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Volumetric, Chromatographic, Refractometric Studies on the Esterification of Methanol with Acetic Acid in the Presence of Cation-Exchange Resins

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Esterification of methyl alcohol with acetic acid catalysed by commercially available polymeric ion-exchange resins Amberlyst-15, Dowex 50 W and Amberlite IR-120 was carried out in the temperature ranging between 323–338 K. Mesh sizes and divinylbenzene contents had virtually no effect on the rate the data of which were correlated with a second-order homogeneous reaction. The samples were analysed with gas chromatography, refractometry and volumetry. The reproducibilities were the order of ±2.89%, ±5.07% and the order of ±6.58% respectively for the volumetric, chromatographic and refractometric methods.

Conversions for the esterification reactions have long been known to be limited by a slow reaction rate and the existence of reversible reactions. To accelerate the reaction rate, the use of solid acid catalysts has received great attention [1]. Homogeneous catalysis can be carried out using an ion-exchange resin containing the catalyst ion as its counter ion. The reaction mechanism and kinetic orders remain those of homogeneous catalysis [2]. The preliminary mathematical modelling of the observed esterification kinetics was based on second order kinetics which principally could be applied to both homogeneous and heterogeneous catalysts [3].

In the present study we chose a known reaction as a model and this reaction between methanol and acetic acid over a catalytically active synthetic resin is

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as follows:

$$\mathrm{CH_3COOH + CH_3OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CH_3COOCH_3 + H_2O} \quad (1)$$

HAc MeOH MeAc Water

The aim of this communication is to find that which method (volumetry, chromatography and refractometry) is more useful and sensitive for the model reaction. Furthermore, the important variables such as mesh size, divinylbenzene content, temperature, different catalysts affecting the rate of the reaction were studied.

Ion-exchange resins and other chemicals used of analytical grade purity were supplied by Sigma-Aldrich, Merck A.G.

The experimental assembly consisted of a 0.25 $\mathrm{dm^3}$ reactor fitted with a reflux condenser to prevent any loss of products. The reaction vessel was kept in a stirred constant temperature bath where the temperature could be controlled within an accuracy of ±0.1 K by a controller. Amberlyst-15(macroporous), Dowex 50 W (microporous) and Amberlite IR-120 (microporous) were used to assess their efficacy in this reaction. In a typical experiment 10% (by mass) catalyst concentration of all resins was used at a molar ratio of acetic acid to methanol of 1 : 1 at 333 K (700 rpm). The liquid samples were analysed by using a gas chromatography (UNICAM model 610 series) equipped with flame ionisation detector (FID) and the Supel-Q-Plot, porous divinylbenzene polymer; 30.0 m × 320.0 μm ID × 0.5 μm F column. Nitrogen was used as the carrier gas. In the second method, liquid samples were titrated with the standard NaOH solution together with the phenolphthalein indicator. In the last method, the refractive indexes of the liquid samples were measured by Abbe digital refractometer (ATAGO DR-A1 Model).

The external and the internal diffusion don't generally control the overall rate in the ion-exchange resin catalysed process unless the viscosity of the reactant mixture is very high or the speed of agitation is very low [4, 6] and the ion-exchange resins having small particles (500–570 μm) aren't been chosen as catalysts. The effect of divinylbenzene content on the rate of reaction was studied by conducting the reactions with Dowex 50 W having 2%, 4% and 8% DVB under otherwise the similar conditions. As the %DVB contents increase, the acetic acid conversion was found to decrease slightly. Table 1 shows the values of k_1 for different cases.

The activity order of the catalysts was determined as follows: Amberlyst-15 > Dowex 50 W > Amberlite IR-120. In a macroporous resin the pores are so large that the reactants are able to diffuse into the pores and the products to diffuse out without any resistance. Therefore the concentrations of the reactants in the bulk and inside the pores are almost the same and thus led to a homogeneous reaction in the liquid phase [5, 7]. When the catalyst used was a macroporous ion-exchange resin, a homogeneous reaction could be assumed. Amberlite IR-120 has a tighter pore structure as compared to the others and

Table 1. According to Eq. (3), the calculated rate constants of the model reaction carried out with different types of catalysts, different mesh sizes of catalysts and different DVB contents of catalysts by the volumetric method and the suitability of the kinetic equation to the experimental data.

Catalyst type	k_1 ($\times 10^3$ dm^3 mol^{-1} min^{-1} $\pm$%2.89)	R^2
Amberlyst-15	4.60	0.9996
Dowex 50 W × 4	3.56	0.9984
Amberlite IR-120	2.11	0.9956
Dowex 50 W × 2	3.64	0.9944
Dowex 50 W × 4	3.56	0.9984
Dowex 50 W × 8	3.49	0.9956
Dowex 50 W × 4 (50–100 mesh)	3.56	0.9984
Dowex 50 W × 4 (100–200 mesh)	3.62	0.9960
Dowex 50 W × 4 (200–400 mesh)	3.50	0.9959

Table 2. According to Eq. (3), the calculated rate constants of the model reaction carried out with different methods, standard deviations and the relative errors for these methods.

Experimental method	k_1 ($\times 10^3$ dm^3 mol^{-1} min^{-1} ± std. error)	% error
volumetric	5.19 ± 0.15	2.89
chromatographic	3.75 ± 0.19	5.07
refractometric	3.19 ± 0.21	6.58

there is likely to be substantial intraparticle diffusional resistance [8, 9]. The rate of model reaction (1) can be written by using the homogeneous model in terms of the fractional conversion of the acetic acid.

$$\frac{\mathrm{d}X_{\mathrm{HAc}}}{\mathrm{d}t} = k_1(1 - X_{\mathrm{HAc}})^2 - k_2(X_{\mathrm{HAc}})^2 \tag{2}$$

$$\ln \frac{X_{\mathrm{HAc},e} - (2X_{\mathrm{HAc},e} - 1)X_{\mathrm{HAc}}}{X_{\mathrm{HAc},e} - X_{\mathrm{HAc}}} = 2k_1 \left(\frac{1}{X_{\mathrm{HAc},e}} - 1 \right) C_{\mathrm{HAc},0}\, t \tag{3}$$

$$\ln k_1 = \ln A - \frac{E_A}{R} \left(\frac{1}{T} \right) . \tag{4}$$

According to Eq. (4), the activation energy was found to be 48.16 kJ mol^{-1}. Rate constants of the model reaction followed by different methods are given in Table 2. The sensitivity order of these experimental methods was determined as follows: volumetric > chromatographic > refractometric.

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