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Esterification of n-Butanol with Acetic Acid Catalyzed by a Cation Exchange Resin

Effect of the Catalytic Activity on Reaction Kinetics

Z. Gomzi and S. Zrnčević

Faculty of Technology, University of Zagreb, Zagreb, Croatia, Yugoslavia

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The kinetics of the esterification of n-butanol with acetic acid have been studied in a batch and in a tubular reactor. The best model for obtaining the esterification rate with a partially wet ion exchanger (27% water contents) is obtained by assuming a pseudo-homogeneous system, while the kinetics of dry ion exchangers is best represented by a model derived from assumptions based on a heterogeneous system.

A separate study of the induction period in a tubular reactor shows the considerable influence of the water content on reaction kinetics. This is manifested by a change of the catalytic activity during the reaction. Change of the catalytic activity can lead to erroneous interpretation of experimental results and to derivations of inadequate kinetic expression. It is shown that change of ion exchanger activity in the induction period is caused by diffusion of reactants into resin particle.

INTRODUCTION

The kinetics of esterification with ion exchangers in a liquid phase have been investigated for numerous reactions. There is, at present, no unified opinion about the kinetics of these reactions. The majority of the authors prefers Helfferich's classical explanation which states that the liquid phase catalysis with ion exchangers is pseudohomogeneous[1-3]. Kinetic expressions derived from this assumption correspond to formulas used for homogeneous catalytic systems. Only several authors have tried to explain the kinetics as heterogeneous catalytic reactions[4,5].

Experimental results obtained by a number of investigators show that the initial reaction time in batch reactors can be explained by the pseudohomogeneous model[6,7]. Dissagreement between the pseudohomogeneous model and the data has been explained in several ways. The reaction kinetics in the induction period is explained by introducing the assumption that the ion exchangers have a special structure and by the transport phenomena which accompanies sorption of the reactants[8,9]. It should be noted that liquid phase dehydrations with ion exchangers are usually considered as heterogeneous catalytic reactions[9,10].

Gates at al.[8] assumed a shrinking core model for the induction period of dehydration of the t-butyl alcohol. According to their assumptions, the reaction rate is essentially determined by the water content in the resin and the reacting mixture. They used macroreticular and standard ion exchangers.

The induction period was determined only with the standard resin. Absence of the induction period in experiments with a macroreticular ion exchanger were ascribed to a large internal surface and to the absence of diffusion effects within the resin particle.

In a subsequent work[7] the authors state that reaction in the absence of water was catalyzed by fixed —SO_3H groups in a macroreticular ion exchanger. Water added to the reactant (*t*-butyl alcohol) competed for —SO_3H groups inhibiting the reaction. After more water was added the reaction was catalyzed by hydrated protons in a resin matrix. The global rate is represented by an equation assuming rates at high and low water content.

This work deals with the adequacy of the heterogeneous and pseudo homogeneous model for the esterification of *n*-butanol with acetic acid by means of a standard ion exchanger. Experiments were carried out in a batch reactor with both dry and wet resin. The induction period was investigated separately in a tubular reactor.

EXPERIMENTAL METHODS

Experiments were carried out with a commercial ion exchanger Ionenaustauscher I (cation microporous resin on the base of polystyrene with 8% DVB as crosslinking agent). Prior to an experiment, the ion exchanger was converted in H^+ form[12] and a part of it was dried for 24 hours at 115 °C, the rest was dried in air to 27% water.

A three necked flask was used as a batch reactor. It was equiped with a mechanical stirrer and a thermometer. A constant temperature of 55 °C was maintained by an ultrathermostat.

A tubular reactor assembly shown in Figure 1. was used to study the induction period at 55 °C. Apart from measuring the acid concentration, the level of the resin bed in the reactor was measured. Reaction mixtures in both cases were analyzed by titrating acetic acid with NaOH in the samples.

RESULTS AND DISCUSSION

Two sequences of experiments were carried out in the batch reactor, one with the partially dry resin (27% water) and the other with the completely dry ion exchanger. In both cases the amount of resin and the initial reactant ratios were varied from 2 to 8 g and 0.1 to 10, respectively. Study of the induction period in the tubular reactor was carried out with the initially dry ion exchanger, quantities varied between 2 to 8 g and flow rates between 1 to 3 ml/min.

Kinetic analysis

Pseudohomogeneous system assumption. Kinetic expressions of irreversible first and second order reaction, as well as second order reversible reaction have been tested. Such models are used for the kinetics of esterification in homogeneous systems.

Heterogeneous system assumption. Models based on Hougen- Watson-kinetics have been selected. Active sites in the ion exchangers are H^+ ions in —SO_3H groups. Reaction occurs in the adsorbet layer between H^+ ions and reactants. Ester is produced through several intermediate steps. It was assumed that the basic reaction mechanism is identical to the one in the homogeneous systems[11]. Hence, the following monomolecular mechanism ($A_A C_1$) is proposed:

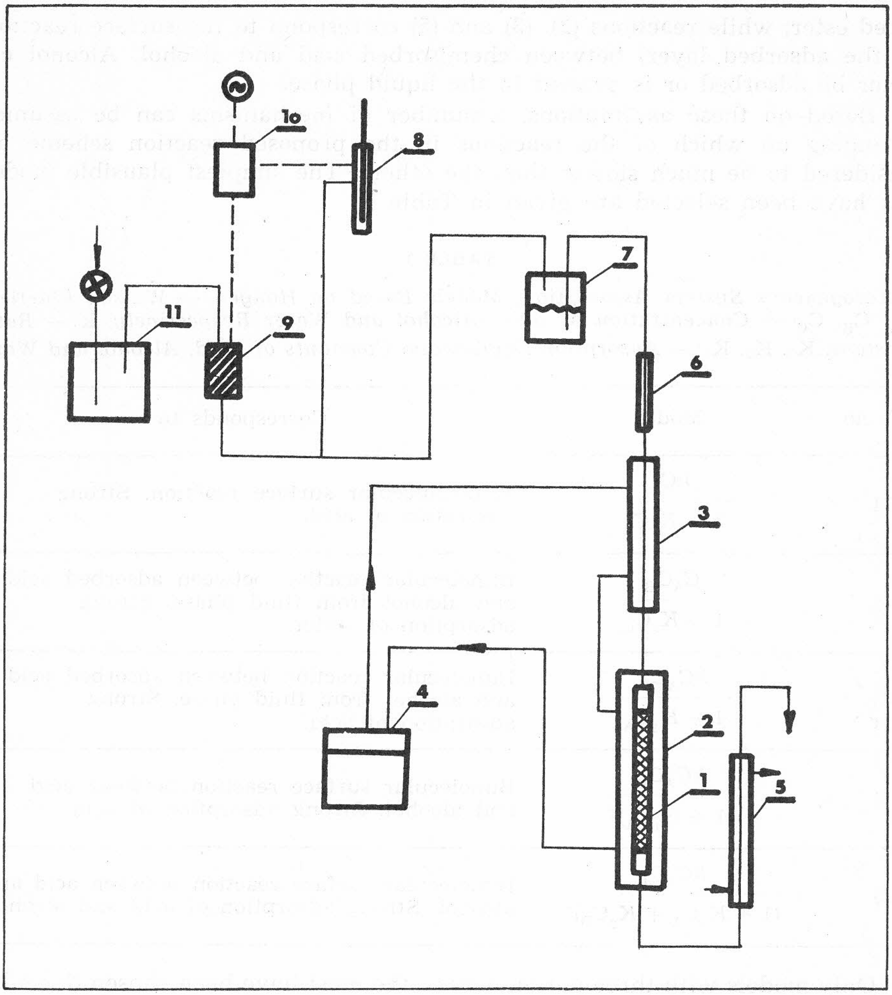

Figure 1. Tubular reactor assembly. 1 — tubular reactor, 2 — thermostated chamber, 3 — preheater section, 4 — ultrathermostat, 5 — water cooled condenser, 6 — capillary, 7 — reactant storage, 8 — contact manometer, 9 — electromagnetic valve, 10 — relais, 11 — pressured air.

$$RCOOH + H^+ \rightleftharpoons RCOO^+H_2 \tag{1}$$

$$RCOO^+H_2 \rightleftharpoons RCO^+ + H_2O \tag{2}$$

$$RCO^+ + R_1OH \rightleftharpoons RCOO^+HR_1 \tag{3}$$

$$RCOO^+HR_1 \rightleftharpoons RCOOR_1 + H^+ \tag{4}$$

In a bimolecular mechanism ($A_A C_2$) which is more probable, reactions (2) and (3) occur simultaneously, i. e.

$$RCOO^+H_2 + R_1OH \rightleftharpoons RCOO^+HR_1 + H_2O \tag{5}$$

From the point of view of the heterogeneous catalysis, the reactions (1) and (4) correspond to chemisorption of the acetic acid and desorption of produced ester, while reactions (2), (3) and (5) correspond to the surface reactions (in the adsorbed layer) between chemisorbed acid and alcohol. Alcohol can either be adsorbed or is present in the liquid phase.

Based on these assumptions, a number of mechanisms can be assumed, depending on which of the reactions in the proposed reaction scheme are considered to be much slower than the others. The simplest plausible models that have been selected are given in Table I.

TABLE I

Heterogeneous System Assumption. Models Based on Hougen — Watson kinetics. C_A, C_B, C_C — *Concentration of Acid, Alcohol and Water Respectively,* k — *Rate Constant,* K_1, K_2, K_3 — *Adsorption Equilibrium Constants of Acid, Alcohol and Water*

Eq. no.	Model	Corresponds to
1	$\frac{kC_A}{1+K_1C_A}$	Monomolecular surface reaction. Strong adsorption of acid.
2	$\frac{C_AC_B}{1+K_3C_C}$	Bimolecular reaction between adsorbed acid and alcohol from fluid phase. Strong adsorption of water.
3	$\frac{kC_AC_B}{1+K_1C_A}$	Bimolecular reaction between adsorbed acid and alcohol from fluid phase. Strong adsorption of acid.
4	$\frac{kC_AC_B}{(1+K_1C_A)^2}$	Bimolecular surface reaction between acid and alcohol. Strong adsorption of acid.
5	$\frac{kC_AC_B}{(1+K_1C_A+K_2C_B)^2}$	Bimolecular surface reaction between acid and alcohol. Strong adsorption of acid and alcohol.

Only models with three parameters at the most have been chosen (k_1 — k_3), even though a number of more complicated models could have been employed. However, the true values of the constants in the multiparameter models are difficult to determine if there is only one variable (in this case concentration). Calculations were made on a UNIVAC 1110 computer at the Computer Centre of the University of Zagreb.

The computer program contained: a) fitting of experimental data X_A-time to a sixth order polynomial, b) reaction rate calculation from the polynomial for given conversion and time, c) parameter estimation algorithm.

Objective functions were defined as a sum of squares of differences between calculated reaction rates from the experimental data and the predicted rates from the mathematical models. Marquardt's algorithm was used as the optimization routine. It is applicable for nonlinear estimation problems and is known to have excellent convergence properties in a broad parameter range.

The selection of the best model was based on the comparison of standard deviations of reaction rates for different models. Altogether we performed 30 experiments, 16 with the dry and 14 with the wet ion exchanger. Table II shows the calculated average standard deviation from all experiments for eight chosen mathematical models (three for the homogeneous and five for the heterogeneous system).

TABLE II

Calculated Standard Average Deviations of Selected Models for Experiments with Wet and Dry Ion Exchangers

Model	σ_{av}/σ_{av}, min	
	dry	wet
irreversible reaction first order	2.69	3.53
irreversible reaction second order	2.67	3.41
reversible reaction second order	2.88	1.00
heterogeneous model		
No. 1	4.50	3.90
No. 2	2.01	3.76
No. 3	1.89	3.38
No. 4	1.00	3.42
No. 5	1.92	3.44

The table shows that the model no. 4 has the minimum average standard deviation for experiments with the dry ion exchanger, while the model based on second order reversible reaction is the best approximation of the data obtained with the wet ion exchanger. Model 4 describes a heterogeneous reaction with the slowest step being the surface reaction between chemisorbed acid and adsorbed alcohol.

The above results demonstrate the significance of water content in the resin prior to an experiment. Different kinetic interpretations of the esterification reactions given by the previous authors can be probably attributed to this fact. Tartarelli at al.[1] used a simple second order irreversible reaction to describe esterification of *n*-butanol with oleinic acid with the air dry ion exchanger. On the other hand, Rodriguez and Setinek[5] describe reesterification of *n*-propanol with ion exchanger dried in vacuum at 100—120 °C as heterogeneous, assuming that the slowest step is a surface reaction between adsorbed alcohol and ester.

In this work, we used the ion exchanger with different initial water content. It can be assumed that different initial water concentration cause different kinetic behaviour.

In Figure 2. experimental data are shown, conversion versus time ($X_A — t$), measured in the batch reactor obtained with dry ion exchanger.

It is well known that the ion exchanger significantly solvates polar organic and inorganic solvents like alcohols and water. There is also sorption of organic acids. Since the catalytic reaction with dry resin occurs simultaneously with the solvation and sorption, it follows that there is a period of resin

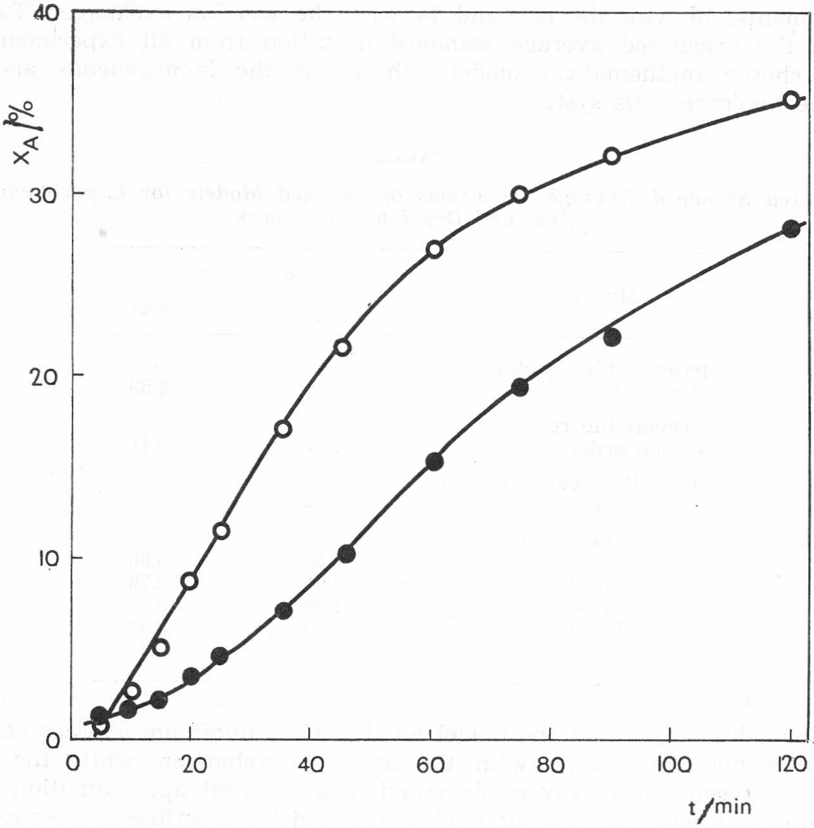

Figure 2. Conversion versus time in batch reactor, equimolar ratio butanol-acetic acid, 55 °C (● — dry resin, ○ — wet resin).

swelling in the reaction mixture. These processes change the initial catalytic activity of resin until some sorption equilibrium steady state is reached. This initial period of solvation of the ion exchanger in a reaction mixture we studied in a tubular reactor.

Kinetic analysis of the induction period. Steady state reached in a tubular reactor depends on residence time of the reactants, if all other parameters are constant. The flow rate in experiments was between 1 to 3 ml/min so that the maximal residence time was 10 min. Conversion was measured from the moment of charging the reactor with the catalyst. Also, the time dependence of the catalyst bed height was measured. At typical result of an experiment is shown in Figure 3.

Figure 3. shows that the reactor reaches a steady state in not more than 10 min if the wet ion exchanger already has been used (curve 2), while with dry resin the steady state is reached after 90 min. (curve 1). Steady state conversion is the same, regardless of the initial catalyst state (wet or dry). Hence, the dry catalyst changes its activity during the induction period until an equilibrium state is reached. The shape of curve 1 and 2 shows that the stationary conversion is obtained when the resin hight becomes constant, i. e.

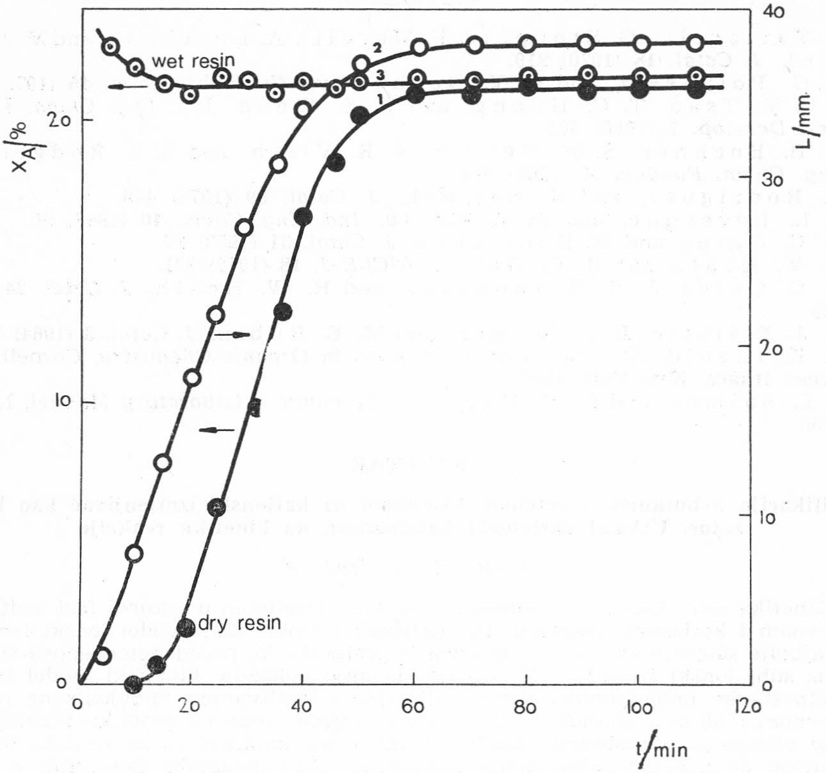

Figure 3. Time dependence of the catalyst height and conversion in tubular reactor.

when swelling stops. Furthermore, the shapes of the curve are identical and therefore the rate of the activation and the rate of sorption are proportional.

The experimental results show the induction period of 90 min. The same period also exists in the batch reactor (Figure 2.), where simultaneous reaction with activation occurs. However, a kinetic analysis of the batch reactor data has been carried out with the assumption that catalyst activity was constant. Since this assumption is not correct, a good agreement between data approximation, based on such a model and experimental data, does not justify the acceptance of such a model. On the contrary, the experiments with the wet ion exchangers show that the physically most justified model also fitts the data very well. The best agreement of the heterogeneous model for the case with the dry ion exchanger is probably to simultaneous occurence of the chemical reaction and the catalyst activation. Kinetic analysis with the wet and the dry ion exchanger in the batch reactor, and the kinetic analysis of the induction period show that the model based on the pseudohomogeneous system assumption is the most acceptable. Also, the induction period of this reaction depends on the sorption equilibrium between reactants within a resin bed.

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SAŽETAK

Esterifikacija *n*-butanola s octenom kiselinom uz kationski izmjenjivač kao katalizator. Utjecaj aktivnosti katalizatora na kinetiku reakcije

Z. Gomzi i S. Zrnčević

Kinetika esterifikacije *n*-butanola s octenom kiselinom u tekućoj fazi ispitana je u cijevnom i kotlastom reaktoru. Uz djelomično mokri (27% vode) ionski izmjenjivač najbolje slaganje daje model izveden iz pretpostavke pseudohomogenosti sistema, dok uz suhi ionski izmjenjivač najbolje slaganje pokazuje kinetički model izveden iz pretpostavke heterogenosti sistema. Posebnim ispitivanjem indukcijskog perioda u cijevnom reaktoru ustanovljen je značajan utjecaj vode na kinetiku reakcije. Taj utjecaj očituje se u promjeni katalitičke aktivnosti katalizatora za vrijeme reakcije što dovodi do pogrešnog korištenja eksperimentalnih podataka dobivenih u kotlastom reaktoru u svrhu izvođenja kinetičkog izraza. Promjena aktivnosti ionskog izmjenjivača u indukcijskom periodu uzrokovana je difuzijom reaktanata u zrno ionskog izmjenjivača.

TEHNOLOŠKI FAKULTET
SVEUČILIŠTA U ZAGREBU,
ZAGREB

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