

## ESTERIFICATION OF ACETIC ACID WITH STYRENE: ION EXCHANGE RESINS AS CATALYSTS

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*Esterification of acetic acid with styrene was carried out in the presence of cation exchange resins as catalysts in the temperature range 20–60 °C. The reaction was accompanied by dimerization of styrene. The selectivity with respect to the ester (1-phenylethyl acetate) was greatly influenced by the catalyst, solvent and operating conditions. Some experiments were carried out in the presence of homogeneous catalysts such as 98% H<sub>2</sub>SO<sub>4</sub> and p-toluene sulfonic acid (PTSA) to find their utility for obtaining the ester. Optimum conditions for realising high selectivity with respect to the ester have been delineated. Monodisperse K2661 was found to be the best catalyst amongst those studied, in so far as the selectivity with respect to the ester was concerned.*

Keywords: cation exchange resin; esterification; styrene; 1-phenylethyl acetate; monodisperse K2661

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### INTRODUCTION

The anhydrous esterification of carboxylic acids with olefins in the presence of acid catalysts has been the subject of investigation by many research workers. Both homogeneous and heterogeneous catalysts have been used for this purpose. If the esterification reaction is accompanied by a side reaction then there is a distinct advantage of using the heterogeneous catalysts over their homogeneous counterparts because heterogeneous

catalysts, such as ion exchange resins, may suppress undesirable side reactions to a great extent. The other advantages of heterogeneous catalysts are that they can be easily separated from the reactant–product mixture and they eliminate the corrosive environment that is often encountered with homogeneous catalysts. Apart from these advantages, the distribution characteristics of the reactant and product between the bulk liquid phase and the ion exchange resin matrix sometimes plays an important role in achieving high selectivity with respect to the desired product.

1-Phenylethyl acetate is widely used in the perfume industry and constitutes part of sev-

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eral very successful and well-known perfumes [1].

This work was undertaken to find the suitability of macroporous ion exchange resins Amberlyst 15 and Monodisperse K2661 in the anhydrous esterification of acetic acid with styrene and to map the best operating conditions for producing predominantly 1-phenylethyl acetate.

## PREVIOUS STUDIES

Limited information is available in the literature on the use of cation exchangers as catalysts for the preparation of 1-phenylethyl acetate.

Malewski and Lewandowski [2] claimed that 1-phenylethyl alcohol esters can be prepared by the addition of  $C_{1-9}$  acids to styrene in the presence of Wofatit KPS catalyst.

Cervený *et al.* [3] have studied the possibility of the preparation of 1-phenylethyl acetate by direct addition of acetic acid to styrene catalyzed by Ostion KS in the acid

cycle. They reported that the reaction proceeds with difficulty even in the presence of a strong acid catalyst.

Martinez de la Cuesta *et al.* [4] studied the kinetics of the addition of acetic acid to styrene in the presence of  $HClO_4$ . They studied the effect of temperature and the effect of styrene concentration and catalyst on the reaction.

Nakayama *et al.* [5] claimed that 1-phenylethyl acetate can be prepared in one step by the oxidation of PhEt with  $O_2$  in the presence of  $Ac_2O$ .

In a recent study, Patwardhan and Sharma [6] reported the esterification of carboxylic acids with different olefins such as propylene, isobutylene, *etc.*, with ion exchange resins as catalysts.

## EXPERIMENTAL

The cation exchangers Amberlyst 15 and Amberlyst XN-1010 were obtained from Rohm and Haas Co., Philadelphia; monodis-

TABLE 1  
Physical properties of different cation exchangers

Physical property	Amberlyst		Nafion H (NR-50)	Monodisperse	
	15	XN-1010		K2661	K2631
Shape	beads	beads	beads	beads	beads
Bead size distribution mm (min. 90%)	0.5	<sup>a</sup>	<sup>a</sup>	0.6	0.6
Internal surface area ( $m^2/g$ )	55	540	~ 0.8	40	40
Weight capacity (meq/g)	4.75	3.3	0.91	1.35 <sup>b</sup>	1.3 <sup>b</sup>
Porosity (Vol.%)	36	50	non-porous	50	50
Cross-linking density (%)	20-25	85	<sup>a</sup>	14-25	14-25
Temperature stability ( $^{\circ}C$ )	120	120	200	130	120

<sup>a</sup> Data not available.

<sup>b</sup> In accordance with DIN standards.

perse K2661 and K2631 were obtained from Bayer, Germany. Nafion NR-50 was obtained from Du Pont. All the ion exchange resins were washed with acetone to remove impurities adhering to the surface and then dried at 100 °C under vacuum (1–2 mmHg for 4–5 h). Glacial acetic acid was obtained from M/S. S. d. Fine. Chem. Pvt. Ltd. Styrene was obtained commercially and was washed with aqueous alkali and was distilled before use. The physical properties of the different ion exchangers are listed in Table 1.

All the experiments were carried out in a 0.05 m i.d. fully baffled, mechanically agitated contactor. A six bladed glass disc turbine impeller was used for agitation. For maintaining a constant reaction temperature, the reactor was kept in a constant temperature bath. The temperature was maintained at the desired value  $\pm 1^\circ\text{C}$ . Complete addition of styrene to the acid-catalyst slurry was considered as the starting time of the reaction.

Analysis of the samples was done in a gas chromatograph (PE8500) with a flame ionization detector. A 3.5 m stainless steel column packed with 10% OV-17 supported on chromosorb WHP was used. The injector and detector were kept at 300 °C. The oven temperature was programmed from 100 to 300 °C with a ramp rate of 0.25 °C/s. Nitrogen was used as the carrier gas at a flow rate was 0.5 ml/s.

The reaction samples were washed with excess water to remove unreacted acetic acid and the organic layer was dried over  $\text{Na}_2\text{SO}_4$ . The moisture free organic layer was then injected into the GC. The material balance was checked by determining the saponification value of the ester. Characterization of the products was done on an FTIR spectrophotometer (Bruker IFS 88).

## RESULTS AND DISCUSSION

**Mechanism of the reaction:** The reaction mechanism involves the formation of the carbonium ion corresponding to the alkene used in the presence of an acidic catalyst. The oxygen atom of the hydroxyl group of the acid molecule then attacks the carbonium ion to give the ester [7]. On the other hand, the carbonium ion may add with another molecule of the alkene to give alkene dimers. The mechanism of the reaction is shown in Fig. 1.

### *Effect of speed of agitation*

The speed of agitation (700 to 2200 rpm) had no effect on the rate of reaction. Also, the value of the apparent rate constant of the overall process at the highest temperature (60 °C) employed for the reaction was well below the calculated value of the solid-liquid mass transfer coefficient, based on the correlation developed by Levins and Glas-tonbury [8]. This further endorses the fact

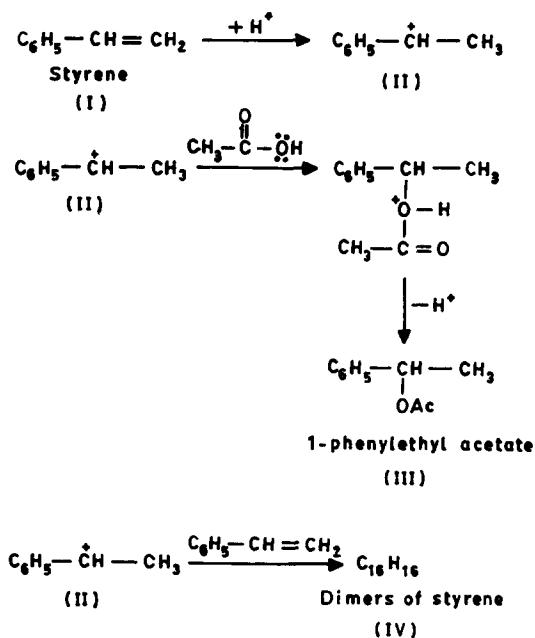


Fig. 1. Mechanism of the reaction.

that in the range of stirrer speeds employed, the reaction was free from external mass transfer resistance.

#### Effect of particle size

There was no change in the rate of reaction as the particle size was varied from 0.3 to 0.6 mm, leading to the conclusion that there was no macropore diffusional limitation. This observation was cross-checked with the help of the interruption test suggested by Helfferich [9]. Microgel diffusion limitation may well be present, but it appears that swelling of the gel-type regions occurs in the presence of acetic acid leading to the accessibility of the acid groups and free mobility of all the components of the reaction mixture and it is reported in the case of hydration of isobutylene that the microgel effectiveness factor for Amberlyst-15 is unity [10,11].

#### Effect of catalyst loading

The rate of reaction was found to vary linearly with the catalyst loading in the range 2.5 to 10% (w/w). Increased catalyst loading means more sulphonic acid groups are available, leading to the formation of greater numbers of carbonium ions per unit time, which in turn, increases the rate of reaction.

#### Kinetic model

In the case of catalysis by ion exchange resins, the distribution of the reactants and products between the bulk liquid phase and the resin phase (where the reaction occurs) should be considered in formulating the kinetic equation.

The distribution coefficient of component  $i$  can be written as  $\lambda_i = \bar{m}_i/m_i$  where  $\lambda_i$  is the molal distribution coefficient of component  $i$ ,  $\bar{m}_i$  and  $m_i$  are the concentration of component  $i$  in the resin phase and in the bulk liquid phase, respectively.

Distribution coefficients were measured by

TABLE 2

Distribution coefficient for the ion exchange resin catalyzed esterification of acetic acid with styrene <sup>a</sup>

Component	Distribution coefficient
Styrene	1.45
Acetic acid	0.97
1-Phenylethyl acetate	1.85

<sup>a</sup> Temperature: 40 °C.

the Helfferich method [12]. At a particular time, the resin phase was carefully removed from the bulk liquid phase by filtration and the contents of the resin phase were analyzed by the usual analytical procedures. The values of the distribution coefficients of the different components are listed in Table 2.

#### Model proper

The reaction network is shown in Fig. 2, where S, A, SA and S<sub>2</sub> represent styrene, acetic acid, 1-phenylethyl acetate and styrene dimers, respectively;  $k_1$  and  $k_2$  are the forward and backward rate constants, respectively, for the esterification reaction and  $k_3$  is the rate constant for the dimerization of styrene.

Esterification was found to be first order with respect to both styrene and acetic acid. Dimerization was found to be first order with respect to styrene (this has also been observed by Higashimura and Nishii [13]).

So the overall rate of reaction can be written as

$$-\frac{dC_S}{dt} = k_1 C_S \lambda_S C_A \lambda_A - k_2 C_{SA} \lambda_{SA} + k_3 C_S \lambda_S$$

$$= K_1 C_S C_A - K_2 C_{SA} + K_3 C_S \quad (1)$$

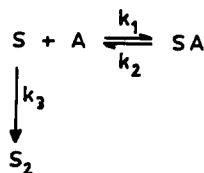


Fig. 2. Network of the reaction.

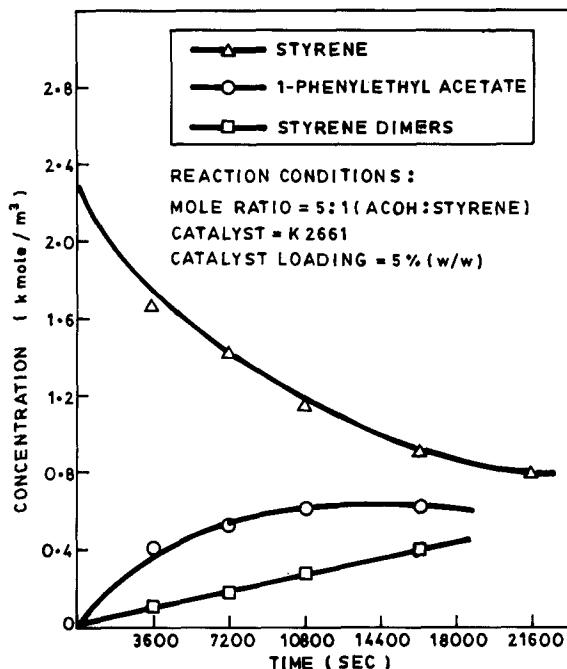


Fig. 3. Concentration profiles of different components at 40°C.

where  $K_1 = k_1 \lambda_S \lambda_A$ ,  $K_2 = k_2 \lambda_{SA}$  and  $K_3 = k_3 \lambda_S$ .  $C_S$ ,  $C_A$  and  $C_{SA}$  are the bulk liquid phase concentrations of styrene, acetic acid and 1-phenylethyl acetate, respectively.  $\lambda_S$ ,  $\lambda_A$  and  $\lambda_{SA}$  are the distribution coefficients of styrene, acetic acid and 1-phenylethyl acetate, respectively.

The net rate of formation of ester can be written as

$$\begin{aligned} \frac{dC_{SA}}{dt} &= k_1 C_S \lambda_S C_A \lambda_A - k_2 C_{SA} \lambda_{SA} \\ &= K_1 C_S C_A - K_2 C_{SA} \end{aligned} \quad (2)$$

The rate of formation of dimers can be written as

$$\frac{dC_S}{dt} = \frac{1}{2} k_3 C_S \lambda_S = \frac{1}{2} K_3 C_S \quad (3)$$

The values of the apparent rate constant  $K_1$ ,  $K_2$  and  $K_3$  can be determined with the help of an iterative procedure by matching calculated and experimental concentrations at different reaction times.

The differential equations represented by eqns. (1), (2) and (3) were solved by a fourth order Runge-Kutta method for the conditions used in the experiments. The differences between the experimentally determined and calculated concentration values of the various components at different reaction times were minimized with the help of least-square method by adjusting the values of the apparent rate constants at a particular temperature.

The experimental concentration profiles of different components are shown in Fig. 3.

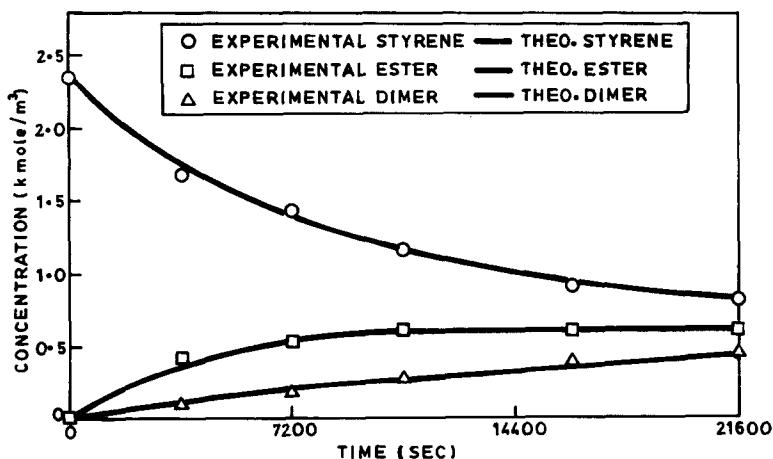


Fig. 4. Comparison between theoretical and experimental concentration profiles of different components at 40°C.

TABLE 3

Values of the apparent rate constants <sup>a</sup>

Rate constant	Value
$K_1$ ( $\text{m}^3\text{kmol}^{-1}\text{s}^{-1}$ )	$1.274 \times 10^{-5}$
$K_2$ ( $\text{s}^{-1}$ )	$9.409 \times 10^{-5}$
$K_3$ ( $\text{s}^{-1}$ )	$3.338 \times 10^{-5}$

<sup>a</sup> Temperature: 40 °C; catalyst: monodisperse K2661; catalyst loading: 5% (w/w).

The comparison between theoretical and experimental concentration profiles of different components is shown in Fig. 4. The values of the apparent rate constants at 40 °C are given in Table 3.

#### Effect of temperature

The effect of temperature on the overall rate of reaction is shown in Fig. 5. The variation in the reaction temperature from

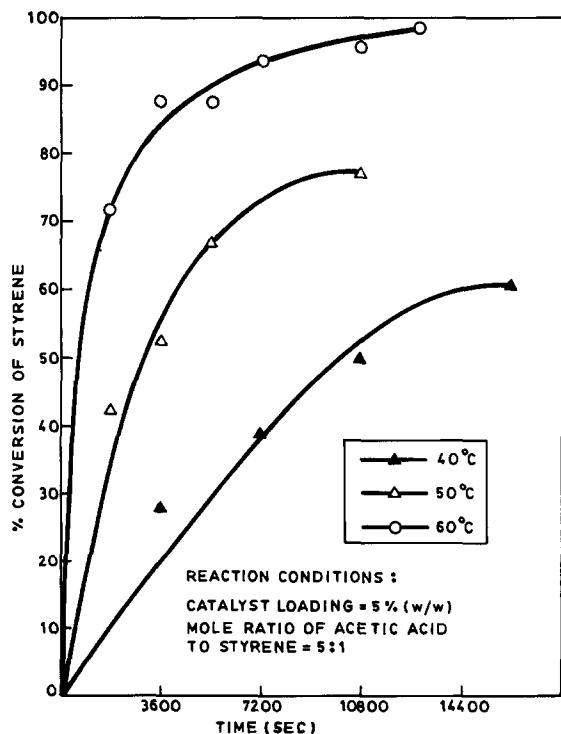


Fig. 5. Effect of temperature on the overall rate of reaction in the presence of monodisperse K2661 as the catalyst.

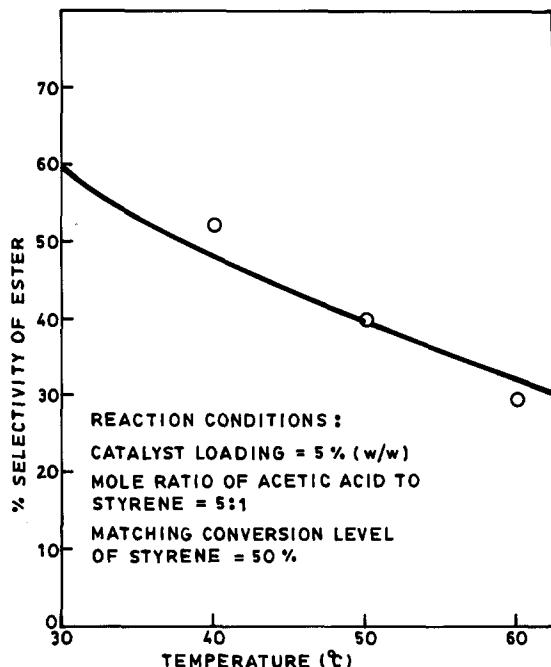


Fig. 6. Effect of temperature on the selectivity of the ester in the presence of monodisperse K2661 as the catalyst.

40 to 60 °C increased the rate of reaction but decreased the selectivity of the ester. From this observation it is clear that the dimerization of styrene has a higher activation energy relative to the esterification reaction. Decreasing the temperature from 40 to 20 °C decreased the reaction rate without much improvement in the selectivity of the ester. The effect of temperature on the selectivity of the ester is shown in Fig. 6.

#### Effect of catalyst

The results obtained with different catalysts are shown in Fig. 7. The highest reaction rate amongst the cation exchange resins tried was obtained with K2631. The reasons for this behaviour are not clear. Amberlyst XN-1010 was the least reactive which may be due to its low weight capacity and high crosslinking density (85%). Due to the high crosslinking density, most of the sulfonic acid

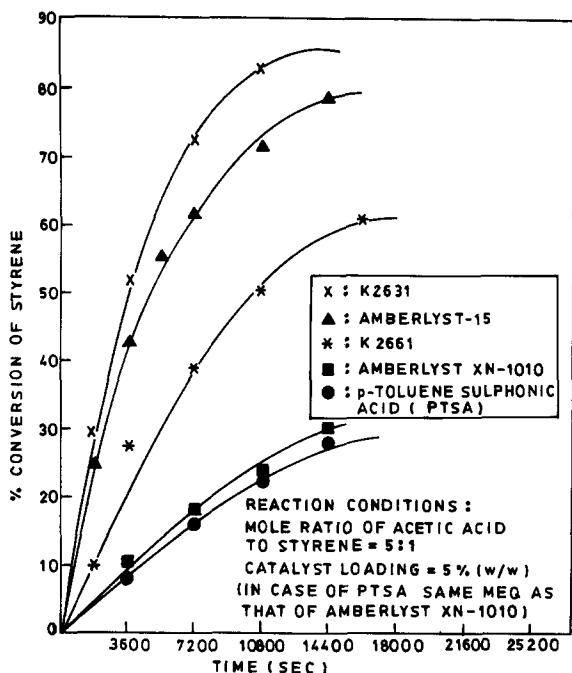


Fig. 7. Effect of different catalysts on the overall rate of reaction at 40 °C.

groups are on the surface. It is known that surface sulfonic acid groups can be less reactive than those in the gel phase [6,14,15]. This results in a lower reactivity of Amberlyst XN-1010. Monodisperse K2661 was the best catalyst so far as selectivity of the ester was concerned. Homogeneous catalysts such as 98%  $H_2SO_4$  and PTSA showed almost the same reactivity as Amberlyst XN-1010 with the same amount of acid groups. The effect of different catalysts on the selectivity of the ester is given in Table 4.

#### Effect of mole ratio

The mole ratio of acetic acid to styrene was varied from 1:1 to 7:1 to assess the effect of mole ratio on the selectivity of the ester. As the mole ratio was increased from 1:1 to 3:1, the selectivity of the ester jumped from 37 to 60% for the same conversion level (35%) of styrene. Further increments in the

TABLE 4

Effect of different catalysts on the selectivity of the ester <sup>a</sup>

Catalyst	Selectivity (%)
Amberlyst 15	56
Amberlyst XN-1010	52
Monodisperse K2661	65
Nafion H (NR 50)	30
98% $H_2SO_4$	43
PTSA	43
K2631	55

<sup>a</sup> Reaction conditions: temperature 40 °C; mole ratio of acetic acid to styrene, 5:1; catalyst loading 5% (w/w) in the case of cation exchangers and the same meq as that of Amberlyst 15 in the cases of 98%  $H_2SO_4$  and PTSA. Matching conversion level of styrene, 30%.

mole ratio had a marginal effect on the selectivity of the ester.

Here, selectivity of the ester is defined as the ratio of the net rate of the formation of the ester to the overall rate of the consumption of styrene. So,

$$s = - \frac{dC_{SA}}{dC_s} = \frac{K_1 C_S C_A - K_2 C_{SA}}{K_1 C_S C_A - K_2 C_{SA} + K_3 C_S}$$

[from eqns. (1) and (2)].

$$= \frac{1}{1 + (K_3 C_S) / (K_1 C_S C_A - K_2 C_{SA})}$$

$$= \{1 + [K_3(1 - X_T)] / (K_1 C_{S0}(1 - X_T)(M - X_A) - K_2 X_A)\}^{-1}$$

where  $X_T$  is the total conversion of styrene and  $X_A$  is the conversion of styrene to 1-phenylethyl acetate.  $M = C_{A0}/C_{S0}$  = mole ratio of acetic acid to styrene.

It is clear from the above expression that as  $M$  increases, selectivity increases.

#### Effect of the mode of addition

Some experiments were carried out in a semi-batch mode (styrene was added over a period of time to the acid-catalyst slurry

from a dropping funnel) to study the effect of the mode of addition on the selectivity of the ester. No further improvement in selectivity was obtained with this mode of addition when the mole ratio of acetic acid to styrene was kept at 5:1.

#### *Effect of solvent*

It is known that solvents can greatly influence the reaction rate and selectivity. It was thought that some non-polar aromatic solvents could favour the distribution of acetic acid in the resin phase to a great extent and thereby increase the selectivity. Ethylbenzene was used as the solvent as it would be available in the styrene manufacturing plant. In the presence of monodisperse K2661 as catalyst, the selectivity of the ester with and without solvent was 80 and 65%, respectively for the same conversion level (30%) of styrene at 40 °C. In the literature the selectivity of the ester at 40 °C is reported to be 55% (Cervený *et al.* [3]). But in the presence of solvent, a 23% decrease in reactivity was observed under otherwise identical conditions.

#### *Effect of inhibitor*

It was thought that a small amount of inhibitor may suppress the dimerization of styrene leading to an increase in the selectivity of the ester. *p*-*tert*-Butyl catechol and hydroquinone were used as inhibitors. There was no effect on the rate of the reaction and selectivity of the desired product. This was also observed by Cervený *et al.* [3].

#### *Effect of moisture in the catalyst and effect of water in the reaction mixture*

The presence of moisture in the catalyst and the presence of water in the reaction mixture had a detrimental effect on the reaction. In both cases the rate of the reaction

decreased drastically without affecting the selectivity of the ester. The cause of the decrease in the reaction rate was described by Zundel [16] with the help of infrared spectroscopic studies. According to Zundel, at a low concentration of water in the resin phase, three sulfonic acid groups are attached to one water molecule. Thus, available active sites decrease, resulting in a sharp decrease in the reaction rate.

#### *Effect of alcohol*

*tert*-Butanol has been used as oligomerization inhibitor [in the etherification reaction between propylene glycol and isobutylene over strongly cation exchange resin catalysts] to suppress the formation of the by-product diisobutylene (Matsumoto *et al.* [17]). Chaudhuri and Sharma [18] have confirmed this in the case of  $\alpha$ -methylstyrene (AMS) dimerization. So it was thought that a small amount *tert*-butanol may affect the selectivity of the ester. In the present case, it reduced the rate of reaction to 25% of that in the absence of alcohol with an 11% improvement in the selectivity of the ester at the same conversion level (40%) of styrene. The loading of the alcohol was 5% (w/w) of the total reactants.

#### *Effect of repeated use of the catalyst*

The ion exchange resins were used repeatedly and after an interval of time, the conversion level of the reactant was checked. There was no change in conversion level and selectivity after five batches.

## CONCLUSIONS

The anhydrous esterification of acetic acid with styrene can be carried out satisfactorily in the presence of cation exchange resins as the catalyst.

Monodisperse K2661 was superior to other cation exchangers as it suppressed the dimerization of styrene. For realising high selectivity with respect to the ester and with a reasonable rate, the reaction should be carried out at 40 °C in the presence of ethylbenzene as solvent. The mole ratio of acetic acid to styrene should be between 3 and 5. The ion exchange resins can be used repeatedly without affecting the rate of the reaction and selectivity of the ester.

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