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Synthesis of a new sulphonated cation exchange resin and its application in catalysed hydrolysis of esters

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Samples of an acidic cation exchanger have been prepared by sulphonation of acrylonitrile butadiene styrene copolymer previously cross-linked with phenol-formaldehyde resin. The samples having a cation exchange capacity of 3.48 meq g^{-1}, are being introduced as new catalysts in the hydrolysis of ethyl acetate. The synthesized cation exchanger shows good thermal and chemical stability. Hydrolysis rate constants (K_r values) for the catalysed reaction have been determined. The efficiency of the resin catalyst, q, is shown to be a function of resin concentration.

1. Introduction

Acidic cation exchangers in H$^+$ form will catalyse many reactions which are normally catalysed by solubilized acids in homogeneous systems. Literature on the hydrolysis itself is quite extensive [1–10], and several investigators indicated that resins act more efficiently as catalysts than the corresponding acid catalytic reactions. It was observed [4] that considerable specification of the cation exchanger may be obtained by introducing acidic or basic groups to the exchange matrix. Thus it may be possible to prepare a resin that would catalyse certain reactions. The present work is mainly concerned with the hydrolysis of esters in the presence of a new strong acidic cation exchanger, synthesized by sulphonation of acrylonitrile butadiene styrene copolymer which has been previously cross-linked with resol. This cation exchanger has been introduced in the H$^+$ form as a catalyst in the hydrolysis of ethyl acetate.

2. Experimental procedure

Acrylonitrile–butadiene–styrene copolymer (ABS) (Ugikral-SN, France) was used as a substrate for the synthesis. All chemicals used were of Analar grade.

Standard solutions for the analytical work were prepared by either direct weighings of Analar grade reagents or by indirect standardizations. Demineralized water (DMW) was prepared by passing distilled water through a cation exchanger packed in a column.

2.1. Apparatus

A thermostatically controlled electric oven was used for drying the samples. Infrared measurements were made by using a Pye Unicam SP-1100 spectrophotometer. The standard suspension polymerization apparatus used in catalyst preparation consisted of a 1 litre three-necked cylindrical flask fitted with a variable mechanical stirrer, a thermometer, and a reflux condenser.

2.2. Preparation of the catalyst

A suspension of the (ABS) copolymer (95 g) in benzene was introduced in the standard suspension polymerization apparatus and a solution of the cross-linking agent phenol-formaldehyde resin (resol), 5 g, was then added with continuous stirring at 70° C until a completely homogeneous solution was obtained. The blended copolymer was obtained after evaporation of the solvent at room temperature and cut into small fragments. The swollen blended copolymer (36 g) in sulphuric acid (70 ml) and 0.5 g silver sulphate as a catalyst, were then refluxed for 30 min. The resulting product was hydrolysed in water by boiling for 60 min. The resin obtained was then thoroughly washed with water until neutral, and finally vacuum dried to constant weight.

2.3. Cation-exchange capacity

The resin was first conditioned [11], then converted to the H$^+$ form by treating it with excess 0.1 M hydrochloric acid, and its capacity determined as described in the literature [12]. The selected mesh size of the ion exchange resin was 250 to 420 μm. The resin was dried at room temperature and stored in a desiccator. The exchange capacity of the obtained resin as determined [12, 13] was 3.48 meq g^{-1}.

2.4. Chemical composition

The infrared spectrum of the synthesized sulphonated acrylonitrile–butadiene–styrene copolymer cross-linked with 5% resol is shown in Fig. 1. The band at 700 cm^{-1} is assigned to the C=S group while the weak

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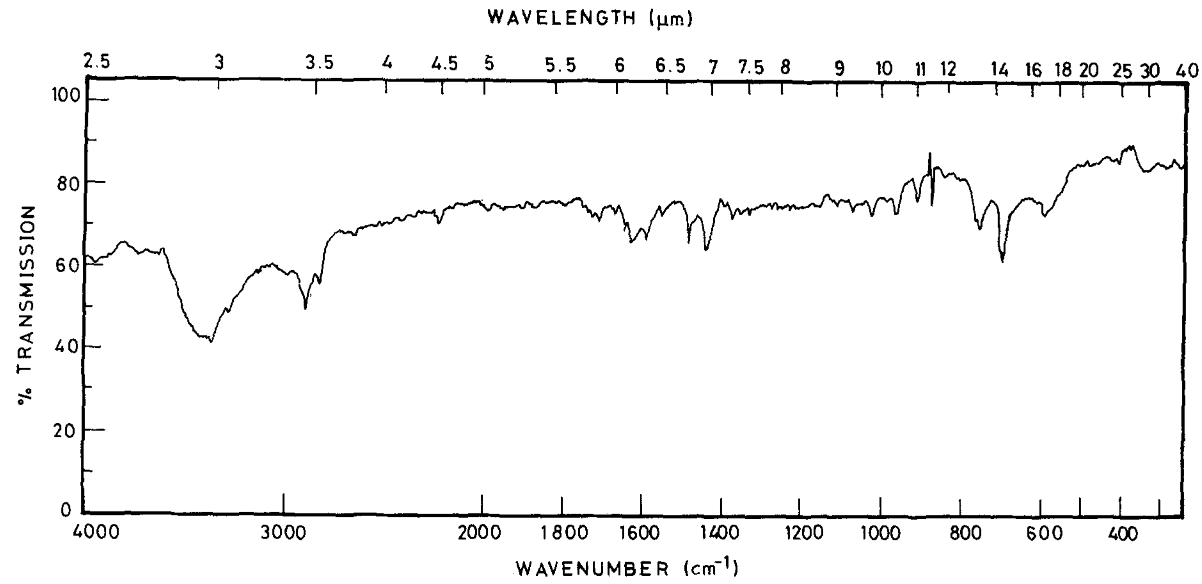

Figure 1 Infrared spectrum of sulphonated resin catalyst (5% resin).

band at 1650 cm^{-1} is probably due to the presence of CH_3 groups. The broad band characteristic of OH groups is indicated at 3500 cm^{-1}. The two bands due to the SO_3^{2-} group appeared at 1440 and 1490 cm^{-1}.

Elemental analysis of the exchanger was found to be C = 54.4%, H = 5.5%, S = 6.4% and N = 2.8%.

2.5. Chemical stability

A sample of 1.0 g exchanger was used for all the following experiments.

(I) Treatment with soda (0.1 N) and mineral acids (1 N). The resin was soaked in each of the above solutions for 24 h; the loss in its capacity ranged from 2.27% to 6.89% in the case of mineral acids and was found to be 16.9% on soda treatment.

(II) Treatment with different organic solvents. The resin was kept separately in acetone, ethanol and isopropanol for 24 h at 25° C. The loss in capacity was between 0 and 1.15%.

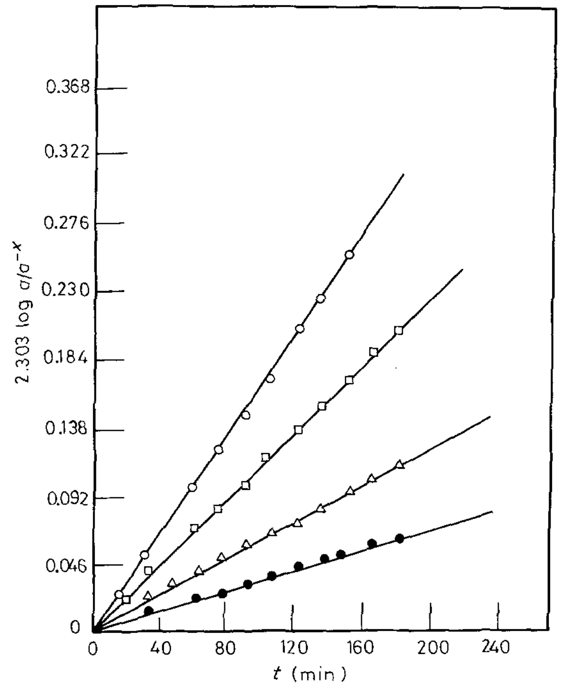

Figure 2 The effect of temperature on the rate constant. (○) 65° C, (◇) 55° C, (△) 45° C, (●) 35° C.

(III) Treatment with boiled water. The decrease in resin capacity after soaking in boiling water for about 10 h was 3% to 5%.

(IV) Effect of heat. Heating the resin for 48 h at 170° C caused a 1% to 2% loss in its exchange capacity.

2.6. Kinetic studies

Reaction rates of hydrolysis were determined for the resin (H^+ form)–water mixtures to which the calculated amount of ethyl acetate was added. Various ester concentrations ranging from 0.1 M to 0.4 M were also used and rates determined at 35, 45, 45, 55 and 60° C (±0.1° C), using the continuous operation method [14]. The effect of catalyst concentration was also studied, 150 ml ester solution being used for each determination. The liberated acid was titrimetrically determined with a standard solution of sodium hydroxide.

3. Results and discussion

The hydrolysis of ethyl acetate in the presence of the cation exchange catalyst was found to be a first-order reaction. Linear plots of 2.303 log $a/a - x$ against time for the resin catalyst are shown in Fig. 2. Values for first-order rate constants, K_r, as determined from these slopes are given in Tables I to III. These values are in good agreement with those reported in the literature [8, 15]. First-order reaction rates with respect to ester concentration were also reported by Bernhard *et al.* [5] for the hydrolysis of aliphatic esters catalysed by ion-exchange resin, and similar HCl-catalysed homogeneous reactions [16].

The effect of ester concentration on the rate of hydrolysis at constant temperature (45° C) in the presence of the resin catalyst (3 g) is shown in Table I. A higher value of the rate constant is observed for the

TABLE I Effect of varying concentration of ethyl acetate on catalytic hydrolysis using resin catalyst (3 g) at 45° C

Ethyl acetate	0.1 M	0.2 M	0.3 M
K_r (10^6 sec^{-1})	13.71	10.97	9.60

TABLE II Effect of varying catalyst concentration on the hydrolysis of ethyl acetate (0.2 M) at 45° C

	Weight of resin (g)		
	3	6	9
K_r (10^6 sec^{-1})	10.97	24.00	41.30
Efficiency, q	0.34	0.40	0.45

lower ethyl acetate concentration (0.1 M). This can be explained on the basis that active sites on the synthetic resin catalyst are insufficient to hydrolyse the increasing amount of ester within a definite reaction time, and hence the rate is decreased.

The effect of varying catalyst concentration on the rate of hydrolysis of ester is shown in Fig. 3. The reaction rate constant is found to be directly proportional to the concentration of the resin catalyst (Table II).

The efficiency of the resin catalyst, q, defined as

$$q = \frac{\text{rate coefficient for hydrolysis with acid resin catalyst}}{\text{rate coefficient for hydrolysis in acidic solution}}$$

was shown to be a function of resin concentration, and increases with increasing amount of the resin catalyst. The effect of heating temperature on the rate constant is shown in Table III, higher K_r values being observed at higher temperatures.

TABLE III Effect of varying temperatures on the hydrolysis of ethyl acetate (0.2 M) with resin catalyst (3 g)

	Temp. (° C)			
	35	45	55	60
K_r (10^6 sec^{-1})	5.76	10.97	18.81	28.34

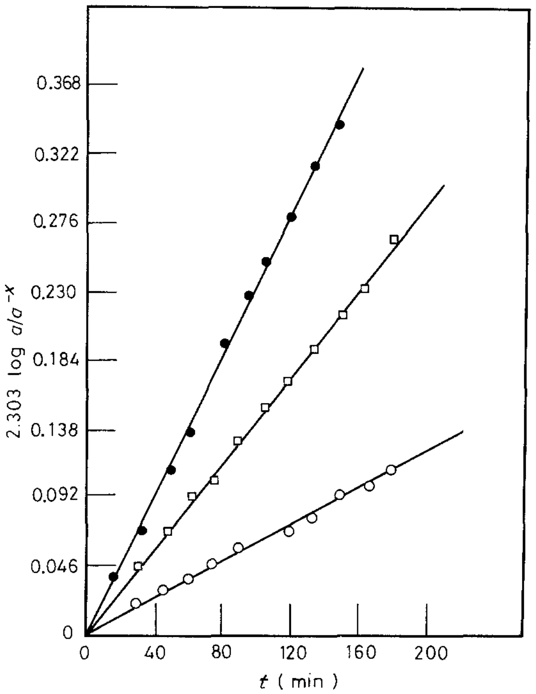

Figure 3 The effect of catalyst concentration on the rate constant. (●) 9 g, (◇) 6 g, (○) 3 g.

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