABLE-1
REUSABILITY OF CATION EXCHANGE RESINS[a]

Cycle	Conversion of acetic acid (%)
1st run	58.2
2nd run	57.8
3rd run	56.3
4th run	55.9
5th run	55.3
6th run	55.0
7th run	54.8
8th run	54.6

[a]Reaction conditions: temperature = 363.15 K, acetic acid: *n*-octanol = 1:1 (molar ratio), reaction time = 3 h.

$$= M_{cat} k_1 \left(C_A C_B - \frac{1}{K_e} C_D C_E \right) \quad (2)$$

where $K_e = \frac{k_1}{k_{-1}}$, M_{cat} is the catalyst loading per unit volume, k_1 is the forward reaction rate constant and k_{-1} is the reverse reaction rate constant. Subscripts A, B, D and E denote acetic aid, *n*-octanol, octyl acetate and water, respectively. The kinetic equations were integrated numerically using a fourth-order Runge-Kutta method. The parameters of the kinetics model were estimated using minimizing the sum of residual squares (SRS) between the experimental and calculated conversion of acetic aid using eqn. 3.

$$SRS = \sum_{samples} (x_{exp} - x_{calc})^2 \quad (3)$$

where SRS is the minimum sum of residual squares and x is the conversion of acetic acid. The subscripts exp and calc denote experimental and calculated values, respectively. The kinetic data during the course of the reaction was analyzed by the nonlinear least-squares method regression.

The pseudo-homogeneous model was used to describe the experimental kinetic data. The comparisons between the measured and calculated conversions of acetic acid at different temperature, catalyst loading and initial molar ratio of reactants were shown in Figs. 7-9, respectively. It can be seen that the calculated conversion of acetic acid by the kinetic model was in good agreement with the experimental data. This indicated that the pseudo-homogeneous model gave a good representation of the kinetic behaviour for the esterification reaction of acetic acid with *n*-octanol in the presence of Amberlyst 15 as catalysts.

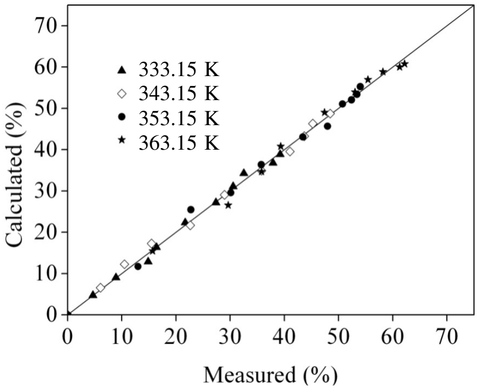

Fig. 7. Comparison between measured and calculated conversion of acetic acid at different temperatures at catalyst loading of 10 % and acid to alcohol molar ratio is 1

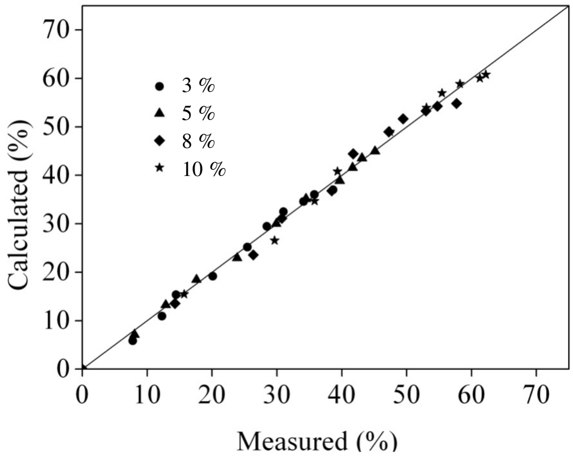

Fig. 8. Comparison between measured and calculated conversion of acetic acid at different catalyst loading at 363.15 K and acid to alcohol molar ratio is 1

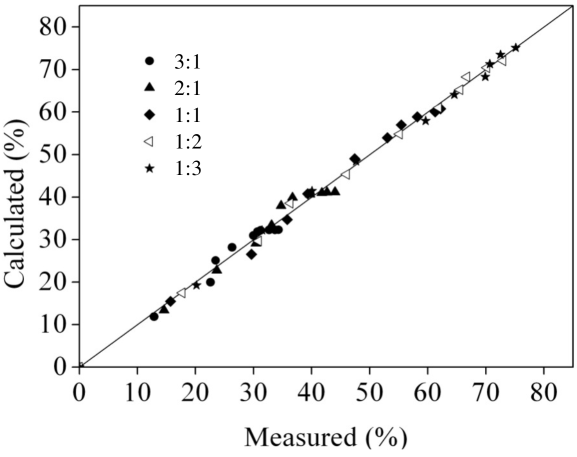

Fig. 9. Comparison between measured and calculated conversion of acetic acid at different initial molar ratios of acetic acid and *n*-octanol at 363.15 K and catalyst loading of 10 %

The temperature dependence of the reaction rate constant k can be expressed by Arrhenius law:

$$\ln k = \ln k_0 - \frac{E_a}{RT} \quad (4)$$

From eqn. 4, plotting ln k *versus* 1/T, straight lines with the slope of ($-E_a/R$) can be obtained and were shown in Fig. 10. The reaction constant (k_1, k_{-1}) and the corresponding activation energy were found to be:

$$k_1 = \exp\left(9.59 - \frac{5641}{T}\right) \quad E_{a_1} = 46.90 \text{ kJ/mol} \quad (5)$$

$$k_{-1} = \exp\left(0.54 - \frac{2735}{T}\right) \quad E_{a_2} = 22.74 \text{ kJ/mol} \quad (6)$$

Conclusion

The esterification of acetic acid with *n*-octanol has been investigated in the presence of Amberlyst 15 cation exchange resins as catalysts, showing excellent performance for the manufacture of octyl acetate. The effect of various parameters, such as agitation speed, particle size, temperature, catalyst loading, initial reactants molar ratio and catalyst reusability

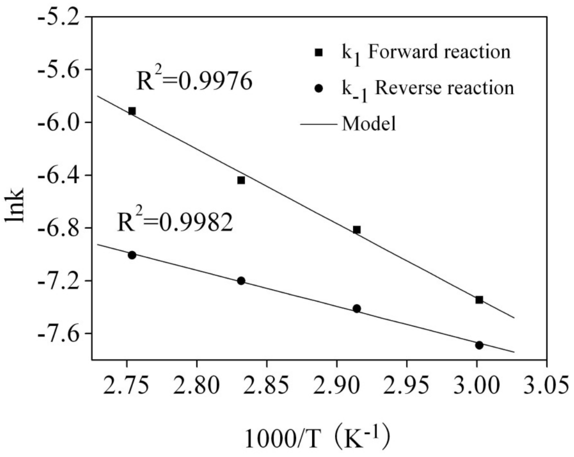

Fig. 10. Arrhenius plot for esterification of acetic acid with *n*-octanol

was studied. There was a linear relationship between the initial reaction rate and the catalyst loading. The conversion of acetic acid increased with the increase of temperature. The kinetics of esterification reaction was studied and the pseudo-homogeneous model was used to correlate the experimental data and gave a good representation for this heterogeneous catalytic esterification reaction system.

Nomenclature

C = concentration (mol/L)
C_{cat} = the catalyst loading (kg/L)
E_{a_1} = activation energy for the forward reaction (KJ/mol)
E_{a_2} = activation energy for the reverse reaction (KJ/mol)
Δ_rH^o = reaction enthalpy (KJ/mol)
k = reaction rate constant (L^2 mol^{-1} g^{-1} min-1)
k_0 = pre-exponential factor (L^2 mol^{-1} g^{-1} min^{-1})
k_1 = forward reaction rate constant (L2 mol-1 g^{-1} min^{-1})
k_{-1} = reverse reaction rate constant (L^2 mol^{-1} g^{-1} min^{-1})
K_e = equilibrium constant of the reaction
M = molar ratio of acetic acid to *n*-octanol
M_{cat} = the catalyst loading unit volume (g/L)
PH = pseudo-homogeneous model
R = gas constant (J/(mol K))
Δ_rS^o = entropy (J/(mol K))
SRS = the minimum sum of residual squares
T = temperature, K
wt/wt = weight of catalyst/ weight of acetic acid
x_{cal} = calculated conversion
x_{exp} = experimental conversion

Subscripts

A, B, D and E for acetic acid, *n*-octanol, octyl acetate and water, respectively.

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