Journal of Population Therapeutics & Clinical Pharmacology

RESEARCH ARTICLE
DOI: 10.53555/jptcp.v29i04.5266

A STUDY ON ESTERIFICATION KINETICS AS A TWO-WAY REACTION

D.U.S.L. Deepthi[1], K.V. Ramesh[2], G.V.S. Sarma[3*]

[1,2,3*]Department of Chemical Engineering, Andhra University, Visakhapatnam–530003, India.
*gvssarma@gmail.com

***Corresponding Author:** G.V.S. Sarma
*Email: gvssarma@gmail.com

Abstract:
The esterification kinetics of the three carboxylic acids viz., n-propionic acid, n-butyric acid and n-pentanoic acid with 2-propanol in the presence of sulphuric acid catalyst, are studied in a temperature controlled and stirred batch reactor. The effect of the different variables on the rates of reaction such as mole ratio of acid to alcohol varied as 0.5 to 1.5, catalyst loading varied from 1.0 to 3.0 weight percent and the reaction temperature ranging between 50°C and 70°C is observed. The experimental data are incorporated in the second order rate equation considering esterification as a two-way reaction. The forward and backward second order rate constants with respect to acids concentration are evaluated using integral method of analysis for the present systems. The correlation equations subjected to non-linear regression analysis in terms of the forward and backward rate constants are obtained. The experimental and the calculated values of both the second order rate constants are compared and the results are found to be in good agreement.

Keywords: Esterification, Kinetics, Rate constant, Reversible reaction.

1. Introduction

Esters have a pleasant characteristic fruity odor and the most common ingredients in organic and biological materials. Esters have extensive applications in the fragrance, polymer and flavor industries. The most employed homogeneous catalysts are mineral acids such as sulphuric acid, hydrochloric acid, hydrogen iodide[1].

Three reacting systems are considered in the present study: (1) n- propionic acid and 2-propanol, (2) n- butyric acid and 2-propanol and (3) n- pentanoic acid and 2-propanol. Iso-propyl propionate esters are the products derived by reacting n- propionic acid with a hydroxyl compound, 2-propanol. Deepthi et al[2] conducted experiments on esterification of n-propionic acid and 2- propanol in a stirred and temperature controlled batch reactor, using homogenous catalyst as sulphuric acid. Isopropyl propionate is the ester formed with the reaction between n-propionic and 2-propanol. The esterification reaction is shown in equation (1).

$$CH_3CH_2COOH + (CH_3)_2CHOH \overset{H_2SO_4}{\rightleftharpoons} CH_3CH_2COO(CH_2)_2CH_3 + H_2O \quad \ldots(1)$$

A similar study on esterification of n-pentanoic acid and 2- propanol carried out by Deepthi et al[3], wherein the following reaction occurred.

$$CH_3(CH_2)_3COOH + (CH_3)_2CHOH \overset{H_2SO_4}{\rightleftharpoons}$$

$$CH_3(CH_2)_2COO(CH_2)_3CH_3 + H_2O \qquad \ldots(2)$$

The data from these two studies are designated as systems(1) and (3) respectively were interpreted as a one-way reaction by the authors[2,3] and they reported the rate constants accordingly. However, in their another work, pertaining to the kinetics of system(2), which followed reaction equation according to equation (3). Deepthi et al[4] reported that the data can also be analyzed as a two-way reversible reaction. As per their work, the inspiration for this study was derived from Beula and Sai[5].

$$CH_3(CH_2)_2COOH + (CH_3)_2CHOH \overset{H_2SO_4}{\rightleftharpoons}$$

$$CH_3(CH_2)_3COOCH_2CH_3 + H_2O \qquad \ldots(3)$$

Theory

Deepthi et al[6] derived equation(4) to represent the data pertaining to forward reaction rate constant k_1.

$$\ln\frac{\{MX_{Ae}+X_A[M-(M+1)X_{Ae}\}}{\{M(X_A-X_{Ae})\}} = [\frac{2M}{X_{Ae}} - (M+1)]\,K_1C_{A0}t] \ldots (4)$$

$$Y = \ln\frac{\{MX_{Ae}+X_A[M-(M+1)X_{Ae}\}}{\{M(X_A-X_{Ae})\}} \qquad \ldots \quad (5)$$

The argument of the ln in the LHS of equation (4) has been designated as Y. The graphs were plotted for Y vs t for different catalyst concentrations, temperatures and mole ratio for the reacting systems under consideration.

From k_1, the rate constant for backward reaction k_2 is obtained using the following equations.

$$k_2 = \frac{k_1(1-X_{Ae})(M-X_{Ae})}{{X_{Ae}}^2} \qquad \ldots \qquad (6)$$

2. Materials and methods

n-propionic acid, n-butyric acid, n- Pentanoic acid, 2-propanol, sulphuric acid, sodium hydroxide, oxalic acid and phenopthalein were the chemicals used in this study. The kinetic experiments were conducted in a 500 ml three neck round-bottom flask, placed on a magnetic hot plate stirrer with temperature control ($\pm 0.2^0$C) and stirring speed control (0–1500 rpm). The measured quantities of the acid and 2-propanol were taken separately in two conical flasks. Accurate quantities of sulphuric acid catalyst were added to the flask constituting acid. The 2-propanol in the flask was transferred to the reaction vessel and the temperature was increased to the required temperature. The speed of the stirrer was maintained at 200 rpm. The conical flask containing carboxylic acid and catalyst mixture was heated separately to the same temperature. When the desired temperature was reached, the mixture of butyric acid and catalyst was transferred to the reaction flask of 2- propanol. The resulting mixture of required mole ratio was acheived. At zero time, samples of 2 ml was drawn using pipette into the conical flask containing 20 ml of 1.0 N sodium hydroxide and 20 ml of distilled water. The samples drawn at regular time intervals were titrated and the concentration of unreacted acid was estimated using standard titration analysis. The equilibrium samples were taken corresponding to a reaction time of 24 hours. Several experiments were carried out at different ranges of temperatures 50°C, 60°C and 70°C; the mole ratios 0.5, 1.0 and 1.5; catalyst concentrations 1.0, 2.0 and 3.0 weight percent.

The unreacted carboxylic acid concentration attained was determined by titration analysis with standard solution of 1.0 N sodium hydroxide against 0.5 N oxalic acid using phenolphthalein

indicator. The sulphuric acid catalyst equivalent titer was estimated by taking equal proportions of distilled water for acid and 2- propanol in a separate conical flask and approximate quantities of sulphuric acid catalyst was added. The conversion of the acid in the experiment was thus determined. The effect of various independent variables such as molar ratio of reactants, catalyst concentration and reaction temperatures were evaluated by employing full factorial design of experiments.

3. Results and Discussion

For the system(1) under consideration, the data for rate constant k_1 are analyzed and represented as Y versus t in Figures 1, 2 and 3. A graph drawn between Y and t on semi log graph sheet is shown in Fig.1. Three plots in this figure correspond to three different values of catalyst concentration viz., 1.0, 2.0 and 3.0 by wt percent employed in the present work. One can observe from these plots that there is a good fit of data points. In a similar way Fig.2 is drawn for three different values of mole ratio and Fig.3 for three different temperatures.

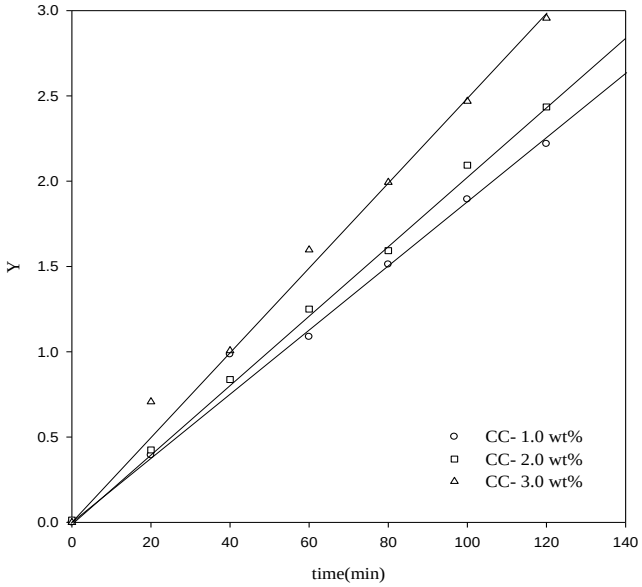

Fig.1. Test of the rate equation {T= 70^{o}C; MR= 1.0}

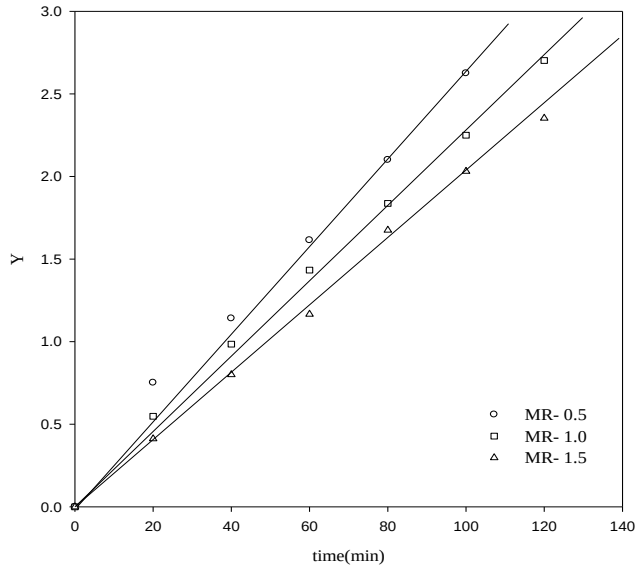

Fig.2. Test of the rate equation {CC = 2.0 wt%; T = 70^{o}C}

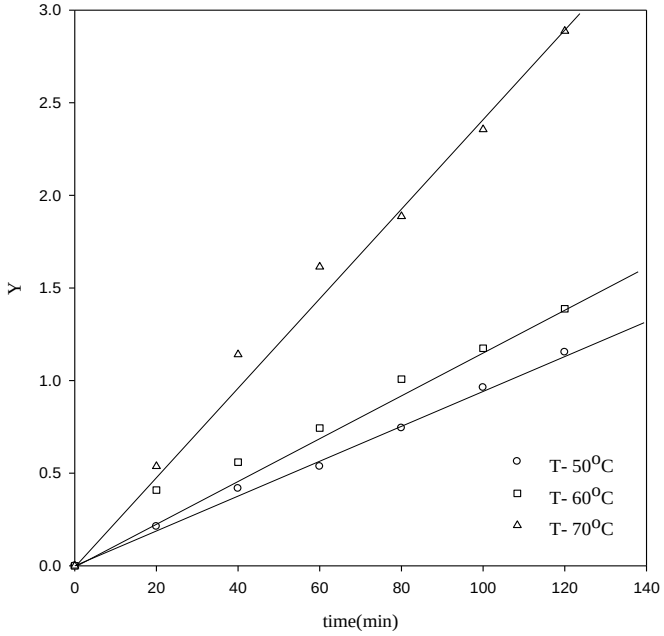

Fig.3. Test of the rate equation {MR = 1.5; CC = 2.0 wt %}

The entire data are subjected to regression analysis and the following equations were obtained for the rate constants.

$$k_1 = 1.653\ (MR)^{1.287}(CC)^{1.178}\ e^{-1336/T} \quad \ldots (7)$$

Average deviation = 6.101 percent
Standard deviation = 7.401 percent

$$k_2 = 0.1054(MR)^{-0.0598}\ (CC)^{0.8055}\ e^{-500.1/T} \quad \ldots (8)$$

Average deviation = 6.157 percent
Standard deviation = 7.647 percent

The experimental and calculated k_1 and k_2 values are compared and presented in Figs.4 and 5 respectively.

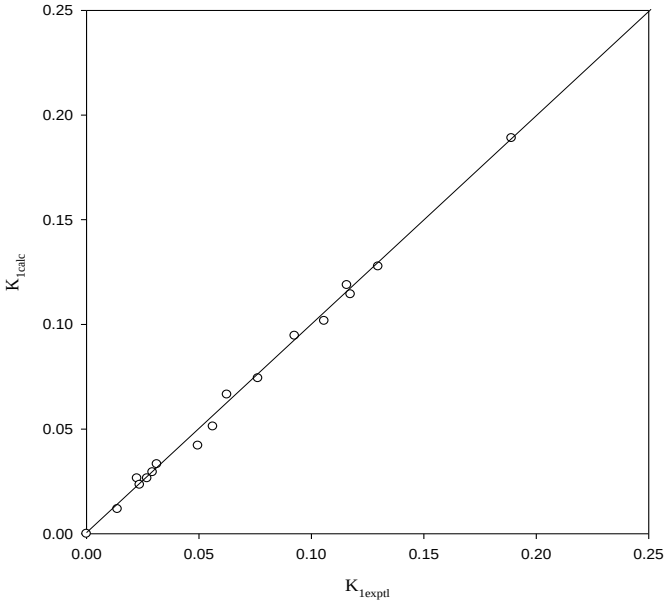

Fig.4. Comparison of experimental and calculated values of k_1- for system(1)

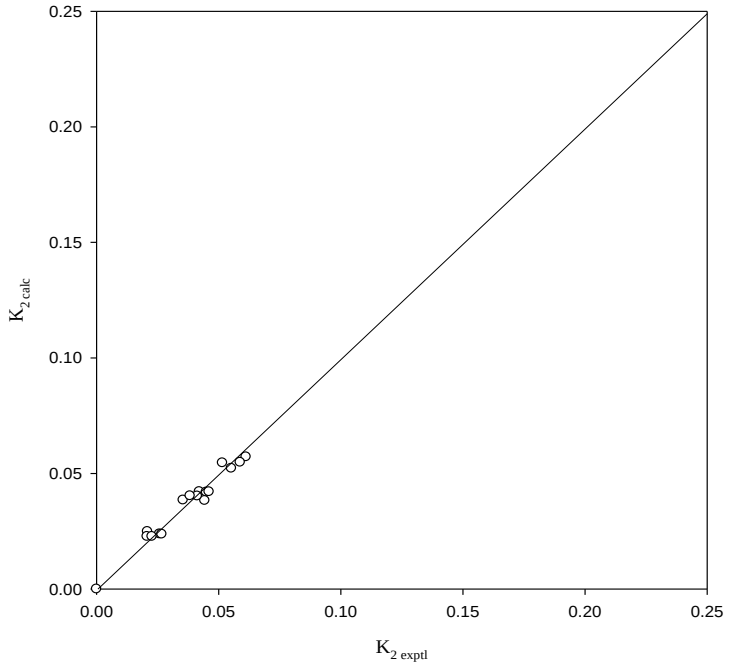

Fig.5. Comparison of experimental and calculated values of k_2- for system(1)

However, for system(2), Deepthi et al[4] reported similar observations and also correlation equations obtained from regression analysis for both the rate constants.
The present data obtained for system(3) were analyzed in the lines of system(1) and the corresponding graphs and equations are presented here under.

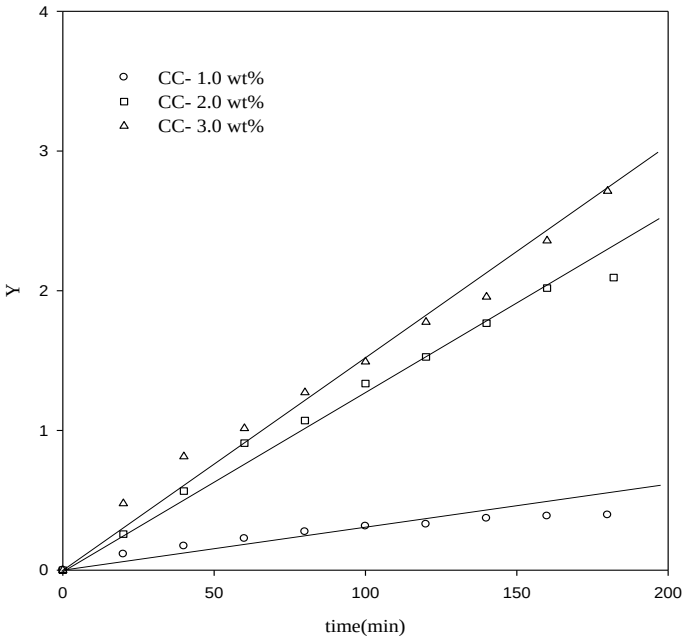

Fig.6. Test of the rate equation {T= 70^{o}C; MR= 1.0}

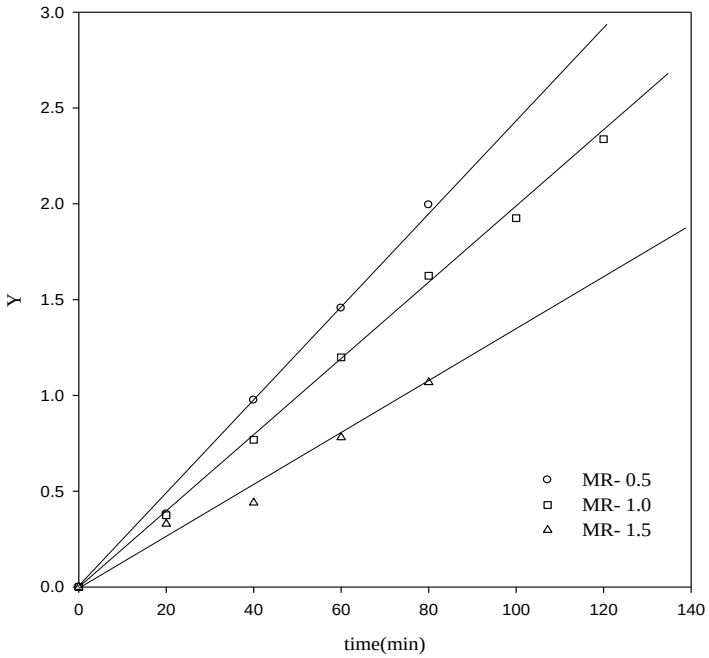

Fig.7. Test of the rate equation {CC = 2.0 wt%; T = 70^{o}C}

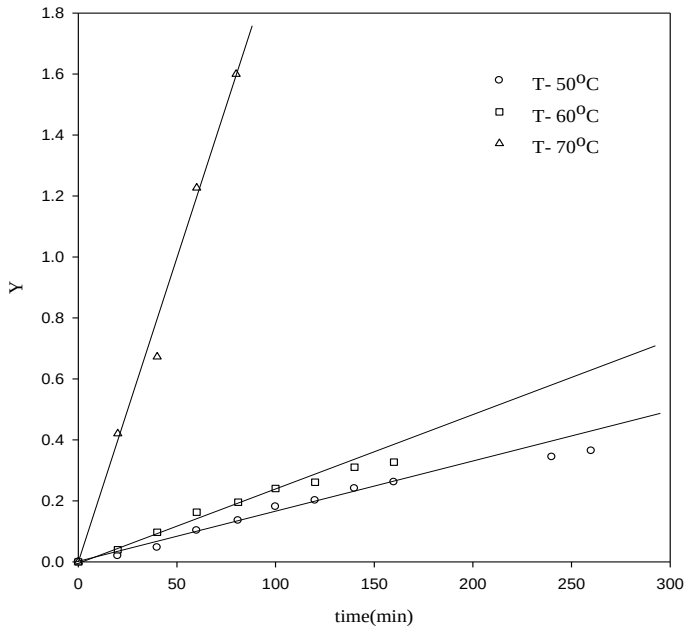

Fig.8. Test of the rate equation {MR = 1.5; CC = 2.0 wt %}

A close examination of plots of the Figures 6, 7 and 8 also reveals the similar observations pertaining to system(3).

Applying regression analysis to the data the following equations were obtained for the rate constants.

$$k_1 = 0.2711 \times 10^7 \, (MR)^{1.635} (CC)^{0.6692} e^{-6320/T} \quad \ldots (9)$$

Average deviation = 6.795 percent

Standard deviation = 9.651 percent

$$k_2 = 0.4058 \times 10^{-3} (MR)^{0.8775} \, (CC)^{-1383} \, e^{1487/T} \quad \ldots (10)$$

Average deviation = 7.811 percent

Standard deviation = 10.12 percent

The experimental and calculated k_1 and k_2 values are compared and presented in Figs. 9 and 10 respectively.

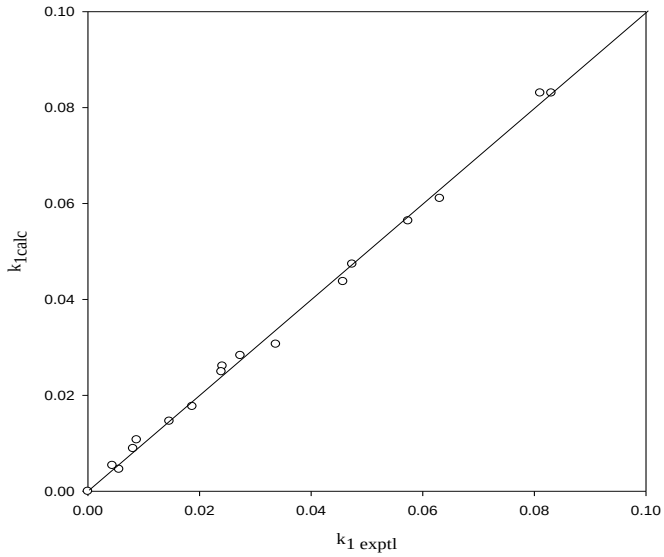

Fig.9. Comparison of experimental and calculated values of k_1- for system(3)

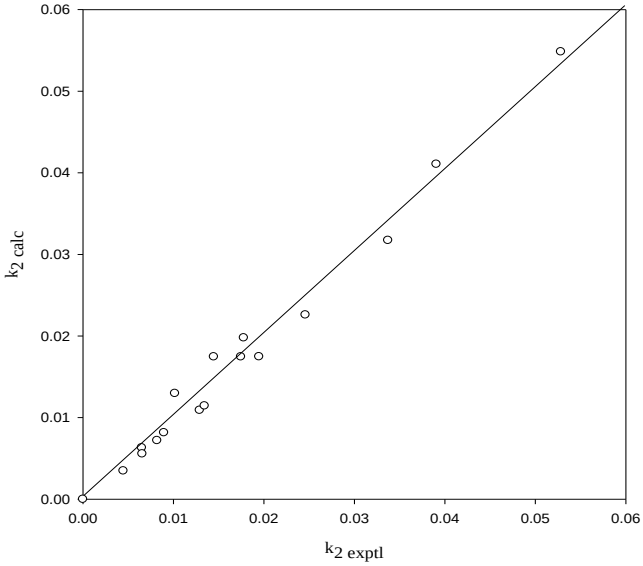

Fig.10. Comparison of experimental and calculated values of k2- for system(3)

The summary of equations of forward and backward rate constants for the three systems was presented here under in Table 1.

Table 1. Rate constants obtained for the three reacting systems**.**

S.No	System	Equation
1	n- Propionic acid and 2- Propanol	$k_1 = 0.05536(MR)^{0.8861}(CC)^{0.5385}e^{49.59/T}$ $k_2 = 357.6(MR)^{0.5987}(CC)^{-0.44}\,e^{-2914/T}$
2	n- Butyric acid and 2- Propanol	$k_1 = 1.653\,(MR)^{1.287}(CC)^{1.178}\;e^{-1336/T}$ $k_2 = 0.1054(MR)^{-0.0598}\;(CC)^{0.8055}\;e^{-500.1/T}$
3	n- Pentanoic acid and 2- Propanol	$k_1 = 0.2711 \times 10^{7}\,(MR)^{1.635}(CC)^{0.6692}e^{-6320/T}$ $k_2 = 0.4058 \times 10^{-3}(MR)^{0.8775}\;(CC)^{-1383}\,e^{1487/T}$

Comparison studies of 2-propanol with the three different carboxylic acids

By inspecting the plots of the Fig. 11, one can notice that, the conversion exercised by each acid was nearly same. Thus it can be understood that, in case of these chosen acids, the conversion mainly dependent on 2-propanol reactivity. Hence, there is no significant variation by the varied chain length. Same observations can be made from Fig.12 drawn for different mole ratio, temperature and catalyst concentration.

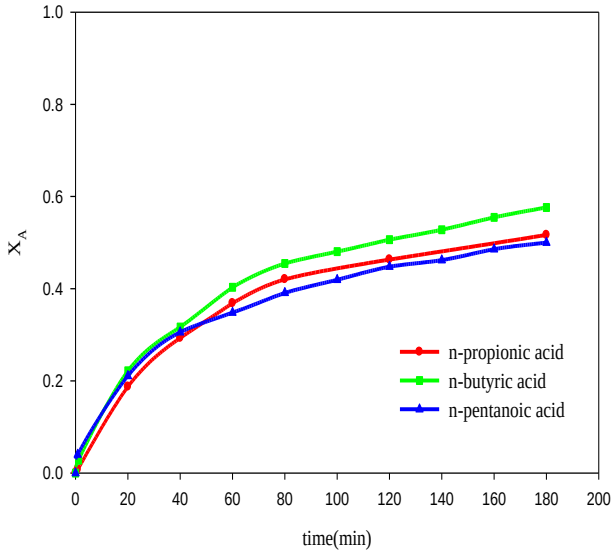

Fig. 11 Comparison of 2-propanol conversion with three different carboxylic acids {MR=1.0; T=70^{0}C; CC=2.0 wt% }

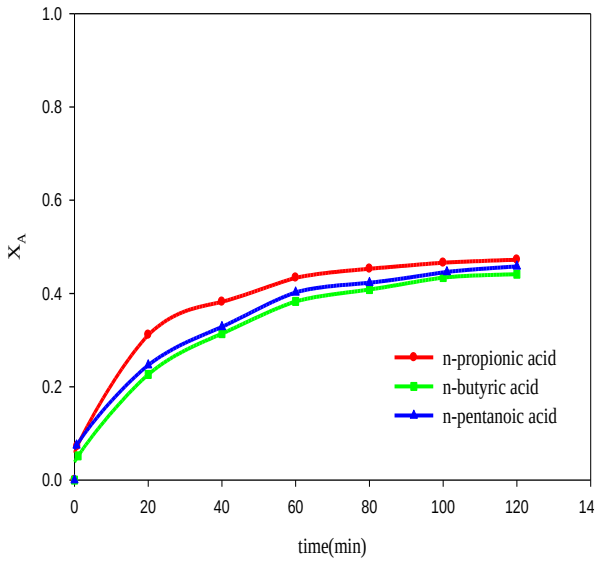

Fig. 12 Comparison of 2-propanol conversion with three different carboxylic acids {MR=1.5; T=70^{0}C; CC=2.0 wt%}

4. Conclusion

Kinetic data on esterification of 2-propanol with three different carboxylic acids viz., n-propionic acid, n-butyric acid and n-pentanoic acid have been analyzed as two way reversible reaction. It was observed that entire data for each reacting system successfully fit into the reversible reaction

kinetics. Both forward reaction rate constant and backward reaction rate constant were obtained and were subjected to regression analysis by expressing them as function of mole ratio, catalyst concentration and temperature.

References

1. R. Robert, T. Salmi, A. Vuori, H. Haario, J. Lehtonen, A. Sundqvist, and E. Tirronen. "Development of a kinetic model for the esterification of acetic acid with methanol in the presence of a homogeneous acid catalyst. *Chemical Engineering Science* 52, no. 19: 3369-3381(1997).
2. D.U.S.L. Deepthi, G.V.S. Sarma, K.V. Ramesh. "Kinetic studies of esterification of n-propionic acid and 2-propanol with sulphuric acid catalyst." Journal of Emerging Technologies and Innovative Research, 6(2) 200-207(2019).
3. D.U.S.L. Deepthi, G.V.S. Sarma, K.V. Ramesh. "Kinetic studies of esterification of n-pentanoic acid and 2-propanol with sulphuric acid as a catalyst." International Journal of Research and Analytical Reviews, 6(2) 512-519 (2019).
4. D.U.S.L. Deepthi, K.V. Ramesh, G.V.S. Sarma. "Kinetic and thermodynamic Modeling of esterification of 2- propanol and n- butyric Acid." Journal of Chemical Health Risks, 2024(in press).
5. Beula, C., & Sai, P. S. T. Kinetics of esterification of acetic acid and ethanol with a homogeneous acid catalyst. *Indian Chemical Engineer*, *57*(2), 177-196(2015).
6. D.U.S.L. Deepthi, "Kinetic and thermodynamic of esterification of 2-propanol with different carboxylic acids", Ph.D. Thesis, Andhra University, India (2023).