

heteropolyoxometalates compounds [21-23], chromium and iron compounds [24-27].

Taking into account the advantages of heterogeneous catalysis, Anne Cauvel and co-workers tested the possibility of replacing the amines with other heterogeneous catalysts obtained through the immobilisation of some primary and tertiary aminic functions on mesoporous mineral supports [28].

The esterification reaction of carboxylic acids with epichlorohydrin over anion exchange resin catalysts is less studied [29-32]. These catalysts have numerous advantages such as their easy separation from the reaction mixture through filtration or decantation, possible regeneration and no need for additional work-up (neutralization, washing).

In previous papers, the authors studied the catalytic activity of some strong base styrene-divinylbenzene anion exchange resins in the addition reaction of carboxylic acids to epichlorohydrin [31,32]. The aim of this work is to test the effectiveness of polyacrylic anion exchange resin Purolite A 860S and to compare its catalytic activity with the activity of Purolite A 500 styrene-divinylbenzene anion exchange resin.

EXPERIMENTAL

Materials

Epichlorohydrin (1-chloro-2,3-epoxypropane) was dried over anhydrous sodium sulphate and vacuum distilled. Acetic acid of 99.5% purity was purchased from Merck. The anion exchange resins Purolite A 500 and Purolite A 860S were supplied by Victoria S.A. Purolite (Romania). The most important physical and chemical properties of these resins are given in Table 1.

Before use, the Purolite A 500 and Purolite A 860S catalysts were dried at 353 and 333 K, respectively.

Procedure

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 400 rpm.

Carboxylic acid and epichlorohydrin were loaded into the reactor and then heated to the desired temperature. Finally, a given amount of catalyst was added. This was considered as the zero time of reaction. Fatty acids were determined by titration against standard alcoholic solution 0.10 M of NaOH in the presence of phenolphthalein as indicator. Acetic and acrylic acids were titrated against standard aqueous solution 0.10 M of NaOH using a mixed indicator phenolphthalein-bromthymol blue.

Characterization of catalysts

Swelling experiments

3 cm³ of dried resins (V_i) were placed into a byrett. The reaction mixture (acetic acid/epichlorohydrin molar ratio 1:1) or heptan were added until the complete covering of catalyst beads. The final volume of resins (V_f) was determined after 24 h (enough time for complete resin swelling). The swelling degree was calculated according to the relation:

$$\text{Swelling degree (\%)} = 100 \frac{V_f - V_i}{V_i}$$

Determination of pore volume

The total pore volume was calculated with the following equation:

$$V_p = (1/\rho_{ap}) - (1/\rho_r)$$

The apparent density (ρ_{ap}) was determined with a mercury pycnometer. The real density (ρ_r) was measured in *n*-heptane.

Table 1. Physical and chemical properties of the anion exchange resins

Physical and chemical characteristics	Purolite A 500	Purolite A 860S
Polymer Matrix	Macroporous polystyrene crosslinked with divinylbenzene	Macroporous polyacrylic crosslinked with divinylbenzene
Functional Groups	Quaternary ammonium salts	Quaternary ammonium salts
Physical Form and Appearance	Spherical beads	Spherical beads
Ionic Form	Cl ⁻	Cl ⁻
Moisture Retention, Cl ⁻ form (%)	50-56	66-72
Total Exchange Capacity (meq/ml min)	0.9	0.8
Particle size range (μ m)	400-1000	600-800
Maximum Operating Temperature (°C)	100	80
Shipping weight (g/l)	680	680-735

Samples analysis

The reaction products were identified by gas chromatography/mass spectrometry (GC/MS) using a 5890 Hewlett Packard series II chromatograph. A DB1 capillary column (15 m length, 0.25 mm diameter, 0.1 μm film thickness) was used for separating the reactants and products. The conditions of GC analysis were: injector temperature 250 $^{\circ}\text{C}$, oven temperature program 30(1)-5-160, amount of sample injected 0.10 μl , carrier gas nitrogen at a flow rate of 5 ml/min, splitting ratio 1:10. Quantitative gas chromatographic analyses were performed on a GC/FID coupling. A flame ionization detector (FID) was used at 250 $^{\circ}\text{C}$. The external standard method was used in order to quantify the amounts of the chemical species.

Characterization of products

3-chloro-2-hydroxypropyl acetate (b.p. 133 $^{\circ}\text{C}/21$ mm Hg) and 1-chloro-3-hydroxypropan-2-yl acetate (b.p.168 $^{\circ}\text{C}/20$ mm Hg) were separated by vacuum fractionation and identified by $^1\text{H-NMR}$, IR and MS. The spectral data of the two isomeric hydroxyl-alkyl esters were presented in another paper [32].

RESULTS AND DISCUSSIONS

Effect of carboxylic acid nature

Initial researches focussed on the efficiency of two anion exchange resins Purolite A 500 and Purolite A 860S used as catalysts in the addition reaction of some carboxylic acids to epichlorohydrin. For both catalysts the reaction rate depended on the strength of the acid used decreasing in the following order: acrylic acid, acetic acid, caprylic acid, palmitic acid

acid (Figure 1). The results obtained can be explained by the reaction mechanism which involves two subsequent steps. In the first step, the ionic exchange between carboxylic acid and quaternary ammonium groups with formation of carboxylate ion takes place. In the second step, the addition of carboxylate ion to oxirane ring occurs. The rate of ionic exchange is much slower than the addition of carboxylate ion and depends on a dissociation constant of the acid.

In previous papers [31,32] the authors showed that the esterification reaction of carboxylic acids with epichlorohydrin over anion exchange resins follows a second order overall kinetics; the partial orders of the reaction are 1 with respect to the catalyst and epichlorohydrin and 0 for the carboxylic acid. The values of rate constants for the two catalysts used, calculated from the integrated form of reaction rate $-\ln(1 - x_A)$ versus time are shown in Table 2.

Table 2. The values of rate constants for the reaction of epichlorohydrin with carboxylic acids; molar ratio acetic acid-epichlorohydrin: 1:1.2; stirring speed: 400 rpm.; catalyst loading: (10 g catalyst/100 g reaction mixture); temperature: 366 K for Purolite A 500 and 348 K for Purolite A 860S

Carboxylic acid	Rate constants, $k \times 10^4$ (min^{-1})	
	Purolite A 500	Purolite A 860S
Acrylic acid	10.00	15.92
Acetic acid	7.00	12.17
Caprylic acid	6.17	9.08
Palmitic acid	5.50	8.17

From the data presented in the above table one can notice the high values of reaction rates obtained for Purolite A 860S under low reaction temperatures

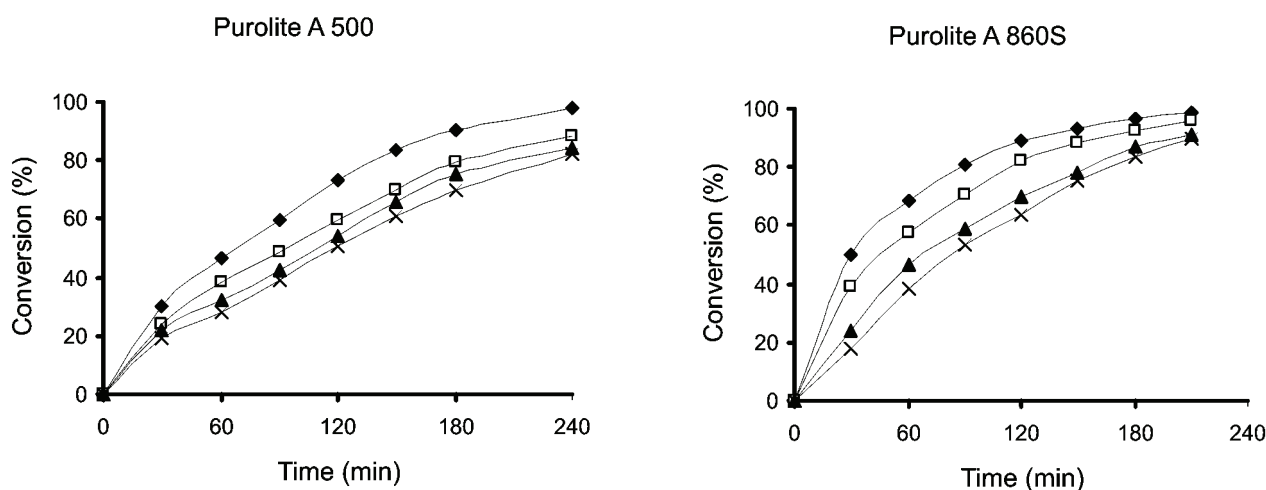


Figure 1. Variation of carboxylic acid conversions with time; molar ratio acetic acid-epichlorohydrin 1:1.2; catalyst loading: 10 g catalyst/100 g reaction mixture; temperature: 366 K for Purolite A 500 and 348 K for Purolite A 860S; stirring speed: 400 r.p.m.; x - palmitic acid; \blacktriangle - caprylic acid; \square - acetic acid; \blacklozenge - acrylic acid.

(348 K). The higher catalytic activity of Purolite A 860S resin can be justified by the polar nature of the polymer matrix (pointed out through higher swelling degree values in polar solvents - acetic acid/epichlorohydrin) and through its higher porosity (Table 3).

Table 3. Swelling degree for anion exchange resins

Catalyst	Swelling degree (%) in acetic acid-epichlorohydrin mixture	Swelling degree (%) in heptan	Cumulative pore volume (mm ³ /g)
Purolite A 500	55	6.25	379
Purolite A 860S	90	1.43	515

Influence of reaction parameters

The effect of reaction parameters on the yields of the chlorohydroxypropyl esters was studied taking as a model the esterification of acetic acid with epichlorohydrin.

Effect of temperature

The reaction was studied in the temperature range from 338 to 348 K for Purolite A 860S catalyst and between 343-366 K for Purolite A 500 catalyst,

maintaining the other parameters unchanged (reaction time 5 h, molar ratio acetic acid-epichlorohydrin: 1:1, catalyst loading: 10%, stirring speed: 400 rpm).

Analysing the experimental data, it results that the reaction yield was favourably influenced by the increasing of temperature (Table 4). Higher variations for the reaction rates with the increase of temperature were obtained for the Purolite A 500 catalysed reactions.

The values of the ratio between the two isomeric esters decrease with the increase of temperature because the higher temperatures favourise the formation of abnormal ester.

Effect of catalyst loading

The catalyst loading varied from 0 to 12.5% (weight of catalyst/total weight of reactants). The effect of the catalyst amount is shown in Figure 2.

The plot from Figure 2 shows a significant increase in the reaction rate in the range of 0 to 10 % catalyst loadings. Higher catalyst loadings generate only small changes in reaction rates.

Regarding the effect of the catalyst loading on the reaction selectivity there is a slightly decrease of the ratio between the two isomeric esters with the increase of the catalyst amount (Table 5).

Table 4. The effect of temperature on the yields of the two isomeric esters; reaction time: 5 h, molar ratio acetic acid-epichlorohydrin: 1:1, stirring speed: 400 rpm; catalyst loading: 10 g catalyst/100 g reaction mixture

Purolite A 500			Purolite A 860S		
Temperature K	Yield of normal ester %	Yield of abnormal ester %	Temperature K	Yield of normal ester %	Yield of abnormal ester %
343	38.60	3.44	338	59.12	8.62
353	53.00	8.98	343	63.08	10.46
366	66.48	12.31	348	70.13	11.93

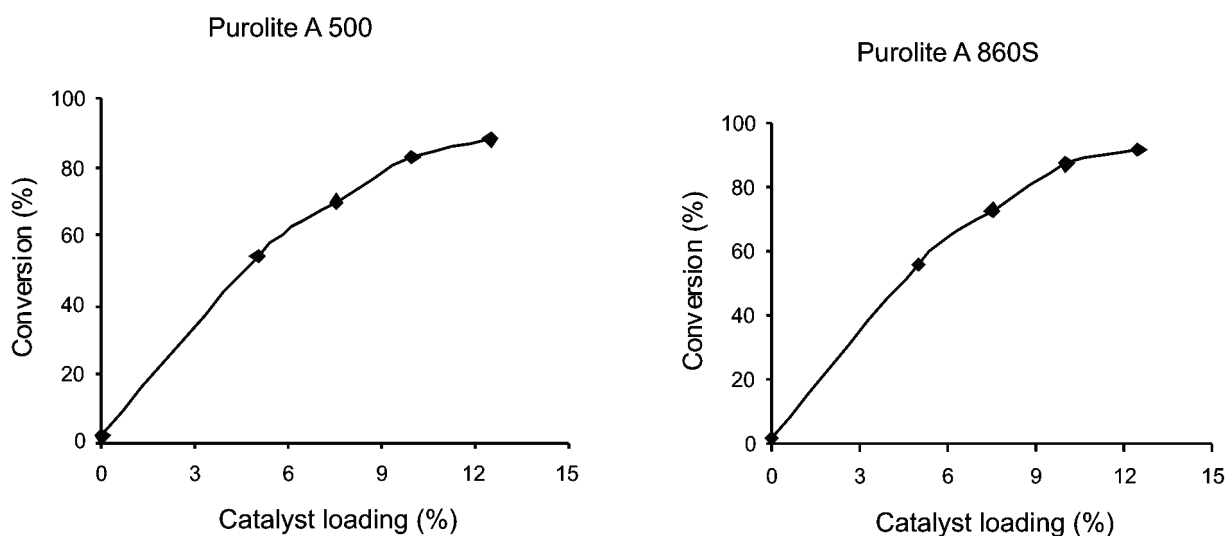


Figure 2. The effect of catalyst loading on acetic acid conversion; molar ratio acetic acid-epichlorohydrin: 1:1; temperature: 366 K for Purolite A 500 and 348 K for Purolite A 860S; stirring speed: 400 rpm.

Table 5. The effect of catalyst loading on the yields of the two isomeric esters; Reaction time: 5 h, molar ratio acetic acid-epichlorohydrin: 1:1, stirring speed: 400 rpm

Catalyst loading, %	Purolite A 500 ^a		Purolite A 860S ^b	
	3-chloro-2-hydroxypropyl acetate, %	1-chloro-3-hydroxypropan-2-yl acetate, %	3-chloro-2-hydroxypropyl acetate, %	1-chloro-3-hydroxypropan-2-yl acetate, %
5.0	45.50	8.12	48.10	7.40
7.5	55.99	10.24	60.08	9.64
10.0	66.48	12.31	70.13	11.93
12.5	67.86	13.08	71.84	12.60

Temperature: ^a366 and ^b348 K

Effect of molar ratio between reactants

The increase of epichlorohydrin/acetic acid mole ratio from 1:1 to 1.5:1 increases the yields of the two isomeric esters for both reactions catalysed by Purolite A 500 and Purolite A 860S respectively (Table 6). At the same time, the ratio between the two isomeric esters decreases with the increase of the epichlorohydrin excess. The decrease is stronger in the case of reactions catalysed by Purolite A 500 due to higher operating temperatures. By using an extra amount of epichlorohydrin (mole ratio epichlorohydrin/acetic acid 2:1) the yield in normal ester decreases owed to the enhancement of the side reactions. High yields in normal ester for the experiments carried out in the excess of acetic acid (acetic acid/epichlorohydrin 1:2) are also obtained, but in this case the reaction rates are lower.

Reusability of catalysts

The catalyst reusability was studied four times, including the use of the fresh catalyst (Figure 3). The catalysts were filtered, washed with distilled water and ethylic alcohol and subsequently heated at 333 K before being reused in subsequent batches.

During the experiments of reusability, the conversion of acetic acid did not vary significantly for the reaction catalysed by Purolite A 500 resin and the selectivity of the reaction remained the same. For Purolite A 860S a decrease in conversion values from 83.1 to 70.2 was observed due to the degradation of catalyst particles during the chemical reactions (it is a well-known fact that the mechanical strength of the acrylic resins is lower compared to the styrene-divinylbenzene resins).

CONCLUSIONS

The reaction rate increases for both catalysts with the increase of temperature, catalyst loading and epichlorohydrin/carboxylic acid molar ratio. The selectivity of the reaction is mainly influenced by the increase of temperature and epichlorohydrin/acetic acid molar ratio. The highest yields in normal ester are obtained for catalyst loadings between 10–12.5 %, temperatures of 348 and 366 K for Purolite A 860S and Purolite A 500, respectively, and epichlorohydrin/acetic acid molar ratios between 1.1–1.5. The lowest values for the ratio between isomeric esters are obtained for Purolite A 500 catalyst (at 366 K tempe-

Table 6. The effect of mole ratio on the yields of the two isomeric esters

Catalyst	Temperature K	Catalyst loading, %	Reaction time min	Molar ratio acetic acid-epichlorohydrin	3-chloro-2-hydroxypropyl acetate, %	1-chloro-3-hydroxypropan-2-yl acetate, %
Purolite A 500	366	10	300	1:1	66.48	12.31
			270	1:1.3	71.09	13.55
			180	1:1.5	74.3	15.04
			150	1:2	68.12	14.71
			300	1.5:1	72.42	12.82
Purolite A 860S	348	10	300	1:1	70.13	11.93
			270	1:1.3	74.26	12.85
			180	1:1.5	77.25	14.2
			150	1:2	70.94	13.4
			300	1.5:1	75.12	12.37

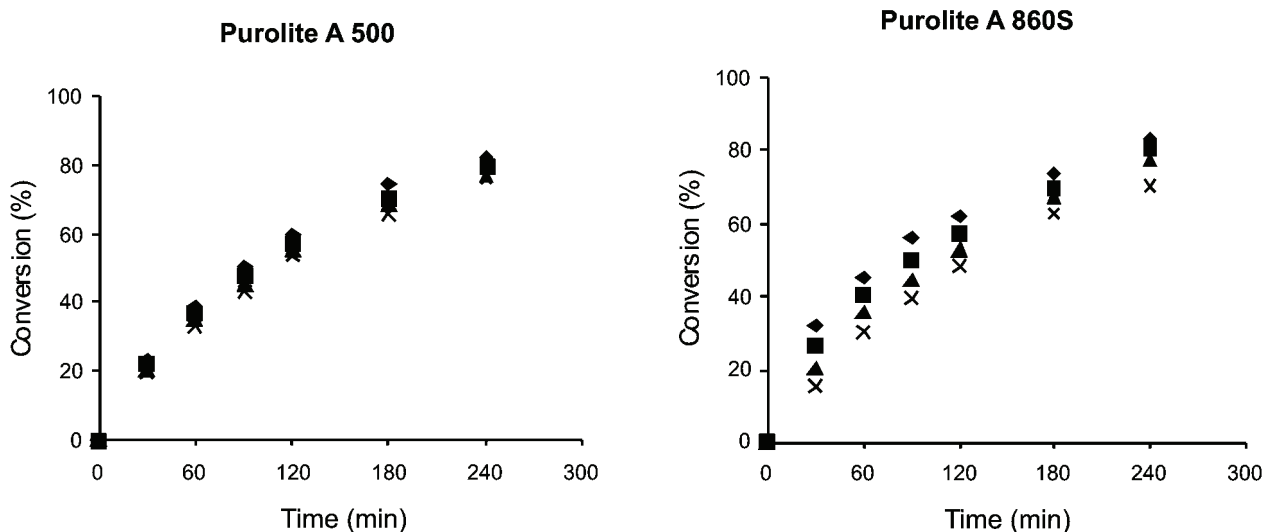


Figure 3. The effect of catalyst reusability on acetic acid conversion; ♦ - fresh catalyst, ■ - first reuse, ▲ - second reuse, x - third reuse.

perature and 2:1 molar ratio epichlorohydrin acetic acid). The higher selectivity obtained by using Purolite A 860S catalyst can be explained by lower operating temperatures (maximum 348 K).

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