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KINETIC STUDY OF AUTOCATALYZED ESTERIFICATION OF LACTIC ACID WITH ALCOHOLS C_2-C_5

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ARTICLEINFO	ABSTRACT
	Lactic acid and their esters are used for the manufacture of biodegradable polymers and green solvents. Lactic acid esters also used in the purification process of lactic acid. The autocatalyzed esterification kinetics of lactic acid with linear chain alcohols C_2-C_5 was studied with isothermal batch experiments at 313-384 K. The effect of various parameters such as molar ratio and the temperature was studied. The activation energy for all forward reactions was almost equal and it was in the range of 47-49 kJ/mol. It was found that the pre-exponential factor decreased as the number of carbons in the linear alkyl chain of alcohols increased. Disciplinary: Chemical Engineering & Sciences

1. INTRODUCTION

Lactic acid is an interesting compound due to the presence of carboxyl and hydroxyl group. Lactic acid and its esters due to the combination of these groups are used in many organic synthesis industries and in various biochemical industries. Lactic acid esters are used as green solvents in cosmetic industries (Häckl and Kunz, 2018). The hydrolysis of alkyl-lactates is an effective way to minimize the cost of lactic acid purification (Datta et al., 1995; Edreder et al., 2011) and to produce pure lactic acid for biodegradable polymers (Edreder et al., 2011). The scientific literature contains some reports (Yixin et al., 2009; Dassy et al., 1994) with the kinetic studies of lactic acid esterification on the heterogeneous acid catalysts. The use of ion-exchange resins is more advantageous as compared to homogeneous catalysts. But the works of Golovanov et al. (2013); Choi et al. (1996) shown inhibiting effects of alcohol and water on the ion-exchange resin catalyst. Heterogeneous catalysts are also expensive.

In this work, the esterification kinetics of lactic acid with linear chain alcohols C_2-C_5 catalyzed

by lactic acid (autocatalyzed) have been investigated.

2. MATERIALS AND METHODS

2.1 RAW MATERIALS

All chemicals used in the study were obtained from Vekton, Russia. Alcohols were additionally purified by the fractional distillation. Final purity of alcohols was: ethanol more than 96.2% by mass, n-propanol, n-butanol, n-pentanol more than 99.8% by mass. The degree of purity was determined using gas chromatography. An aqueous solution of lactic acid (68% by mass) was used. The number of oligomers of lactic acid was measured by titration. It did not exceed 0.2% by mass.

2.2 ESTERIFICATION

The esters were synthesized by esterification of lactic acid with linear chain alcohols C_2-C_5 with azeotropic distillation in the presence of benzene. The molar relation of lactic acid to alcohol was 1:5. All esters were purified by a repeated distillation in vacuum. Purities of samples were determined by the gas chromatography. The purity of samples was obtained more than 99% by mass.

2.3 ANALYSIS

In kinetic experiments, the samples were analyzed using a Khromatek-Analitika chromatographic program-apparatus complex based on a Kristall-2000M chromatograph equipped with a flame ionization detector. A capillary column DB-1 (stationary phase dimethylpolysiloxane) was used with a column length of 30 m, an inside diameter of 0.2 mm and a film thickness of 0.5 µm. The temperature of the injector was 523 K, detector temperature was 553 K. The standard temperature program of the column was T=373 K for 20 min followed by a heating rate 20 K·min^{-1} to T=533 K. Helium with a purity of 99.99% was used as the carrier gas helium. The volume of sample was 0.2 µl and flow splitting was 1/80. The amount of condensed substance was determined by GC analysis using an internal standard n-propanol for ethyl, butyl, pentyl lactates and n-butanol for propyl lactate.

2.4 KINETIC MEASUREMENTS

The reaction kinetics was studied in a three-necked glass reactor of 250 ml capacity fitted with a reflux condenser, a thermometer, and a magnetic stirrer. The temperature was maintained within an accuracy of ±0.5 K by an electric-heated thermostatic oil bath. The equipment and procedure have already been described in detail elsewhere (Choi et al., 1996). The aqueous lactic acid solution was weighed an accuracy of 0.0001 g. It was charge into the reactor and heated to the required temperature. The calculated amount of alcohol weighted accuracy of 0.0001 g was heated and fed into the reaction. This time was considered to be the starting point of the reaction. Samples (100 µl) were taken using a syringe at regular time intervals and mixed with the standard (30 µl). The time of kinetic experiments was 0-240 minutes.

2.5 KINETIC MODEL

Two overall reactions are considered in the kinetic model: esterification of lactic acid with alcohols and the reverse reaction of alkyl-lactates with water. The following kinetic equation to model this type of reaction was used:

$$r = -\frac{dC_{ML}}{dt} = k_1 \cdot C_{LA}{}^a \cdot C_{ROH}{}^b - k_{-1} \cdot C_{ML}{}^c \cdot C_W{}^d \tag{1}.$$

The reaction order was estimated by the method of initial rate in excess of alcohol. At the initial moment of time, the rate of the direct reaction considerably exceeds the rate of the reverse reaction. It can be assumed that the rate of the reverse reaction is negligible. Then equation (1) can be written as

$$r = -\frac{dC_{ML}}{dt} = k_1 \cdot C_{LA}{}^a \cdot C_{ROH}{}^b \tag{2}.$$

The amount of alcohol in reaction mass was in large excess. So the concentration of alcohols remains essentially constant $C_{ROH}{}^b$=const:

$$r = -\frac{dC_{ML}}{dt} = k' \cdot C_{LA}{}^a \tag{3},$$

where $k' = k_1 \cdot C_{ROH}{}^b$.

The reaction constant is expressed using the Arrhenius equation (Aleksandrov et al., 2019)

$$k' = A \cdot e^{-E_A/R \cdot T} \tag{5}$$

where A is the pre-exponential factor, E_A the activation energy, R the gas constant and T is the absolute temperature.

3. RESULTS AND DISCUSSION

3.1 EFFECT OF THE REACTANT MOLAR RATIO

The molar ratio of alcohol to lactic acid was varied from 4 to 10 for the esterification reaction at 383 K. The dependence of the initial rate of esterification versus molar ratio of alcohol to lactic acid is shown in Figure 1.
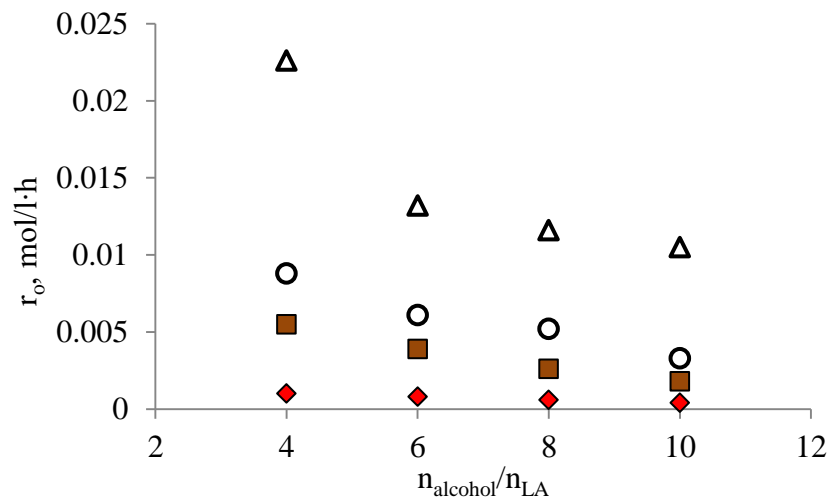

Figure 1: Initial rate of esterification versus the molar ratio of alcohols to lactic acid,
♦ – ethanol; ■ – n-propanol; o – n-butanol; Δ – n-pentanol.

As can be seen in Fig. 1 the initial rate of esterification decrease with the increasing molar ratio of alcohols to lactic acid for all alcohols. The decreases in reaction rate are depending on used alcohol. The large excess of alcohol leads to need a recovery of the product and to increase cost of the reactant. A trade-off between the cost recovery and conversion has to be addressed.

The reaction order for lactic acid was calculated using equation (3). The obtained values were 1.1 ± 0.2, 1.1 ± 0.2; 0.9 ± 0.4 and 1.1 ± 0.4 for esterification lactic acid with ethanol, n-propanol, n-butanol and n-pentanol, respectively. This result generally confirms the total second reaction order for the reagents in esterification (Choi et al., 1996).

3.2 EFFECT OF THE REACTION TEMPERATURE

In order to calculate the activation energy esterification reactions were carried out in the temperature range from 313 to 384 K with a molar ratio of initial reactants 1. Typical results are shown in Figure 2.
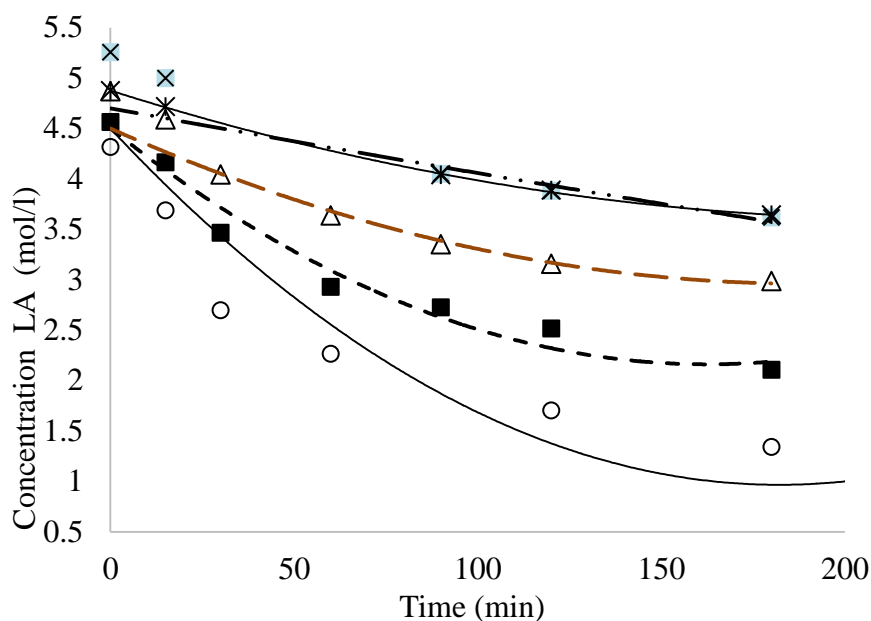

Figure 2. Lactic acid concentration versus time for the esterification with butanol at different temperatures (* - 353K; × - 363 K; Δ - 373 K; ■ - 383 K; ○ - 393K).

It can be seen that the reaction rate increases substantially with the increasing temperature. Rate constants, pre-exponential factors and activation energies for a forward reaction at temperature 323 K were calculated using experimental data and are tabulated in Table 1. Some literature values of activation energy for a similar reactive system also are shown in Table 1.

Table 1: Parameters of the kinetic models for the autocatalytic esterification of lactic acid with alcohols C_2-C_5.

Alcohol	Temperature range, K	k' at 323 K, h^{-1}	A, mol l^{-1} h^{-1}	E_a, kJ/mol	Catalyst	Reference
ethanol	313-353	0.0057	4.00×10^4	45.5±3.1	No	This work
ethanol	328-358	-	-	52.3	Amberlyst 15	Delgado et al. (2007)
_n_-propanol	343-380	0.00675	3.76×10^4	46.7±1.4	No	This work
_n_-butanol	353-393	0.0045	3.23×10^4	48.0±2.3	No	This work
_n_-butanol	333-369	-	-	51.8	Weblyst D009	Dassy et al. (1994)
_n_-pentanol	343-384	0.0025	2.54×10^4	47.4±9.1	No	This work

The activation energies obtained in this work are good agreement taking into uncertainty with literature values for ion-exchange catalyzed esterification. Close values of activation energy for

autocatalyzed and catalyzed esterification show that the amount of lactic acid in the reaction zone is sufficient for the formation of protons H^+ ($pK_{LA} = 3.85$ in aq. at 298 K (Wang et al., 2014)). Also, alcohol and water can deactivation the ion-exchange resin catalyst.

The well-known reaction rate of esterification decreased as the number of carbons in the linear alkyl chain of alcohols increased. The rate constants are related to the pre-exponential factor depending on the number of collisions of molecules and the substituent effects of alcohol. The correlation of pre-exponential factor with the number of carbon atoms in the alcohols (Nc) is shown in Figure 3. The pre-exponential factor is a systematic decrease.
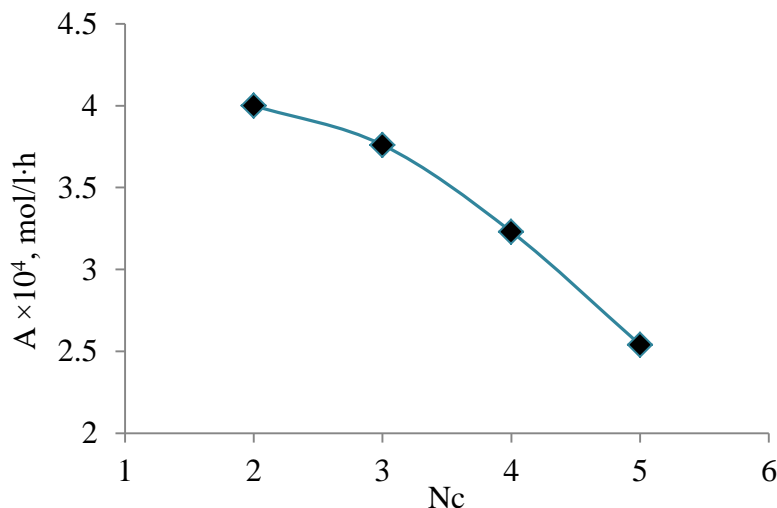

Figure 5: The pre-exponential factor as a function of the number of carbon atoms in the alcohols.

4. CONCLUSION

In this study, the kinetics of the esterification of lactic acid with linear chain alcohols C_2-C_5 without catalyst was experimentally investigated. The reaction rate was found to increase with increasing reaction temperature and to decrease with increasing the molar ratio of the alcohol to lactic acid. The activation energies for all forward reactions were obtained to be in the range of 47-49 kJ/mol. The activation energy of autocatalyzed esterification is close to the activation energy for ion-exchange catalyzed esterification. It was found that the pre-exponential factor decreased as the number of carbons in the linear alkyl chain of alcohols increased.

5. AVAILABILITY OF DATA AND MATERIAL

Data can be made available by contacting the corresponding author.

6. ACKNOWLEDGEMENT

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