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Esterification of palmitic acid with epichlorohydrin on anion exchange resin catalyst

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Abstract: The esterification reaction of palmitic acid with epichlorohydrin catalyzed by an anionic macroporous resin was studied. Purolite A-500 resin proved to be a very effective catalyst in the synthesis of 3-chloro-2-hydroxypropyl palmitate. The effects of certain parameters such as speed of agitation, catalyst particle size, catalyst loading, temperature, initial molar ratio between reactants on the rate of reaction were studied. It was found that the overall rate is intrinsically kinetically controlled. The structure of synthesized ester was confirmed by FTIR and ^{1}H NMR analyses.

Keywords: Palmitic acid, epichlorohydrin, esterification, kinetics, ion exchange resins

1 Introduction

Organic esters are used worldwide in the food, pharmaceutical and cosmetic industries. They are used as monomers for the synthesis of polymers. An important place is occupied by fatty acid esters, using epichlorohydrin as an emulsifier, when they are used in the oil industry or as antistatic agents [1–3].

Ring opening regioselectivity depends on reaction conditions and on the catalyst used. High conversions were obtained with homogeneous catalysts such as tertiary amines and quaternary ammonium salts, but in these cases high amounts of by-products resulted [4, 5]. The highest yields and selectivity were obtained when chromium salts of involved acids were used in esterification reaction [6–16]. The difficulties that occur when

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these catalysts are separated from the reaction mixture represents their major drawback.

Using heterogeneous catalysts (ion exchange resins, zeolites, mesoporous materials) has numerous advantages such as their easy separation from the reaction mixture through filtration or decantation, high selectivity, resuse of the catalyst, as well as their being environmentally friendly [17–24]. Among the heterogeneous catalysts an important role is played by the ion exchange resins.

The aim of this study was to investigate the possibility of using a macroporous strongly basic resin as a catalyst in the esterification of palmitic acid with epichlorohydrin and to establish a kinetic model for this reaction.

2 Experimental

2.1 Materials

Epichlorohydrin (1-chloro-2,3-epoxypropane) was dried over anhydrous sodium sulphate and vacuum distilled. Palmitic acid of 99.5% purity was purchased from Merck. The anion exchange resin Purolite A-500 catalyst was supplied by Victoria S.A. Purolite (Romania). The most important physical and chemical properties of this resin are given in Table 1.

Table 1 Physical and chemical properties of Purolite A-500 anion exchange resin.

Polymer matrix structure	Macroporous, styrene/divinylbenzene	
Functional Groups	R- $N(CH_3)_3^+$	
Appearance	Opaque, spherical beads	
Ionic form	Cl^-	
Moisture holding capacity (%)	53 – 58	
Total Exchange Capacity (ech/ml)	1.15	
Particle size range (mesh)	16 – 50	
Maximum Operating Temperature (°C)	100	
Shipping weight (g/l)	685	
Grading	particle size (μm)	weight percentages (%)
	400 – 500	7.9
	500 – 630	18.37
	630 – 800	30.87
	800 – 1000	42.86

Before use, the catalyst was dried at 353 K for 12 hours.

2.2 Apparatus

The esterification reaction was carried out in a three necked glass flask of 250 ml capacity equipped with a reflux condenser, a sample device and a thermocouple. The temperature was controlled within ± 0.5 °C by a thermostating bath. A magnetic stirrer was used to mix the reactants. The frequency was 600 rpm.

2.3 Procedure

Palmitic acid was loaded into the reactor and then heated to the desired temperature. Finally, preheated epichlorohydrin and a given amount of catalyst were added. This was taken as the zero time of reaction.

The evolution of the reaction was followed by sampling (1 ml sample dissolved in chloroform) at regular time intervals for analysis. The amount of unreacted acid in the samples was determined by titration against standard alcoholic solution 0.1 M of NaOH with phenolphthalein. The content of epichlorohydrin in the samples was determined using the method described by Jay [25].

2.4 Analysis, isolation and characterization of product

The final reaction mixture was analyzed by HPLC chromatography. The analysis was performed at ambient temperature on a ZORBAX SB-C18 (4.6×15 cm) column using a HPLC Varian 9010 pump, an Waters 717 plus Autosampler and an UV-VIS Spectroflow 757 as detector.

The reaction products (purified by vacuum distillation (20 mm Hg and 546 K)) and palmitic acid were dissolved in $CHCl_3$ (about 1.2 mg/mL) and were filtered on 0.45 μm membrane before injection. As eluent an acetonitrile : methanol mixture (75 : 25, v/v) with a flow rate of 1 mL/min was used. The volume of the sample was 30 μL. The chromatogram was recorded at 210 nm.

The recorded chromatogram showed three peaks. The retention times corresponding to the three peaks (which coincide with the retention times of the pure substance taken as standards) were: palmitic acid $1.72 - 1.76$ min, epichlorohydrin $2.02 - 2.2$ min and ester 3.12 min.

The structure of the final reaction product was determined by ^{1}H NMR and FTIR analyses. FTIR spectra of samples which were tablet formed with KBr, were recorded on a DIGILAB FTS 2000 spectrometer (2 cm^{-1} resolution, 24 scan frequency, $4000 - 400$ cm^{-1}). The ^{1}H NMR spectrum was recorded on a Varian EM-39 spectrometer. FTIR spectrum was processed by DIGILAB MERLIN 3.3 program.

In the recorded IR spectrum, the typical vibration bands for 3-chloro-2-hydroxypropyl palmitate were observed: 3440 cm^{-1} ν_{OH}; 2852-2922 cm^{-1} ν_{CH}; 1745 cm^{-1} $\nu_{C=Oesteric}$; 1467 cm^{-1} ν_{CH}; 1170 cm^{-1} $\nu_{C-Oesteric}$; 721 cm^{-1} ν_{CCl}.

The proton resonance signals δ (ppm) noticed in the ^{1}H-NMR spectrum ($CDCl_3$) were: 0.86 (t, 3H, CH_3); 1.54 (m, 26H, $13 \times CH_2$); 2.3 (t, 2H, CH_2); 4.86 (m, 2H, CH_2); 4.13 (m, 1H, CH); 3.6 (m, 2H, CH_2).

3 Results and discussion

The effects of different parameters such as: speed of agitation, catalyst particle size, catalyst loading, molar ratio between reactants and temperature over reaction kinetics were studied.

3.1 Effect of speed of agitation

In order to assess the external mass transfer resistance the stirring speed was varied between 400 and 800 rpm The experimental results are shown in Fig. 1.

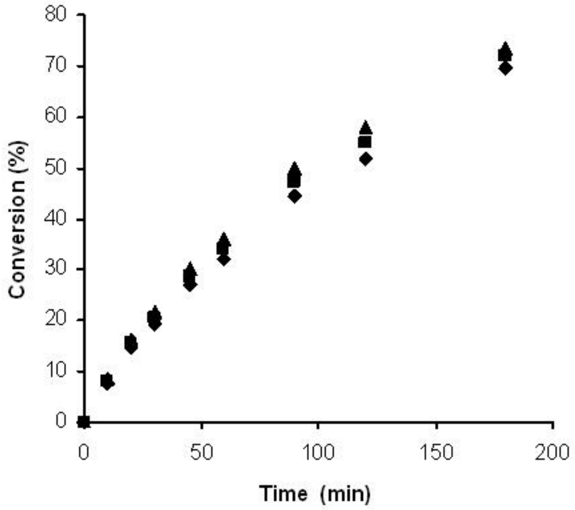


Fig. 1 Effect of speed of agitation on the conversion of palmitic acid; molar ratio palmitic acid - epichlorohydrin 1:1; temperature 368 K; catalyst loading 10 g cat / 100 g reaction mixture; stirring speed: ♦ 400 rot/min; ■ 600 rot/min; ▲ 800 rot/min.

One can conclude that the speed of agitation had no effect on the overall reaction rate, which means there was no external mass transfer limitation. This result is in agreement with the statements of Chakrabarti and Sharma who mentioned in their work that film diffusion control is relatively rare in ion exchange catalyzed reactions since film diffusion is a rather fast process [26]. Such resistance can still occur in exceptional instances when the mixture viscosity is too high or the stirring speed is too low. Therefore, further experiments were conducted at 600 rpm, to be on the safe side.

3.2 Effect of particle size

To evaluate the internal mass transfer resistance a commercial anion exchange resin, Purolite A - 500, was sieved. Four particle size ranges were obtained as can be observed from Table 1.

The change of palmitic acid conversion with time was followed for each particle size range. The results obtained proved that there was no significant effect of particle size on conversion, which suggest the effectiveness factor for this reaction is almost unity and consequently the entire process is intrinsically kinetically controlled. Therefore in subsequent experiments unsieved resin was used.

3.3 The effect of catalyst loading

The effect of catalyst loading on esterification rate is shown in Figures 2 and 3.

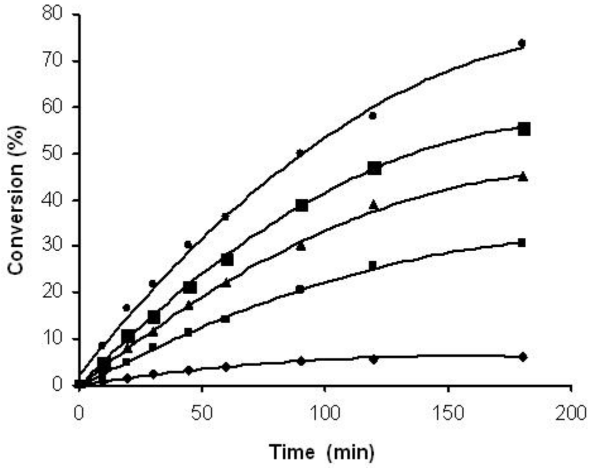


Fig. 2 Effect of catalyst loading on palmitic acid conversion; molar ratio palmitic acid - epichlorohydrin 1:1; temperature 368 K; stirring speed 600 rpm; catalyst loading (g cat / 100 g reaction mixture): ◆ 0; ▪ 2.5; ▲ 5; ■ 7.5; ● 10

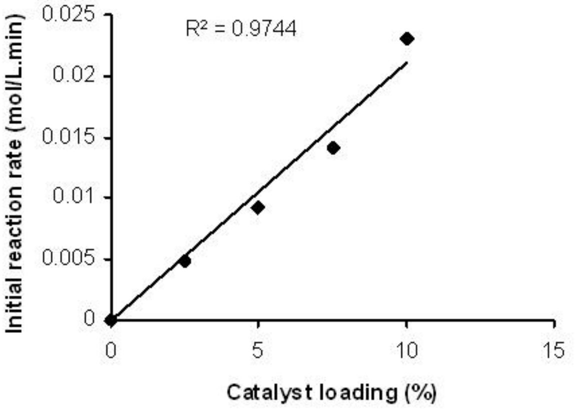


Fig. 3 Initial reaction rate versus catalyst loading; molar ratio palmitic acid - epichlorohydrin 1:1; temperature 368 K; stirring speed: 600 rpm; catalyst loading (10 g cat / 100 g reaction mixture).

The increase of conversion with increasing of the catalyst loading can be explained through the increase of the active sites number. The direct proportionality between the initial reaction rate and the catalyst loading proves that mass transfer resistance is absent. Consequently the reaction rate constant k_1 is a linear function of the catalyst loading c_C and can be expressed based on catalyst loading as: $k_1 = k_R \cdot c_C$.

3.4 Effect of molar ratio between reactants

The molar ratio between epichlorohydrin and palmitic acid was varied from 1 to 4 while the other parameters were kept the same. The increase of conversion with the increase of initial epichlorohydrin - palmitic acid molar ratio can be observed from Fig. 4.

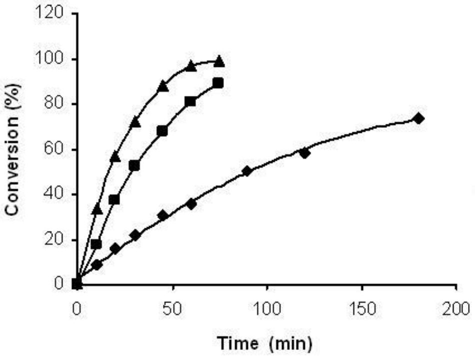


Fig. 4 The effect of molar ratio on palmitic acid conversion; temperature 368 K; stirring speed: 600 rpm; catalyst loading (10 g cat / 100 g reaction mixture); molar ratio: ♦ 1:1; ■ 1:2; ▲ 1:4.

3.5 The effect of temperature

The effect of temperature on conversion under otherwise similar conditions was studied at 348, 353, 358, 363 and respectively 368 K. A sharp increase of conversion with temperature increase was noticed. This increase suggests that external mass transfer is not the rate controlling step. The conversion of palmitic acid versus time was studied. The experimental results are shown in Fig. 5.

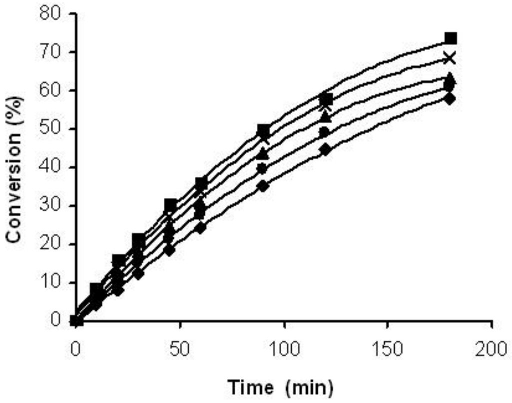


Fig. 5 Effect of temperature on palmitic acid conversion; molar ratio palmitic acid - epichlorohydrin 1:1; stirring speed 600 rpm; catalyst loading (10 g cat /100 g reaction mixture): temperature: ♦ 348 K; ; ● 353 K; ▲ 358 K; × 363 K; ■ 368 K.

3.6 Reaction kinetics

Several kinetic models based on homogeneous or heterogeneous catalysis are used to describe the esterification reactions catalyzed by ion exchange resins. When there is no external mass transfer limitation the general expression of reaction rate r can be written as:

$$r = \eta \frac{k_1 \cdot c_A^{nA} \cdot c_E^{nE}}{\left(1 + \sum_i K_i \cdot c_i\right)^n} \tag{1}$$

where:
η - the effectiveness factor of reaction,
k_1- the reaction rate constant,
K_i - adsorption constant for component i,
c_i - concentration of component i,
c_A - palmitic acid concentration,
c_E - epichlorohydrin concentration,
n_A - partial order of reaction with respect to palmitic acid,
n_E - partial order of reaction related to epichlorohydrin,
The exponent is $n = 2$ for the Langmuir Hinshelwood model, $n = 1$ for the Elley Rideal mechanism and $n = 0$ for the pseudo-homogeneous approach.

In this study the pseudo-homogeneous approach was chosen to represent the experimental data because the adsorption of reactants on resin is weak. When both external and internal mass transfer resistances are absent, the kinetic parameters of intrinsic reaction can be determined. The partial orders of reaction with respect to each reactant were determined by the isolation method. Therefore, in order to establish the reaction order with respect to epichlorohydrin, experiments in an excess of palmitic acid were performed. By this means acid concentration could be considered constant and included into the apparent rate constant k_2.

By this substitution the equation for the reaction rate becomes:

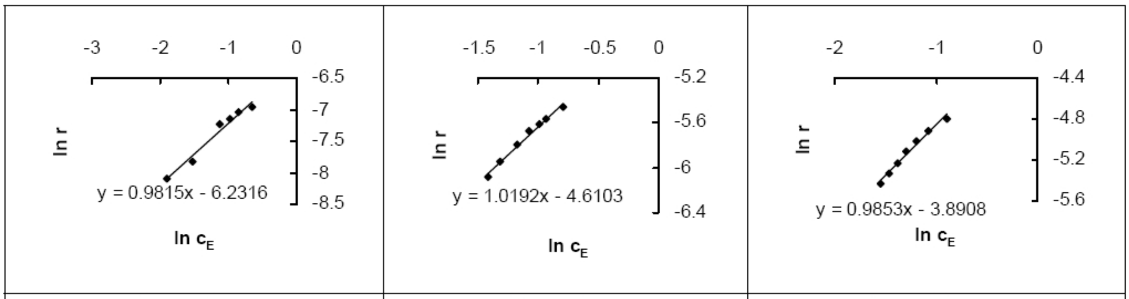
$$r = k_2 \cdot c_E^{nE} \tag{2}$$

where $k_2 = k_1 \cdot c_A^{nA}$.

The reaction order with respect to epichlorohydrin was determined as the slope of the straight line obtained by plotting $\ln r$ against $\ln c_E$. The results obtained for different initial molar ratios of palmitic acid : epichlorohydrin are shown in Fig. 6.

The reaction order with respect to palmitic acid was determined carrying out the experiments in large excess of epichlorohydrin. The plot of palmitic acid concentration against time is a straight line (Fig. 7). This behavior is typical for zero order kinetics. Consequently the expression of the reaction rate can be written as:

$$r = k_1 \cdot c_A^0 c_E^1 \tag{3}$$



Molar ratio = 6:1 | Molar ratio = 8:1 | Molar ratio = 10:1

Fig. 6 The reaction order with respect to epichlorohydrin from plot of ln r against ln c_E.

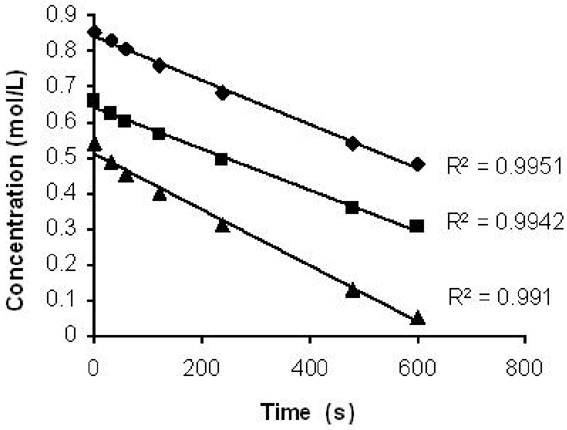


Fig. 7 Change of palmitic acid concentration with time for different molar ratio palmitic acid - epichlorohydrin; speed of agitation: 600 rpm; catalyst loading (10 g cat / 100 g reaction mixture); temperature 368 K, molar ratio: ♦ 1:10; ■ 1:15 ; ▲ 1:20.

The integrated form of equation 3, where concentration was expressed as a function of conversion x_A and taking into account the value of the molar ratio between reactants becomes:

$$-\ln(1 - x_A) = k_1 \cdot t \tag{4}$$

Plot of $-\ln(1 - x_A)$ versus time is a straight line passing through the origin which confirms the validity of the model (Fig. 8).

The value of k_1 from the slope of the straight line (as $tg\alpha/c_{A0}$) was determined, then k_R as a ratio between k_1 and c_c was calculated.

From the Arrhenius plot as $\ln k_R$ versus $1/T$ (Fig. 9), the energy of activation and the preexponential factor were calculated. The value found for energy of activation was 23.025 kJ/mol

This moderate value suggests that the reaction is quite fast and can be controlled by mass transfer factors at higher catalyst loadings.

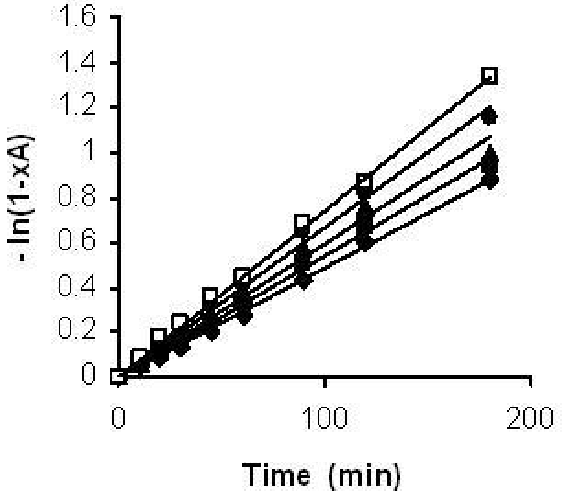


Fig. 8 Integrated form for the equation of reaction rate; molar ratio palmitic acid epichlorohydrin 1:1; speed of agitation 600 rpm; catalyst loading 10 g cat/ 100 g reaction mixture; temperature: ♦ 348 K; □ 353 K; ▲ 358 K; ○ 363 K; ■ 368 K.

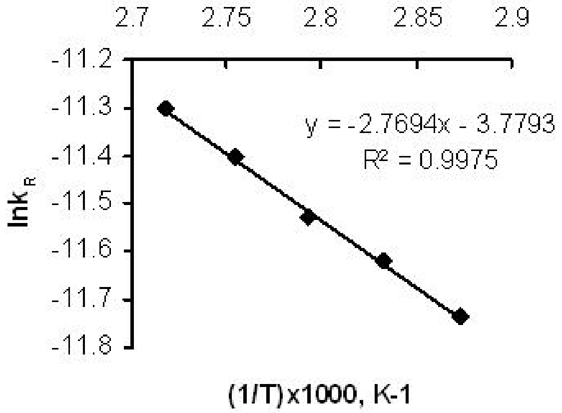


Fig. 9 Arrhenius plot of lnk_R vs (1/T)x 10^3, K^{-1}

3.7 Selectivity of reaction

From experimental data concerning the change of palmitic acid and epichlorohydrin concentrations with time (Fig. 10), no significant differences between their values were noticed (the difference between those two concentrations does not exceed 3-4% after four hours of reaction). This finding, also confirmed by chromatographic analysis, leads to the conclusion that the reaction catalyzed by Purolite A-500 resin is selective.

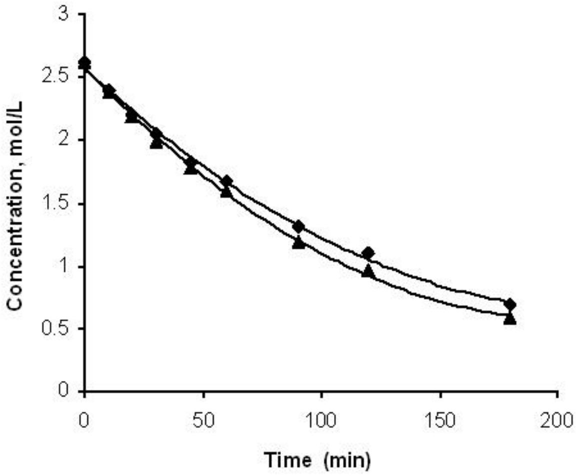


Fig. 10 Changes of palmitic acid and epichlorohydrin concentrations with time ◆ palmitic acid ▲ epichlorohydrin.

3.8 Conclusions

The experimental results obtained for the esterification of palmitic acid with epichlorohydrin in the presence of strongly basic anionic Purolite A-500 are proof that this type of ion exchangers can be successfully used for reactions between organic acids and epoxy compounds. Temperature, catalyst loading and molar ratio of reactants show a marked influence on reaction rate. A pseudo-homogeneous model was used to represent the experimental data. Partial orders of reaction determined through isolation method were zero with respect to palmitic acid and two with respect to epichlorohydrin. The moderate value found for the energy of activation suggests that the reaction is quite fast and can be controlled by mass transfer factors at higher catalyst loadings.

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