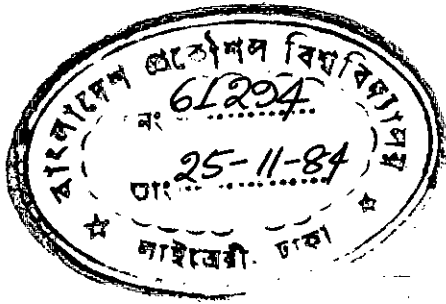


ESTERIFICATION OF ETHANOL AND ACETIC ACID IN A BATCH
REACTOR IN PRESENCE OF SULPHURIC ACID CATALYST.



A Thesis

Submitted to the Department of Chemical Engineering
in partial fulfilment of the Requirements for the

Degree of

Master of Science in Engineering

(Chemical)

Bangladesh University of Engineering & Technology.

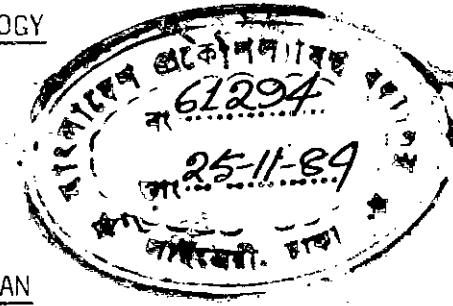
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CERTIFICATION OF THESIS WORK



We, the undersigned, certify that MD. ATAUR RAHMAN candidate for the degree of Master of Science in Engineering (Chemical) has presented his thesis on the subject ESTERIFICATION OF ETHANOL AND ACETIC ACID IN A BATCH REACTOR IN PRESENCE OF SULPHURIC ACID CATALYST, that the thesis is acceptable in form and content, and that the student demonstrated a satisfactory knowledge of the field covered by this thesis in an oral examination held on 18th July, 1984.

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ABSTRACT

The thesis presents the work done on reaction kinetics study and separation process for the esterification of ethyl alcohol with acetic acid in presence of sulphuric acid catalyst. Literature review was made on esterification, esterification by organic acids and catalytic esterification.

An experimental set up has been developed to study the kinetics of reactions and the product separation. The order of reaction have been determined graphically for constant catalyst series and for constant mole ratio series. The reaction rate constant has been found from the following rate equation:

$$k = -\ln\left(1 - \frac{X_A}{X_{Ae}}\right) \left(\frac{M+X_{Ae}}{M+1}\right) \cdot (1/t)$$

The effect of catalyst concentration and mole ratio of reactants on esterification have been studied at constant temperature of $63^{\circ}\text{C} \pm 1^{\circ}\text{C}$. Experiments were also carried out at two other temperatures of 48°C and 75°C . An increase in k - value from 0.0034 to 0.0271 was found with the increase of temperature from 48°C to 75°C . The results are correlated into a single empirical equation for rate constant (k), catalyst concentration (C) and reactants mole ratio (B/A) at a constant temperature, as

$$k = 0.0066 - 0.00592 C + 0.00683(B/A) \cdot C$$

Solvent extraction and fractional distillation has been used for ester separation from the unreacted reactants. Sodium Carbonate solution is used as the solvent. By this method it is possible to produce commercial grade ethyl acetate.

ACKNOWLEDGEMENTS

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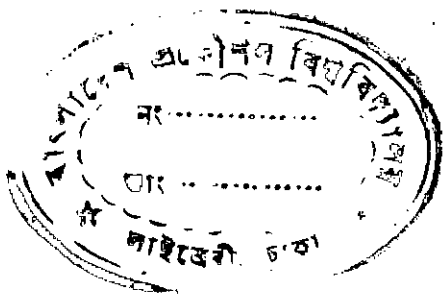
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CHAPTER I

INTRODUCTION AND OBJECTIVES

The importance of making esters is gaining prominence. The wide range of application of esters in chemical process industries has increased the importance of its study. In recent years, the consumption of esters has increased enormously but little had been published on it (both in terms of theory and practice of production). The principles are matters of general knowledge and do not change; the details of their application vary from time to time and from plant to plant and are usually kept secret as long as they are of private advantage.

Esters are organic compounds and are widely used as solvent, as raw material in plasticizer, monomer, medicine and perfume industries. Some nitrate esters, such as nitroglycerins, nitrocellulose are used as explosives. Ethyl acetate is one of the most useful esters. It is being used in large quantities in manufacturing of paint, nitrocellulose lacquers, airplane dopes, artificial flavour; perfume, acetate rayon, smokeless powder, artificial leather and photographic film. In our country large amount is consumed in rayon fiber and paint industry.

The most useful method for the preparation of ester is the reaction of a carboxylic acid and an alcohol catalyzed with a few percent of mineral acid, with elimination of water formed. Although commonly used esters are produced quite efficiently, always there are scopes for research in process development.

The production of esters may be carried out by batch or continuous processing. However, the knowledge of the kinetics of reaction of ethyl alcohol

and acetic acid catalyzed by sulphuric acid coupled with vapor-liquid equilibrium data is a must for every esterification unit design. Because it should allow the calculation and re-design of the reactor and the distillation unit for combined steps of esterification reaction and separation of formed esters.

In the present investigation the esterification of ethyl alcohol and acetic acid will be studied in presence of sulphuric acid catalyst in a batch reactor. The study will also include trials on the separation of the ester. The main objective of the present study may be listed as:

1. Design and construction of a Batch Reactor for esterification of ethyl alcohol and acetic acid with sulphuric acid as a catalyst.
2. Kinetics of the reaction which include the mechanism of the reaction and determination of the order of reaction at constant temperature for the following cases.
 - a) for constant mole ratio of ethanol and acetic acid (B/A).
 - b) for constant weight percent of sulphuric acid catalyst (C).
3. Determination of the rate constant at constant temperature
 - a) for constant B/A.
 - b) for constant C.
4. A method based on solvent extraction and fractional distillation would be used to separate ethyl acetate from the unreacted reactants. For this purpose sodium carbonate solution is a well known solvent for selective absorption of ethyl alcohol from mixture of ethyl alcohol-ethyl acetate.

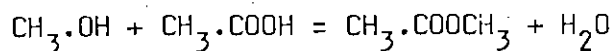
CHAPTER II

LITERATURE REVIEW2.1 ESTERIFICATION:

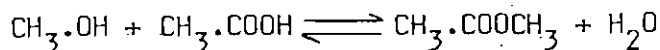
Esters in general are formed where an alcohol is mixed with an acid, but the change, which is a gradual one, is never complete, because the reaction is reversible (1).

When the interaction has proceeded for a certain time, the quantity of ester which is decomposed by the water present is equal to that formed in the same time by the interaction of the acid and the alcohol.

In other words, a condition of equilibrium is established and the equations can be represented by



This is usually expressed by



The equation from left to right is called esterification, and the reverse reaction, hydrolysis.

The proportion of alcohol, which is converted into ester, depends on the nature of the alcohol and of the acid and on their relative quantities and the temperature.

Now, if the water produced during esterification could be removed, or otherwise prevented from decomposing the ester, the desired change, from left to right, should take place more completely. This consideration led to the use of 'dehydrating agents' in the proportion of esters, substances such as zinc chloride, hydrogen chloride or sulphuric acid being added to the mixture of alcohol and acid to 'bind' the water and prevent it from decomposing the

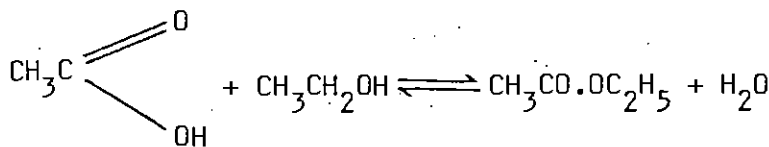
ester. In practice, the results of doing this are very satisfactory and the two methods usually employed in preparing esters of organic acids are:

(a) By passing dry hydrogen chloride into a boiling mixture of the acid and alcohol contained in a flask provided with a reflux condenser. (b) By warming a mixture of the acid and alcohol with concentrated sulphuric acid. In both these processes, when the object is to convert as large a proportion as possible of the acid into its ester, the alcohol is used in very considerable excess.

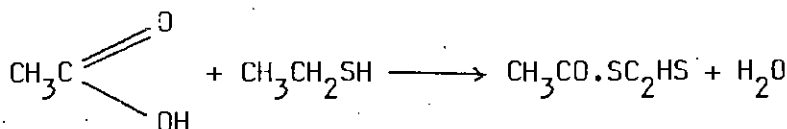
2.2 ESTERIFICATION BY ORGANIC ACIDS

This is esterification in its narrow sense and is what is usually meant when the term esterification is used. It has been extensively studied by both organic and physical chemists. It has been one of the most useful reactions in preparative organic chemistry, one of the best examples of the mass action law and has involved one of the most baffling problems in homogeneous catalysis(3).

The mechanism by which this replacement occurs have been well established. If the direct esterification of an acid, such as acetic, by an alcohol, such as ethanol, is considered, the possibility of breaking is

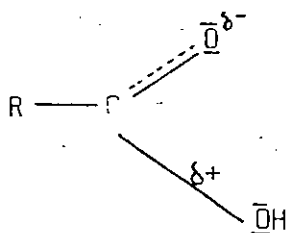


The carbonyl-oxygen bond or the alkyl-oxygen bond is evident. Evidence for the breaking of the carbonyl-oxygen bond was found in the study of the following reaction,



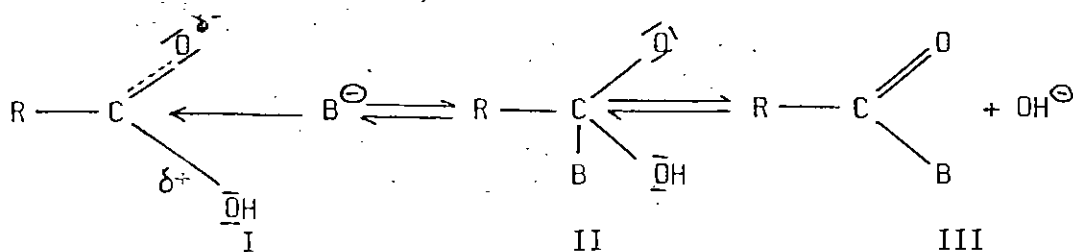
in which water was formed. If the alkyl-sulfur bond had broken, hydrogen sulfide would have been formed. That the carbonyl-oxygen bond is the one broken was confined by the finding that esterification of benzoic acid containing the normal oxygen isotope distribution by methanol enriched with O^{18} produced methyl benzoate containing the heavy oxygen isotope, while the water formed had only the normal isotope distribution.

A generalized explanation for the selectivity of the bond breaking process is found in the electronic structure of the reactants and products. Since oxygen is more electronegative than carbon, the carbonyl carbon is more positive than the carbonyl oxygen. This may be represented as:



Any compound (B) centering a free pair of electrons, whether due to ionization or not, can attack this positive center.

Thus



The transition state can lose the negative charge by loss either of a hydroxyl ion or of the species which originally attacked the positive centre. An equilibrium will be established between starting materials and the final products since the hydroxyl ion produced can attack III to form the same transition state as that from I and II.

Berthelot and Pean de st. Gilles (3) made the first exact measurements on the ethanol-acetic acid-ethyl acetate equilibrium and determined the equilibrium point. Their results showed that the reaction was reversible and that the extent of reaction depended on the relative amounts of each compound present. The equilibrium constant for the reaction is

$$\frac{[\text{Ester}] \times [\text{Water}]}{[\text{Acid}] \times [\text{Alcohol}]} = K$$

Unless activities are used in this expression, the value of K changes with the presence of salts.

Menschutkin (4) made a comparative study of the relative rates of esterification and the equilibrium constants of a large number of acids and alcohols. He found striking differences among primary, secondary and tertiary alcohols, both as to the rates and as to the limits of esterification.

Table (2.1) gives some of his results for acetic acid heated to 155°C with equivalent amounts of various alcohols.

It will be observed that, of all the alcohols studied, methyl shows that greatest initial rate of esterification and the highest limit. The primary alcohols, ethyl, propyl, and butyl, have approximately the same initial rates and limits but are inferior to methyl alcohol in both of these respects. Allyl alcohol is much slower than propyl, the saturated alcohol with the same number of carbon atoms. The presence of the phenyl group in benzyl alcohol has a retarding influence.

Table 2.1 Relative rates of esterification and the equilibrium constants.

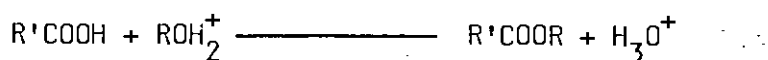
	Alcohol	Percent conversion		K
		1 hr.	Limit	
1.	Methyl	55.59	69.59	5.26
2.	Ethyl	46.95	66.57	3.96
3.	Propyl	46.92	66.85	4.07
4.	Butyl	46.85	67.30	4.24
5.	Allyl	35.72	59.41	2.18
6.	Benzyl	38.64	60.75	2.39
7.	Dimethyl carbinol	26.53	60.52	2.35
8.	Methyl ethyl carbinol	26.53	60.52	2.35
9.	Diethyl carbinol	16.93	58.66	2.01
10.	Methyl hexyl carbinol	21.19	62.03	2.67
11.	Diallyl carbinol	10.31	50.12	1.01
12.	Methanol	15.29	61.49	2.55
13.	Trimethyl carbinol	1.43	6.59	0.0049
14.	Dimethyl propyl carbinol	2.15	0.83	
15.	Phenol	1.45	8.64	0.0089
16.	Thynol	0.55	9.46	0.0192

The secondary alcohols (7 to 12, Table 2.1) are marked by lower than the primary in both initial velocity and limit but vary considerably among themselves. The tertiary alcohols (13 and 14) show little esterification in 1 hr. and hardly any more in 100. In the case of tertiary alcohols, the

limit is seldom if ever reliable, since these alcohols are dehydrated easily to the unsaturated hydrocarbons. Also the esters can decompose to form an unsaturated hydrocarbon and the acid. It is not unusual, with esters to tertiary alcohols, to find less ester present after a long heating period than after a short one. Phenol and thynol which may be regarded as tertiary alcohols but from which water can not be split off, show low initial rates but comparatively high limits.

As was pointed out by Griffin(2) the three classes of alcohols are not always sharply separated as in the above examples, i.e., some tertiary alcohols may be esterified as rapidly and to the same extent as certain secondaries and primary alcohols have been found that do not esterify so readily or so completely as some secondary ones. It may be stated generally that the more branched the carbon chain of the alcohol and the nearer the branches are to the hydroxyl group, the slower will be its esterification and the lower the limit. These effects are due to steric hindrance to the approach of the alcohol to the acid molecule.

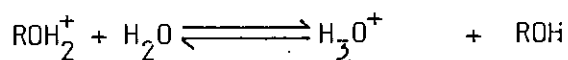
The kinetics of the acid-catalyzed reaction between organic acids and alcohols (4) has best been explained on the basis of Golds Schmidt's equations which was developed by Golds Schmidt and numerous co-workers over the period 1885-1929 and has been further studied by Schmidt(12). Equations were developed based on the assumption that the hydrogen atom from the catalyst first react with the alcoholic hydroxyl to form a complex ROH_2^+ and the latter then reacts with organic acids.



The rate of formation of ester is proportional to the product of the concentrations of the organic acid and the activated alcohol complex.

$$\frac{d(R'COOR)}{dt} = k_1 (R'COOH) (ROH)$$

Since water is formed in the reaction, it will slow up the rate of esterification by reducing the number of available hydrogen ions according to the equilibrium between the alcohol and water complexes.



The equilibrium constant for the reaction is -

$$K = (H_3O^+) (ROH) / (ROH_2^+) (H_2O)$$

If the concentration of alcohol may be considered constant, a factor 'r' may be defined as

$$r = (ROH) / K = (ROH_2^+) (H_2O) / (H_3O^+)$$

Assuming that all the hydrogen ions will be found either as alcohol or water complexes, the above equation for 'r' may be expressed as:

$$r = (ROH_2^+) (H_2O) / (\text{Total } H^+ - (ROH_2^+))$$

If the original concentration of the organic acid is taken as 'a' and X is the concentration of ester formed at time t, and no water is present at the start, the reaction rate is reduced to:

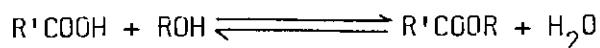
$$\frac{dX}{dt} = \frac{k(a-X)r(\text{catalyst})}{X+r}$$

Integrating the above equation and setting

$X = 0$ when $t = 0$, solution of k yields to :

$$k = (r + a) \ln (a/a - X) - X/(\text{catalyst}) rt$$

The reaction between an organic acid and an alcohol to produce an ester and water according to the equation:



2.3 CATALYTIC ESTERIFICATION

The speed of esterification is susceptible to temperature. The speed doubles for a 10°C rise in temperature. Hence, heat is used to accelerate esterification reactions (2).

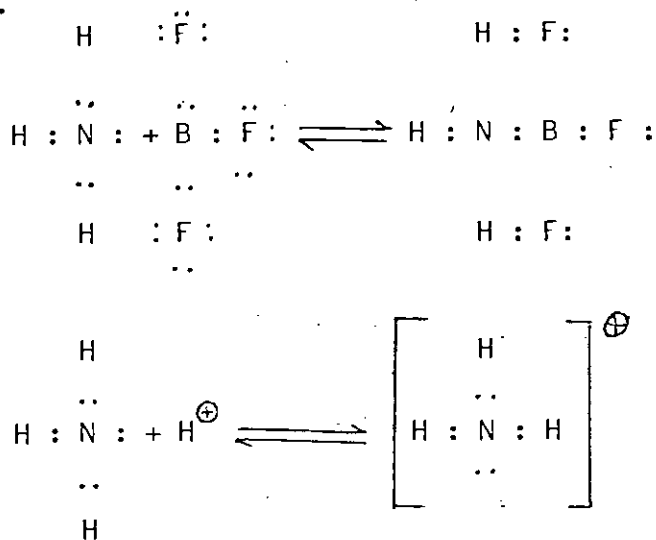
Esterification at atmospheric pressure requires the use of a catalyst. The only exception to the above case being that of a high-boiling alcohol such as glycorol with a high boiling acid such as stearic. The process of esterification is enhanced by the presence of strong acid such as sulphuric or hydrochloric acid.

The catalyst has no effect on the equilibrium point of the reaction. It only enhances the rate of esterification.

Esterification proceeds by attack of an alcohol molecule on the slightly positive carbonyl carbon of an acid. The larger this positive charge, the more rapid the reaction will be. While the nature of the R group attached to the carbonyl group will influence this charge, other methods or catalysts, can be used to increase the positive charge so that a given acid will esterify more rapidly.

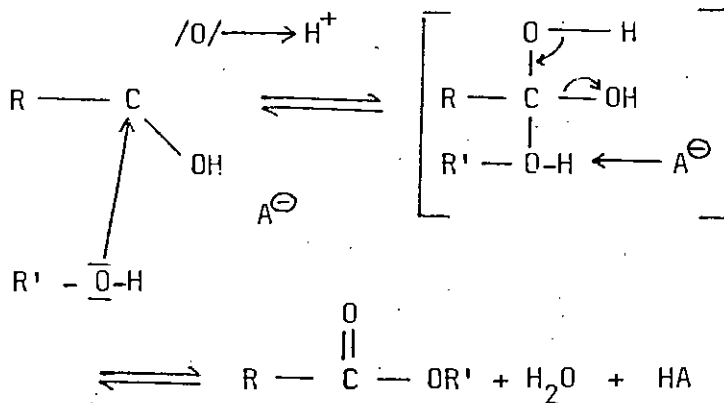
Esterification catalysts are compounds which are acidic in nature.

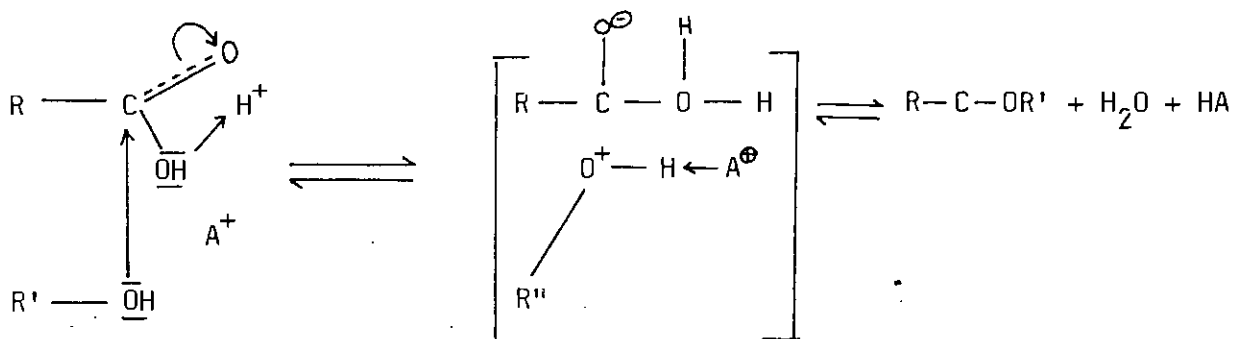
Acidic compounds include those where the central atom has an incomplete external electron shell, so that besides the hydrogen ion, compounds such as boron trifluoride, aluminium chloride or zinc chloride can be considered to be acids.



When an acid (HA) is added to an esterification mixture, the oxygen present will act as base and coordinate with the acid.

The mechanism can be written in two ways depending on which oxygen of the carbonyl group acts as the base.





In certain cases where the acid is sufficiently strong, esterification is self catalysed.

Quite after the speed of the reaction is accelerated by working under increased pressure and hence high temperature can be used.

The figures in Table 2.2 may be considered to represent the relative efficiencies of mineral acids as catalysts in the reverse reaction of esterification.

Table 2.2 Relative Rates of Hydrolysis of methyl acetate with various acids as catalysts.

Acid	Rate of Hydrolysis %	Acid	Rate of hydrolysis %
Hydrochloric	100	Malonic	2.87
Hydrobromic	89.3	Succinic	0.496
Nitric	91.5	Tartaric	2.30
Sulphuric	54.7	Formic	1.31
Ethyl sulphuric	98.7	Acetic	0.345
Ethanosulphuric,	97.9	Chloroacetic	4.3
Benzene sulphuric	99.0	Dichloroacetic	23.0

The commonly used catalysts include hydrochloric and sulphuric acids. The former is very much used in the laboratory because of its efficiency, the latter finds its use in the plant because of its cheapness and lower corrosive effect on metals. Perchloric and phosphoric acids have been recommended as catalysts. Phosphoric acid is less efficient but also less destructive. The sulfuric acids, particularly those containing considerable number of carbon atom are desirable catalysts on account of their high efficiency, solubility in the higher alcohols and acids, and less destructive actions. The most commonly used is p toluene sulfuric acid.

Acid salts, such as potassium bisulphate and salts of strong acids with weak bases have been tried as catalysts. The presence of zinc chloride accelerates the catalytic effect of acids. Zinc and tin chlorides are active catalysts. Various patents claim the use of aluminium, cobalt, lead, magnesium, tin and zinc soaps as esterification catalysts. Catalysts comprising metals such as tin, manganese, lead, silver and copper in the finely divided state are considered to be suitable, zinc being specially favoured. Oxides of aluminium, lead and magnesium also are said to be esterification catalysts.

EXPERIMENTAL3.1 EXPERIMENTAL SET UP3.1.1 BATCH REACTOR

For the experiment to be conducted, a batch reactor is set up. The reactor is a one litre conical flask with liquid sampling provision. For better yield of the reaction a total condenser is fitted. The condenser is permanently fixed to the system. It is a shell tube system in which circulating cooling water flows through the tube side and vapours through the shell side. The reaction temperature is controlled by placing the flask on a hot plate with magnetic stirrer where the power is adjusted by a variable transformer. The temperature is noted with a thermometer placed in the flask. For proper mixing of the reactants, a magnetic stirrer is used. The reactor with its auxiliary units is fixed with a stand by a clamp. Figure 3.1 shows a schematic arrangement of the reactor-set-up.

3.1.2 SEPARATION UNIT

The separation unit is a distillation unit with one partial condenser and one total condenser connected in series. Cooling water is passed through the condensers. Water flow rate should be adjusted in such a way that partial condensation of vapour occurs. This liquid comes in contact with the vapour and thus the mass transfer is increased. The rest of the vapour is condensed in the second condenser and the distillate is collected in a collecting bottle. In the separation unit heat is supplied by a hot plate heater where power input may be varied. A thermometer is used to record the liquid temperature. Figure 3.2 shows a schematic arrangement of the system.

For solvent extraction a separating funnel is used. After extraction the two layers are separated through the bottom stopper of the funnel.

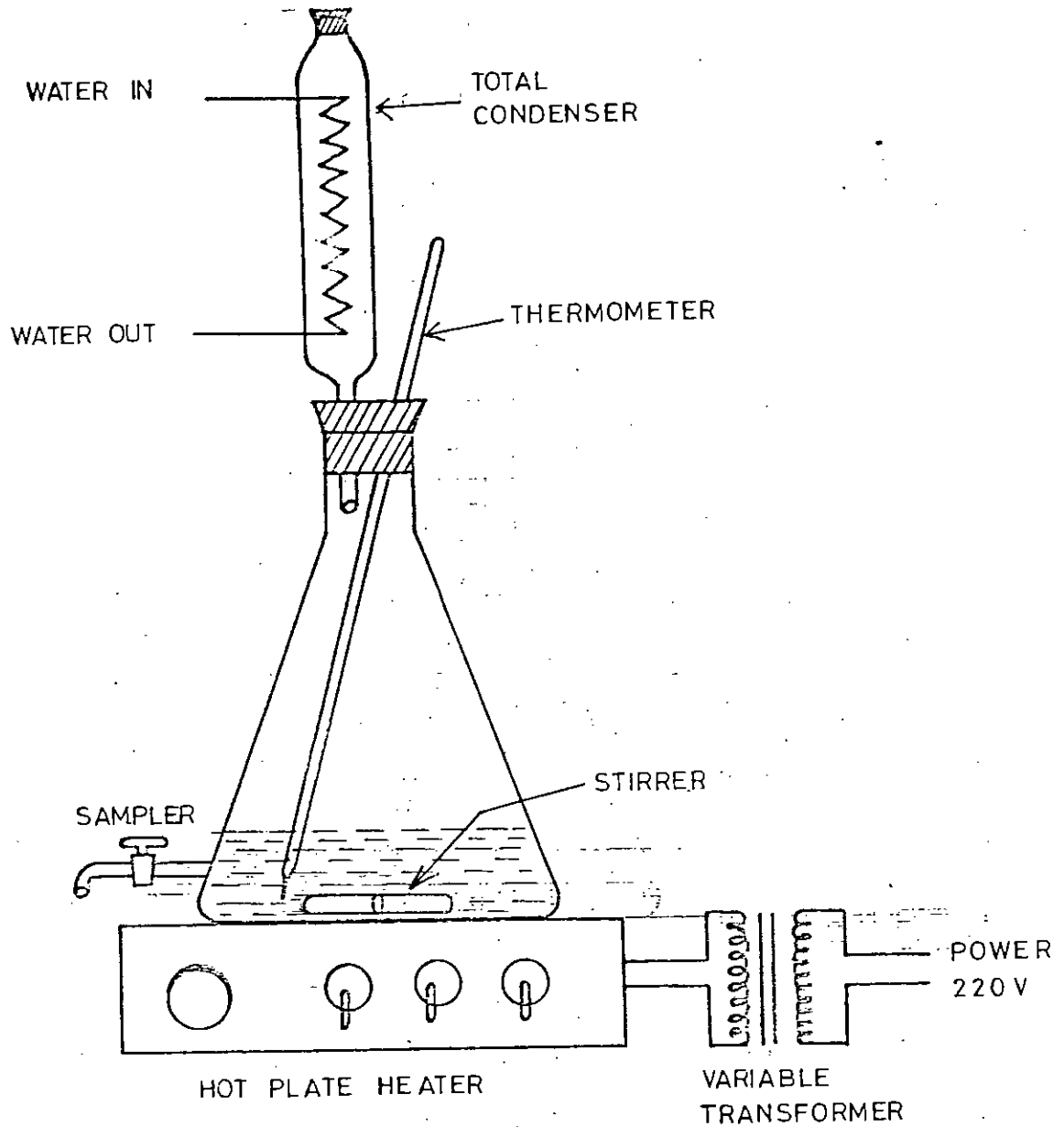


FIG. 3.1 SCHEMATIC ARRANGEMENT OF THE REACTOR SET UP

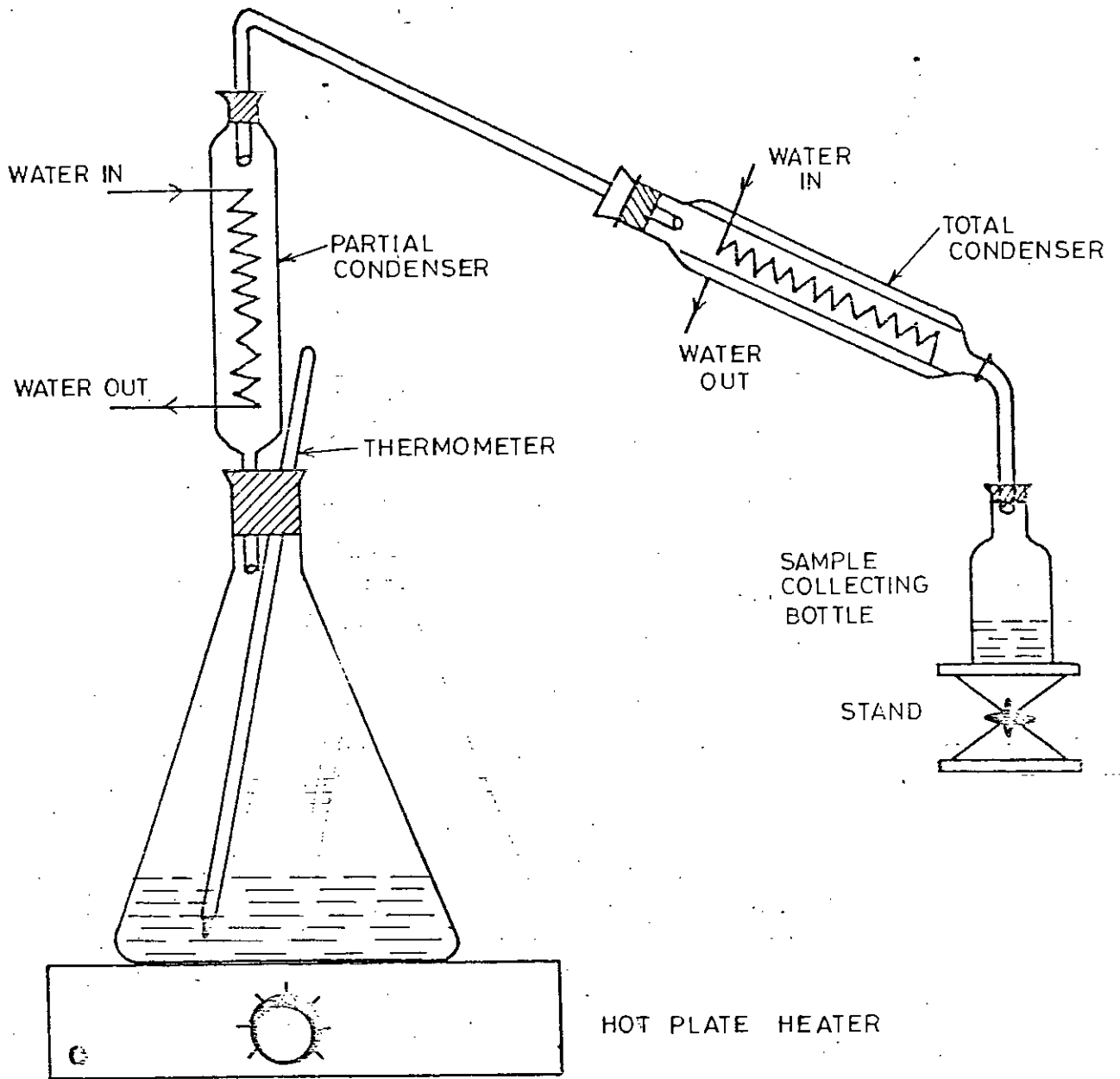


FIG. 3.2 SCHEMATIC ARRANGEMENT OF THE SEPARATION UNIT.

3.2 EXPERIMENTAL PROCEDURE

3.2.1 KINETICS

In each batch the volume of reactants used is approximately 500 cc. Measured volumes in the order of sulphuric acid, acetic acid and ethyl alcohol are taken in the reactor flask. The flask is placed on the hot plate heater and the switches of the heater and the stirrer are put on. Time from this instant is recorded. Within 25 to 30 minutes the temperature of the reaction mixture comes to a steady state value of $63^{\circ}\text{C} \pm 1^{\circ}\text{C}$. The samples of amount 5 to 10 cc. are taken out from the reactor with the help of the sampler at an interval of 30 minutes. 5 cc. of this sample is diluted with distilled water to make 50 cc. solution and titrated immediately against standard sodium hydroxide solution using phenolphthalein as indicator to determine the free acid. Due to the limitation of the heater, experiments are carried out at only three different temperatures (48°C , 63°C and 75°C). One of the runs (Run L) is repeated and reproducibility data of the experiment is presented in the appendix D.

3.2.2 SEPARATION

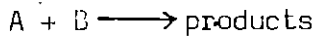
The product from the esterification reaction contains ethyl acetate, ethyl alcohol, water and acetic acid. The purpose of this process is to separate ethyl acetate product. A known quantity of the product mixture is taken in the conical flask of the separation unit. Sample between 78°C to 83°C is collected. Density of the sample is measured. It is assumed that the sample contains only ethyl alcohol and ethyl acetate as their boiling points are close to each other.

A 10% solution of sodium carbonate (commercial grade) in water is prepared and this solution is used as solvent for ethyl acetate extraction. The above distillate is treated with the sodium carbonate solution in various proportions ranging from 1:1 to 1:4. The distillate and sodium carbonate solution are taken in a separating funnel and shaken well for 3 to 4 minutes and then allowed to settle down. Ethyl alcohol is absorbed in the sodium carbonate solution and two distinct layer is formed. The top layer contains mostly ethyl acetate with some ethyl alcohol and water. The bottom layer contains sodium carbonate, water and ethyl alcohol. The top layer is separated out and distilled in the separation unit. Distillate between 78°C to 92°C is collected. The weight of the distillate is taken and the refractive index is measured. The product thus obtained is ethyl acetate with ethyl alcohol and water impurities.

CHAPTER IV
RESULTS AND DISCUSSION

4.1.1 REACTION RATE EQUATION

The actual equation which governs the rate of esterification may be determined by trial and error. Assuming a non-reversible second order reaction,



$$\frac{dx}{dt} = k(A-x)(B-x)$$

Which integrates into,

$$kt = \frac{1}{A-B} \ln \frac{B(A-x)}{A(B-x)} \quad (4.1)$$

Assuming a reversible reaction,

$$dx/dt = k_1(A-x)(B-x) - k_2x(W+x)$$

which can be reduced to the form,

$$dx/dt = k(a+bx+cx^2)$$

This integrates into,

$$kt = \frac{1}{\sqrt{-q}} \ln \frac{2cx+b-\sqrt{-q}}{2cx+b+\sqrt{-q}} - \frac{1}{\sqrt{-q}} \ln \frac{b-\sqrt{-q}}{b+\sqrt{-q}} \quad (4.2)$$

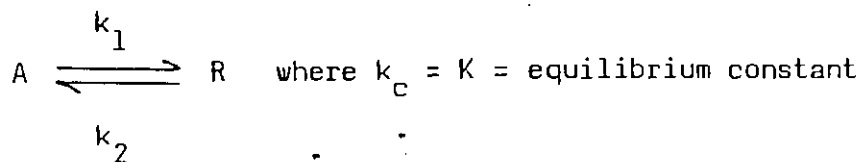
Assuming a second order non reversible reaction, $2A \longrightarrow \text{Products}$

$$\frac{dx}{dt} = k(A-x)^2$$

which integrates into,

$$\frac{x}{A(A-x)} = kt \quad (4.3)$$

Now assuming a first order reversible reaction



Initial concentration ratio $M = C_{R0}/C_{A0}$, the rate equation is -

$$\frac{dC_R}{dt} = -\frac{dC_A}{dt} = k_1(C_{A0} - C_{A0}X_A) - k_2(C_{A0}M + C_{A0}X_A)$$

which on separation and integration yields -

$$-\ln\left(1 - \frac{X_A}{X_{Ae}}\right) = -\ln \frac{C_A - C_{Ae}}{C_A - C_{Ae}} = \frac{M+1}{M+X_{Ae}} k_1 t \quad (4.4)$$

The proper form of the rate equation may be determined graphically by plotting various functions against time and noting which gives a straight line relation: For equation 4.1, $\log \frac{B(A-X)}{A(B-X)}$ vs. t ; for equation 4.2, $\log (2cx + b - \sqrt{-q}) / (2cx + b + \sqrt{-q})$ vs. t ; for equation 4.3, $\frac{x}{A(A-x)}$ vs. t .

The data obtained from the experiments are plotted. Equation 4.3 gives a well defined curve and hence does not apply. The last five points on the curve for equation 4.2 appear to fall on a straight line, but the initial points (0 to 4 hour) fall far off the straight-line relation. Figure 4.1 and 4.2 gives the reaction rate equation tests for equations (4.2) and (4.3) respectively.

For constant mole ratio runs L and M are plotted using equation 4.4, which gives a well defined straight line upto 6 hours (about 90% conversion). At the 6 hour point and above, equation 4.4 no longer holds; the mechanism changes apparently to one approaching equation 4.3 since the reverse reaction, saponification, is beginning to have an effect. This is indicated by the straight line portion of the equation 4.3 above 6 hours. However, in the continuous column

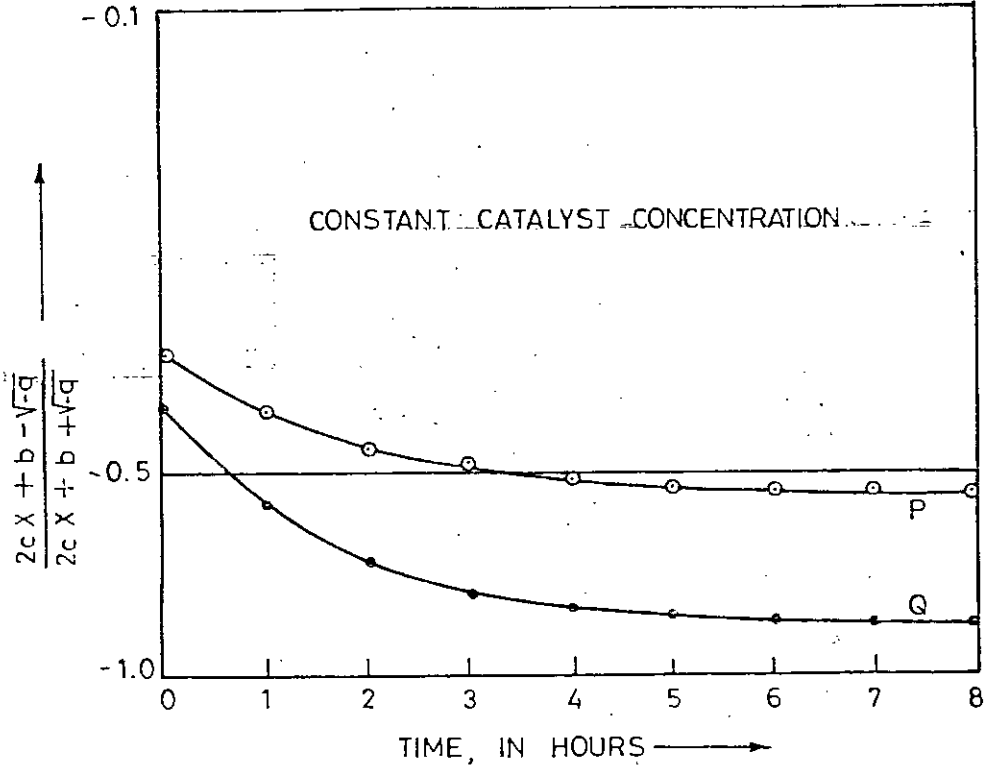
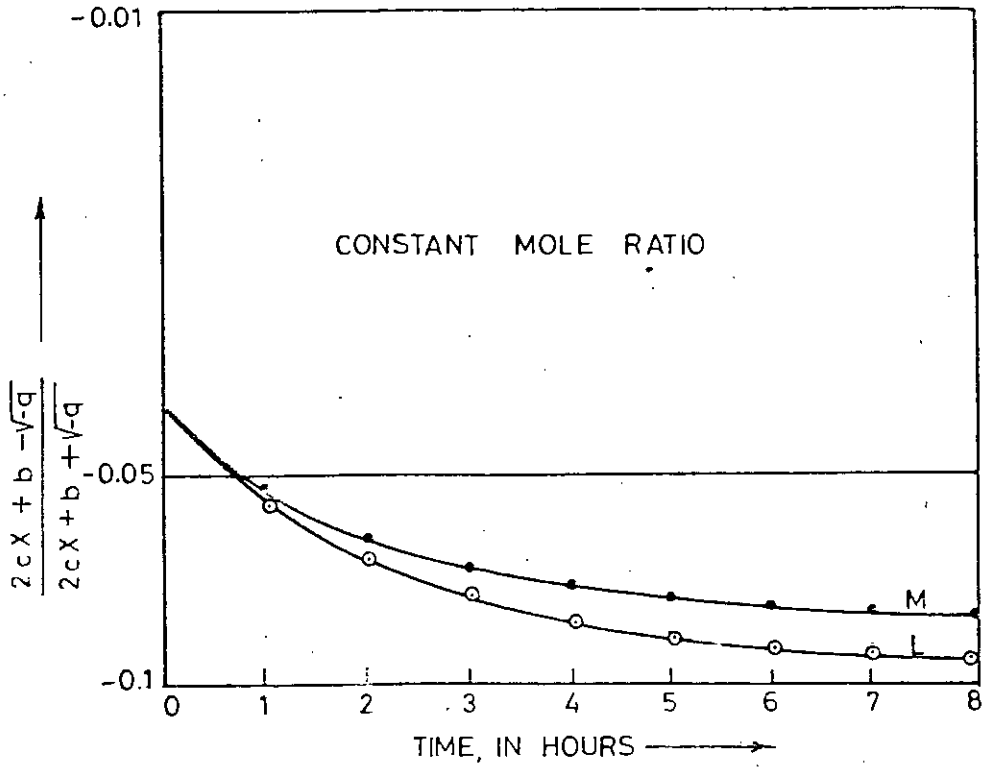


FIGURE 4.1 REACTION RATE EQUATION TEST FOR EQUATION 4.2.

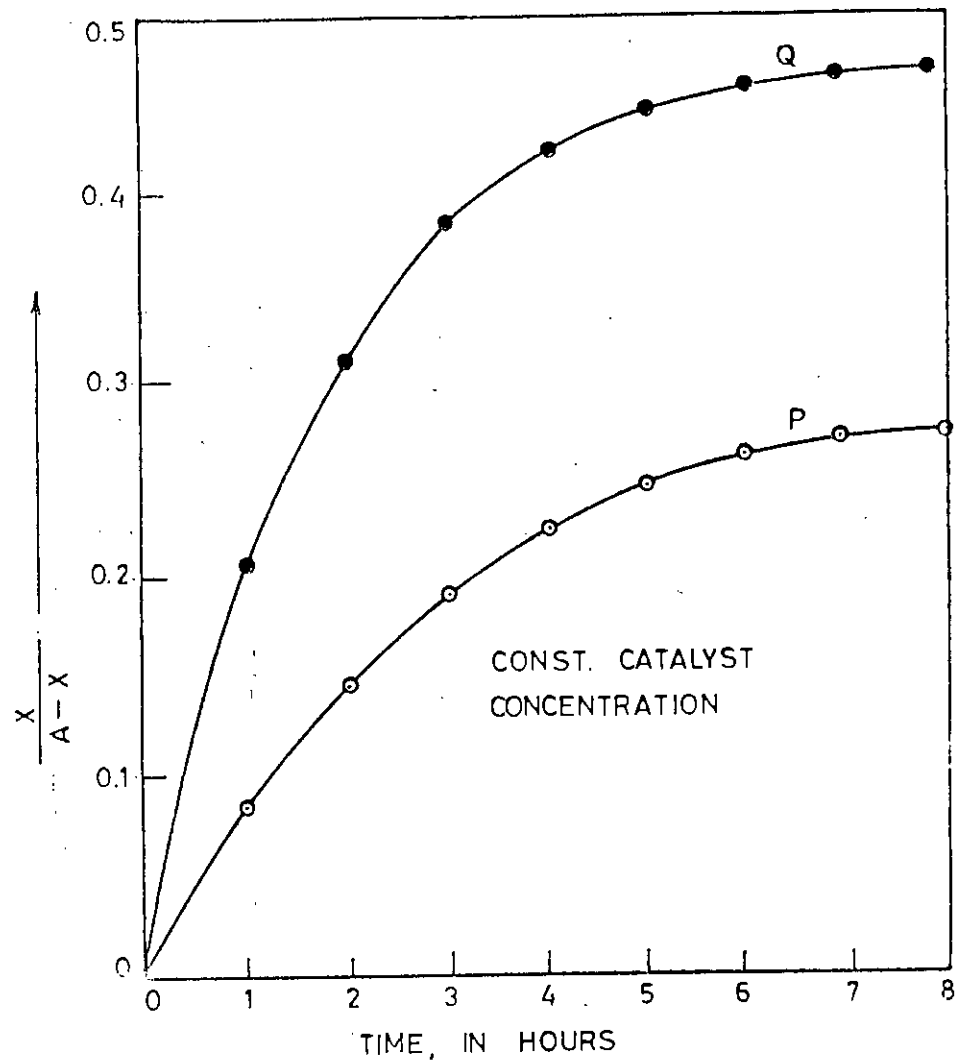
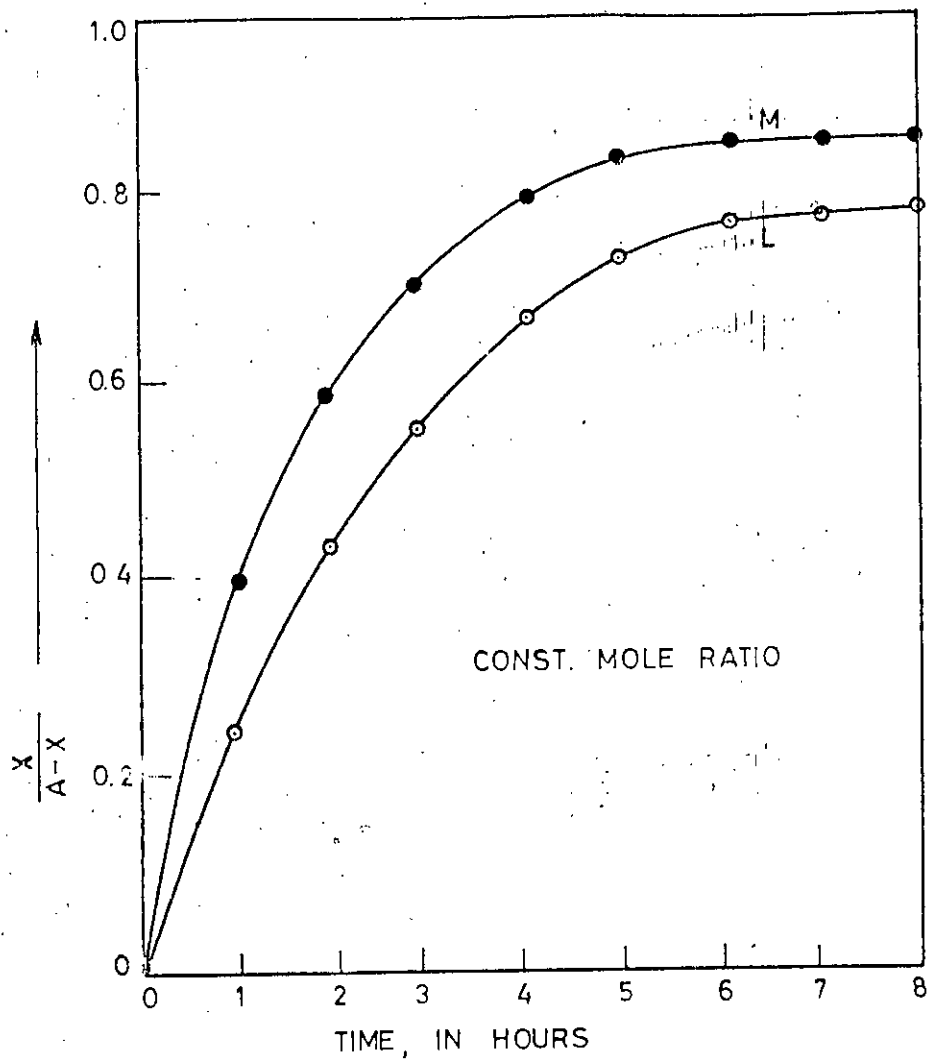


FIGURE 4.2 REACTION RATE EQUATION TESTS FOR EQUATION 4.3

esterification studies reported elsewhere (5), it was desired to reduce the time of contact to about 30 minutes; hence equation 4.4, which gives a straight line relation for the early stages of reaction, applies in the continuous esterifications. Long times of contact and attainment of esterification mass law equilibrium on a given plate are not needed, for a high overall extent of conversion. The agreement is good upto 90% conversion. Table 4.1 summarizes the complete calculations for the experimental data testing equation 4.4. Figure 4.3 shows the reaction rate equation tests for equation 4.4.

For constant catalyst concentration with varying mole ratio, equations 4.1, 4.2 and 4.3 do not apply, since they give a well defined curve. Runs P and Q of this series are plotted using equation 4.4, which gives a well defined straight line. The agreement is good upto 80% conversion. Table 4.2 gives the experimental data testing equation 4.4. Figure 4.4 gives the reaction rate equation tests for equation 4.4.

Table 4.1 Experimental data testing equation 4.4 for constant mole ratio series

RUN L			RUN M		
Time HR	X_A m/l	$1 - \frac{X_A}{X_{Ae}}$	Time HR	X_A m/l	$1 - \frac{X_A}{X_{Ae}}$
0	0	1.000	0	0	1.000
1	0.411	0.539	1	0.568	0.383
2	0.571	0.359	2	0.763	0.171
3	0.725	0.186	3	0.867	0.059
4	0.796	0.107	4	0.904	0.018
5	0.837	0.061	5	0.910	0.011
6	0.873	0.021	6	0.919	0.003
7	0.887	0.005	7	0.921	0
8	0.891	0	8	0.921	0

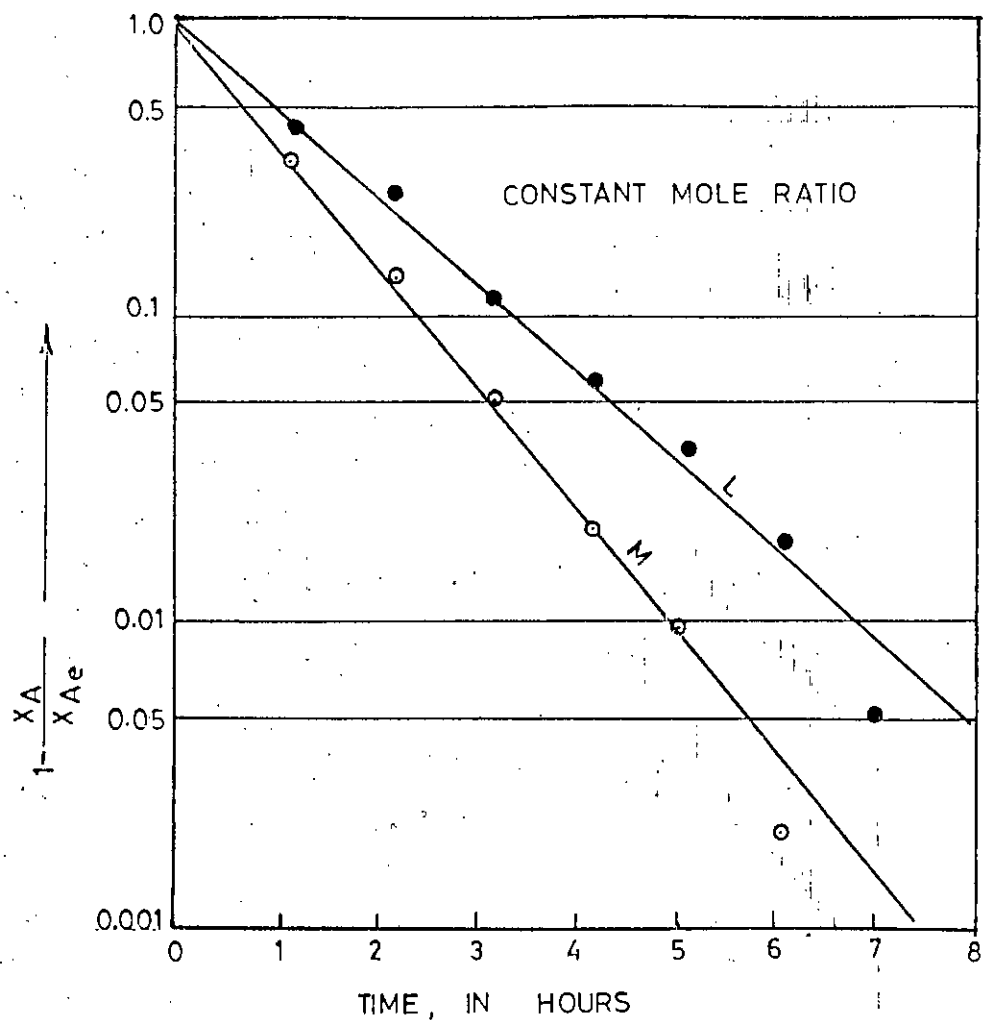


FIGURE 4.3 REACTION RATE EQUATION TESTS FOR EQUATION 4.4

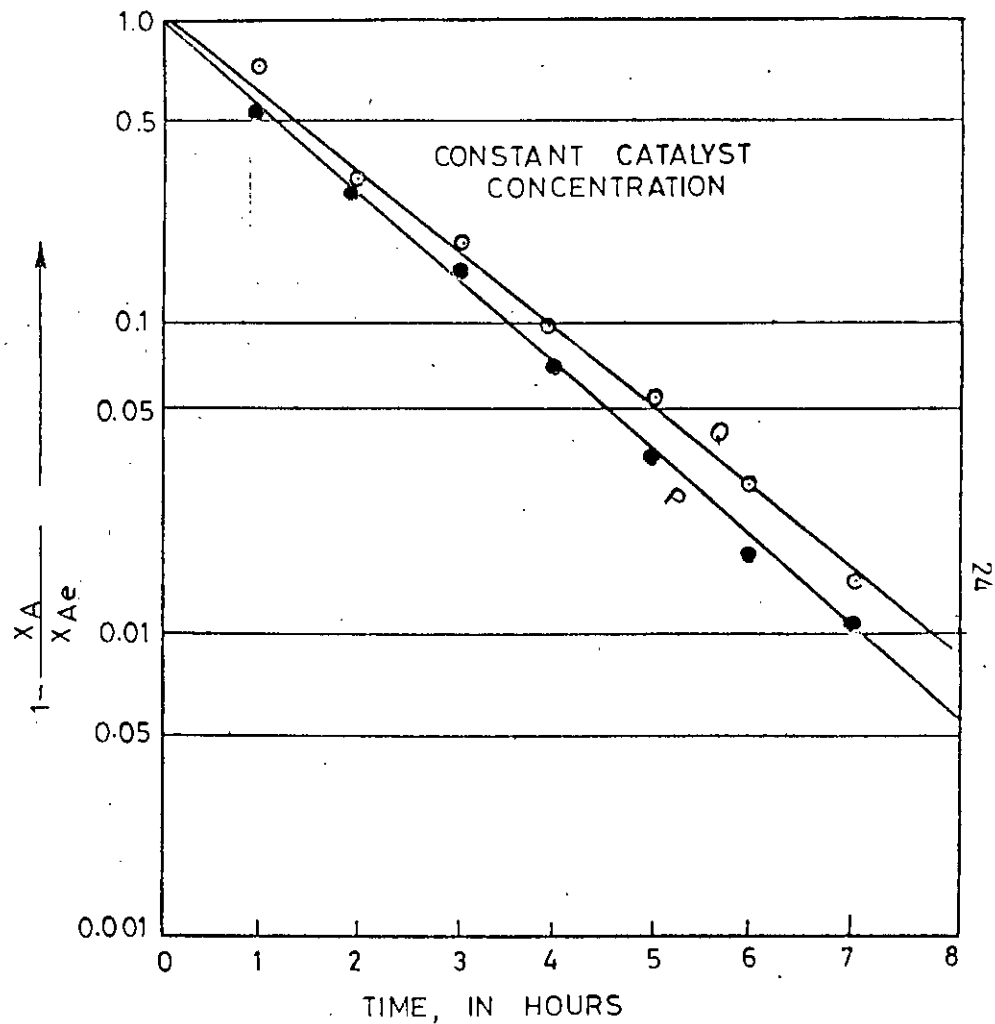


FIGURE 4.4 REACTION RATE EQUATION TESTS FOR EQUATION 4.4

Table 4.2 Experimental data testing equation 4.4 for constant catalyst concentration series.

RUN P			RUN Q		
Time HR	X_A m/l	$X_{Ae} = 0.733$ $1 - \frac{X_A}{X_{Ae}}$	Time HR	X_A m/l	$X_{Ae} = 0.781$ $1 - \frac{X_A}{X_{Ae}}$
0	0	1	0	0	1
1	0.330	0.550	1	0.376	0.519
2	0.503	0.314	2	0.573	0.266
3	0.622	0.152	3	0.652	0.165
4	0.676	0.078	4	0.716	0.083
5	0.701	0.043	5	0.740	0.053
6	0.715	0.024	6	0.755	0.033
7	0.725	0.011	7	0.769	0.015

4.1.2 REACTION RATE CONSTANT:

The dimensions of the rate constant k for the n -th order reactions are $(\text{time})^{-1} (\text{concentration})^{1-n}$, which for a first order reaction becomes simply $(\text{time})^{-1}$ and for second order reaction becomes $(\text{time})^{-1} (\text{concentration})^{-1}$. The value of k was determined from the rate equations at a selected value for time (180 minutes) for all runs. For constant mole ratio, k was calculated using equation 4.4 and for constant catalyst concentration, k was calculated using equation 4.4. Table 4.3 summarizes calculations for reaction rate constant k .

Table 4.3 Calculation of Rate Constant k.

CONSTANT MOLE RATIO:

$$M = 7.59, \text{ where } k = -\ln\left(1 - \frac{X_A}{X_{Ae}}\right) \left(\frac{M+X_{Ae}}{(M+1)t}\right)$$

RUN	A ₀ m/l	Time min.	Wt% Catalyst	Temp. °C	$1 - \frac{X_A}{X_{Ae}}$	$\frac{M+X_{Ae}}{(M+1)t}$	k
K	2.000	180	0.00387	63	0.2322	0.005390	0.00787
L	2.000	180	0.0830	63	0.18622	0.005485	0.00922
M	2.000	180	0.1900	63	0.05854	0.005504	0.015621
N	2.000	180	0.3000	63	0.04104	0.005508	0.01759

CONSTANT CATALYST CONCENTRATION:

Catalyst concentration = 0.0845% by wt., where $k = -\ln\left(1 - \frac{X_A}{X_{Ae}}\right) \left(\frac{M+X_{Ae}}{(M+1)t}\right)$

RUN	A ₀ m/l	B ₀ m/l	Time min.	Mole Ratio	Temp. °C	$1 - \frac{X_A}{X_{Ae}}$	$\frac{M+X_{Ae}}{(M+1)t}$	k
O	8.7014	8.700	180	1	63	0.241	0.00466	0.00663
P	4.000	10.19	180	3.32	63	0.20617	0.005212	0.00823
Q	2.4604	14.76	180	6.00	63	0.165	0.00538	0.00969
R	1.0742	16.11	180	15.00	63	0.067	0.00549	0.0148

4.1.3 EFFECT OF CATALYST CONCENTRATION:

Various investigators have found that the rate of esterification with acid catalysts is proportional to the acid concentration (10,11) or to the hydrogen ion concentration (12). Figure 4.5 shows a linear relation between the rate constant for the runs at 63°C with approximately 7.6 moles of ethanol per mole of acetic acid and between 0.00387 and 0.3% sulphuric acid as catalyst.

4.1.4 EFFECT OF PROPORTION:

According to Watson (11), the rate of esterification is proportional to the concentration of alcohol and acid as well as catalyst. A plot of the rate constants for runs O, P, Q, and R against the molal ratio of ethanol to acetic acid indicated a distinct linear relation. Figure 4.6 shows a linear relation for all of the runs in the proportion series.

4.1.5 EFFECT OF TEMPERATURE:

Experiments were carried out at three different temperatures where the mole ratio of ethanol to acetic acid and the catalyst concentration was constant. Power was supplied to the magnetic stirrer with a Variac transformer.

The temperature-dependent term, the reaction rate constant, has been found in practically all cases to be well represented by Arrhenius' law (13):

$$k = k_0 e^{-E/RT}, \text{ where } k_0 = \text{Arrhenius constant}$$

or,

$$\log k = \left(-\frac{E}{R}\right) \frac{1}{T} + \log k_0$$

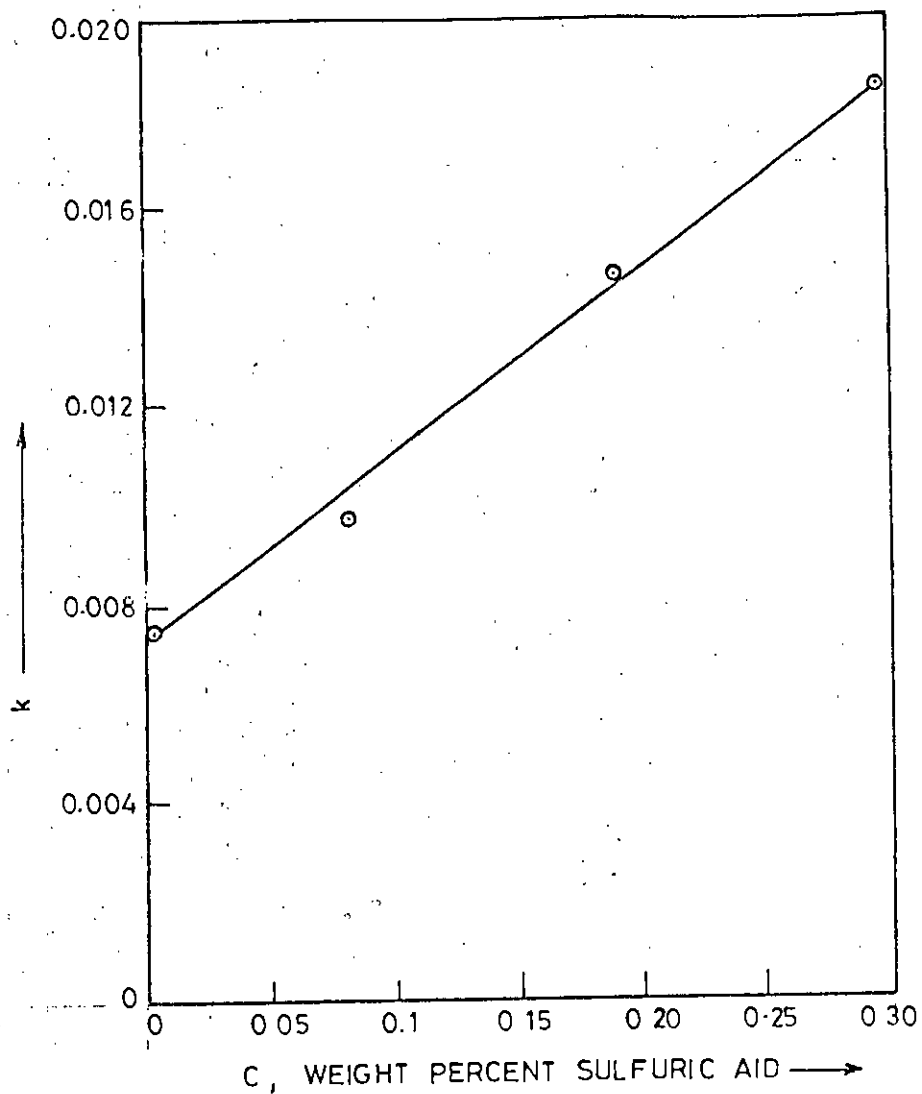


FIGURE 4.5 RELATION BETWEEN REACTION RATE CONSTANT k AND CATALYST CONCENTRATION AT 63°C.

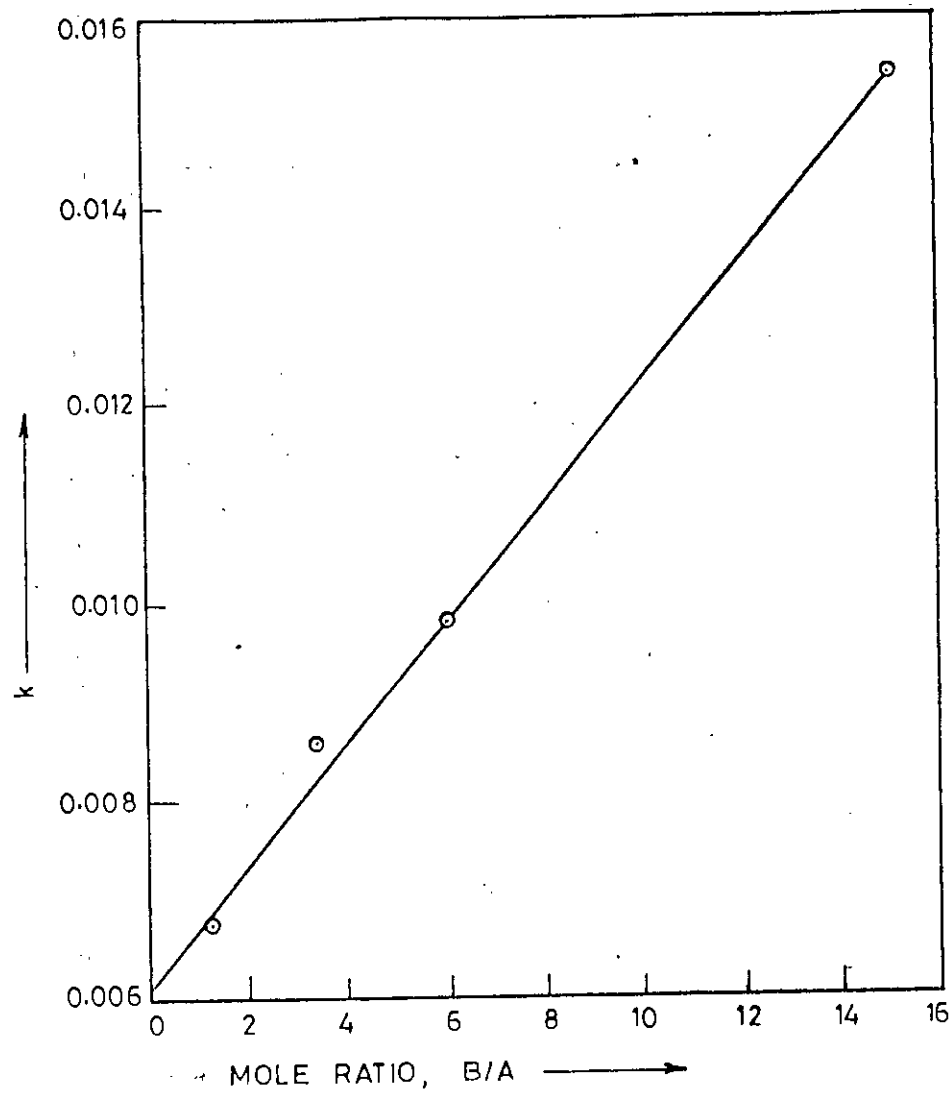


FIGURE 4.6 RELATION BETWEEN REACTION RATE CONSTANT k AND PROPORTIONS OF REACTANTS B/A AT 63°C.

A plot of $\log k$ vs $1/T$ should give a straight line with a slope of $-E/R$ and an intercept of $\log k_0$. Figure 4.7 is a plot of the logarithm of k against the reciprocal of the absolute temperature for data of table 4.4, where variables other than temperature were constant. The activation energy E has been estimated from the slope and its value is 7200.91 cal/gm mole.

Table 4.4 Estimation of k with variation of temperature, where

$$k = - \ln \left(1 - \frac{X_A}{X_{Ae}} \right) \left(\frac{M+X_{Ae}}{(M+1)t} \right)$$

Temp °C	1/T oABS ⁻¹	Time Minute	Mole Ratio M	Wt% catalyst	X m/l	k
48	0.00312	180	0.0845	6	0.3551	0.0034
63	0.00298	180	0.0845	6	0.6521	0.00969
75	0.00287	180	0.0845	6	0.796	0.0271

4.1.6 RATE CONSTANT EQUATION:

The rate of esterification reaction between ethyl alcohol and acetic acid catalysed with sulphuric acid depends upon temperature, catalyst concentration C and proportion of reactants (B/A). At constant temperature, the reaction rate depends upon catalyst concentration and proportion of reactants:

$$k = f(C, B/A)$$

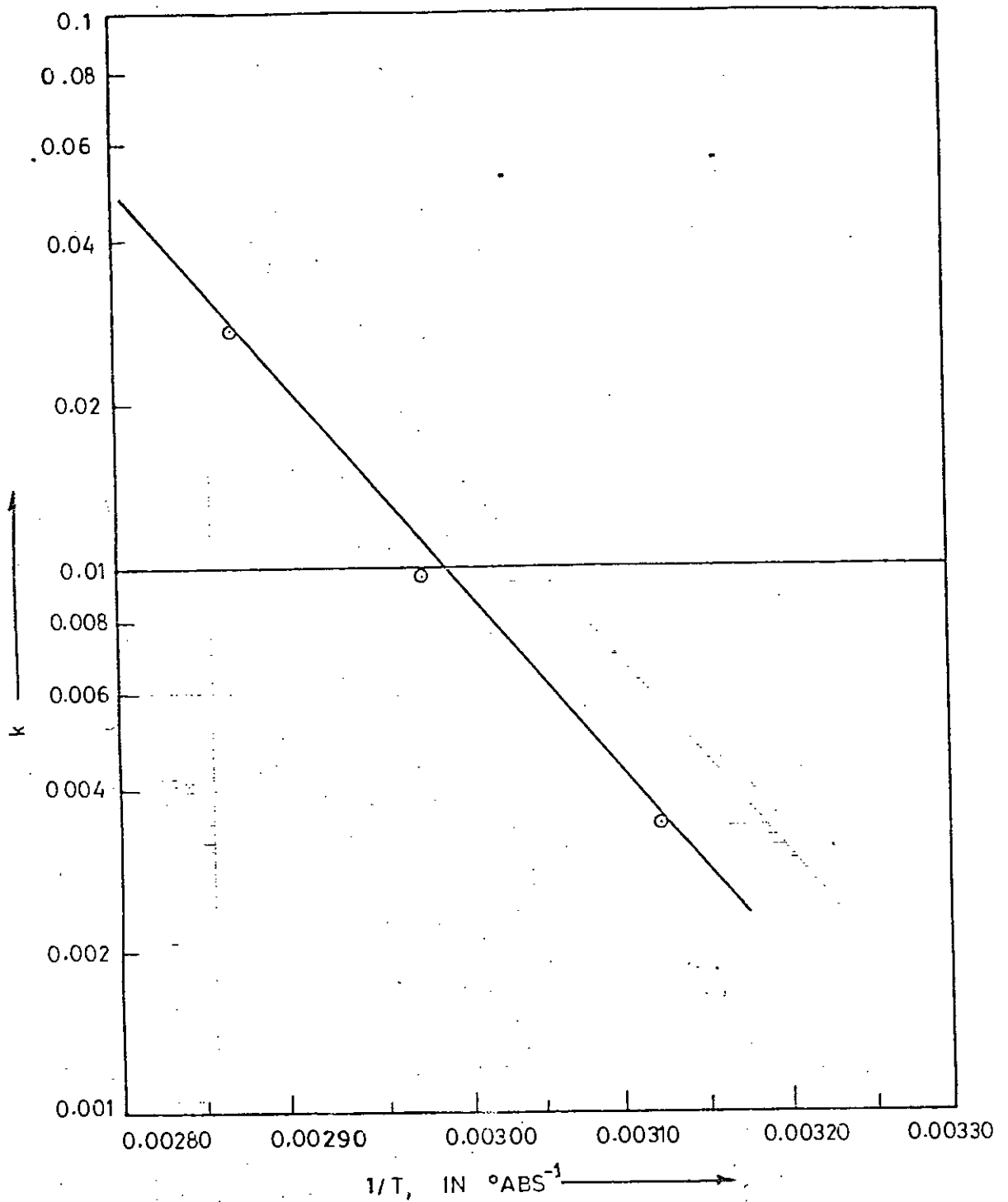


FIGURE 4.7 RELATION BETWEEN REACTION RATE CONSTANT k AND TEMPERATURE WITH 0.0845% CATALYST AND 6.00 MOLES ETHANOL PER MOLE ACETIC ACID.

In figure 4.5, the plot of k vs. C for run of constant mole ratio and in figure 4.6 the plot of k vs. B/A for runs of constant catalyst, both gave a linear relationship, indicating the proportionality of the rate constant with catalyst concentration and proportion of reactants at constant reaction temperature.

From the relations indicated in Figures 4.5 and 4.6, the following empirical equation was deduced to define the constant in terms of catalyst concentration and proportion of reactants, for application in the continuous esterification runs.

$$k = a + bC + c \frac{B}{A} C$$

For constant catalyst series, a plot of k vs. B/A gives a straight line with an intercept of $a + bC$ and a slope of cC . For constant mole ratio series, a plot of k vs. C gives a straight line with an intercept of a and a slope of $c \frac{B}{A} + b$. Thus the constants can be evaluated from the straight line relations. The relation obtained for the best straight line for these data is:

$$k = 0.0066 - 0.00592 C + 0.00683 \frac{B}{A} C \quad (4.5)$$

To check the validity of Equation 4.5, the values of k were recalculated from the molar ratio of ethanol to acetic acid and the catalyst concentration, as summarized in Table 4.4. All of the calculated values for k are in good agreement with the experimental values.

Table 4.5 Comparison of estimated and calculated values of k , at 63°C by the equation

$$k = 0.0066 - 0.00592 C + 0.00683 \frac{B}{A} C; \quad \frac{\text{Liters}}{(\text{Moles})(\text{Min})}$$

RUN	weight per cent of Catalyst (C)	Mole ratio (B/A)	Reaction rate constant k using time $t=180$ minut		
			Calculated k	Estimated k	Difference
K	0.00387	7.59	0.00787	0.00678	+0.00109
L	0.0830	7.59	0.00922	0.01041	-0.00119
M	0.1900	7.59	0.015622	0.01532	+0.000302
N	0.300	7.59	0.01759	0.02038	-0.00279
O	0.0845	1	0.00663	0.00668	-0.00005
P	0.0845	3.32	0.00823	0.008016	+0.000214
Q	0.0845	6.00	0.00969	0.00956	+0.00013
R	0.0845	15.00	0.0148	0.01476	+0.00004

4.1.7 EQUILIBRIUM CONSTANTS:

The equilibrium constant is defined as the ratio of the concentrations of products divided by the concentrations of reactants:

$$K = \frac{[\text{ester}] [\text{water}]}{[\text{ethanol}] [\text{acetic acid}]}$$

To determine the equilibrium constant for the esterification the free acidity was determined. After correction for the catalyst, the amount of unreacted acetic acid remaining could be calculated, which fixed the other compositions. Sample calculations appear in appendix B. The average values for the equilibrium constants are summarized in the following tables.

The concentration of catalyst has markedly no effect on the equilibrium constant with 7.6 moles of ethanol per mole of acetic acid at 63°C.

RUN	Catalyst Wt. %	K
K	0.0464%	0.0730
L	0.0830%	0.1047
M	0.1900%	0.1117
N	0.3000%	0.1130

The equilibrium constant is markedly affected by the proportions of reactants employed, however:

RUN	Molal Ratio Ethanol/Acetic Acid	K
O	1	0.4610
P	3.32	0.2110
Q	6.00	0.1017
R	15.00	0.0448

A decrease in the equilibrium constant for the reaction of acetic acid and ethanol was reported by Poznanski (7,8) who cites a variation in K from 1.0 to 6.8, depending upon the proportions of reactants used. Leys and

Othmer (9) found the average value for the equilibrium constant for the esterification of butanol and acetic acid about 2.35, which was considerably lower than the value of 4.24 reported by Menshutkin (7) for the uncatalyzed reaction at 155°C.

4.2 SEPARATION RESULTS AND DISCUSSION

The separation process may be divided into three stages. In the first stage, the end product obtained from the esterification reaction is distilled for a fraction and the ethyl alcohol and ethyl acetate is separated out from acetic acid and water. In the second stage, ethyl acetate is separated from the ethyl alcohol by solvent extraction with sodium carbonate solution and followed by final separation by distillation.

4.2.1 SEPARATION OF ETHYL ALCOHOL AND ETHYL ACETATE FROM ACETIC ACID AND WATER

A run with 0.0845 per cent by wt. of sulphuric acid catalyst and 3.32 mole ratio of ethanol to acetic acid was chosen. After 8 hours of reaction, the amount of acetic acid converted was found out by titration against standard sodium hydroxide solution. The amount of other products were calculated out from the stoichiometric relation. The components were: acetic acid 67.80 g, ethyl alcohol 360.61 g and ethyl acetate 273.00 g.

The above mixture was distilled. Distillate fractions between 78°C to 83°C, 83°C to 88°C and 88°C to 94°C were collected. Table (4.6) gives the amount of free acetic acid present in each sample.

Table 4.6 Amount of free acetic acid present in the samples.

Initial weight of the mixture : 409.2 g				
Distillate	Vol (ml)	Wt. (g)	Conc. of acid (m/l)	Amount of free acetic acid (g)
Sample 1 78 ^o C to 83 ^o C	471	398.35	0.0282	0.7976
Sample 2 83 ^o C to 88 ^o C	137	113.00	0.069	0.5677
Sample 3 88 ^o C to 94 ^o C	121	98.42	0.1728	1.256
Total acid =				2.6213 g
Bottom product	129	121.51	8.0532	62.38
Bottom product	Amount of water plus others =			59.13 g
			others =	10.54 g

From the above table, the total amount of acetic acid in the top and bottom product was found to be 65g. Comparing to 67.8g of acid originally present, the variation is 2.8g. This may be considered to be within the experimental error range.

The boiling points of the components are: ethyl acetate 77.1^oC, ethyl alcohol 78.4^oC, acetic acid 118.1^oC and water 100^oC. It can be assumed that the first sample (collected between 78^oC to 83^oC) contains only ethyl alcohol and ethyl acetate and it is free from water and acetic acid. The density of the above sample was 0.8458 g/cc and the percentage of ethyl alcohol was 49% and that of ethyl acetate was 51%.

4.2.2 SEPARATION OF ETHYL ACETATE FROM ETHYL ALCOHOL BY SOLVENT EXTRACTION

The method of separation of ethyl acetate from ethyl alcohol is described in chapter 3.2. The results obtained are presented in table (4.7). Since the distillate is collected between 78°C - 92°C, it can be assumed that it is free from water and acetic acid.

Table 4.7 Results for the separation of ethyl acetate from ethyl alcohol.

TRIAL 1 PROPORTION 1:1									
Components	Vol (cc)	Wt (g)	Bottom Layer Wt (g)	Extract Wt. (g)	Phase Vol (cc)	Distillate 78°C-92°C Wt. (g)	Den- sity g/cc	Percentage Ethyl Acetate	Ethyl Alcohol
Ethyl Alcohol	80	62.84							
Ethyl Acetate	100	86.62	178.31	160.62	180	91.94	0.8772	79%	21%
Sodium Carbonate Solution in water	180	233							
TRIAL 2 PROPORTION 1:2									
Ethyl Alcohol	80	62.25							
Ethyl Acetate	100	87.24	429.91	107.18	122	64.60	0.8831	85%	15%
Sodium Carbonate Solution in water	360	388.84							
TRIAL 3 PROPORTION 1:3									
Ethyl alcohol	80	63.34							
Ethyl acetate	100	86.76	640.56	70.40	80	50.02	0.8874	89%	11%
Sodium carbonate Solution in water	540	570.82							
TRIAL 4 PROPORTION 1:4									
Ethyl alcohol	80	62.18							
Ethyl acetate	100	89.09	838.91	68.47	79	50.55	0.8866	88%	12%
Sodium carbonate Solution in water	720	762.11							

For solvent extraction the phase and equilibrium diagram of the system was not available and hence solvent quantity could not be estimated. A 10% sodium carbonate solution was used and the effect of solvent to feed ratio on product composition and recovery was studied. The results show that an 1:1 solvent-feed ratio gives the optimum quantity and composition. The composition of ethyl acetate in the final product is found to be 79%. The overall recovery of the whole separation process is calculated to be about 62%.

Some trial runs were made to recover the absorbed ethyl alcohol from the raffinate carbonate solution by batch distillation. It was found that the regenerated solution contains about 70% ethyl alcohol.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS5.1 CONCLUSIONS

The following conclusions can be made:

1. The reaction involved in the catalytic esterification of ethanol and acetic acid at elevated temperature ($63^{\circ}\text{C} \pm 1^{\circ}\text{C}$, or higher) is of the first order reversible kinetically upto 80% conversion.
2. The rate constant is a linear function of catalyst concentration (C) and mole ratio of reactants ethanol and acetic acid (B/A) at constant temperature and can be represented by the following linear equation:

$$k = 0.0066 - 0.00592 C + 0.00683 \frac{B}{A} C.$$
3. At temperatures in the range of 48°C to 75°C ., the logarithm of the rate constant is proportional to the reciprocal of absolute temperature. A distinct linear relation is also found between the rate constant and catalyst concentration and molal ratio of ethanol to acetic acid. The concentration of catalyst has markedly no effect on the equilibrium constant, but the equilibrium constant is markedly affected by the proportions of reactants employed.
4. Solvent extraction and fractional distillation method can be used for ester separation from the unreacted reactants. Sodium carbonate solution can be used as solvent. A solvent-feed ratio of 1:1 gives the optimum quantity and composition, the purity of ethyl acetate found is 79%. The overall recovery of the whole separation process is calculated to be about 62%.

5.2 RECOMMENDATIONS

The following recommendations may be made for any further work in this subject.

1. Reaction should be carried out at higher temperature range.
2. Experiments should be performed to obtain phase and equilibrium data on ethyl acetate - ethyl alcohol sodium carbonate solution. Other separating procedure such as azeotropic distillation, adsorption etc. may be tried for better product recovery.
3. To study the effect of mole ratio of the reactants on the reaction rate uniquely experiments should be carried out keeping the catalyst concentration constant with respect to the rate controlling reactant.

NOMENCLATURE

A	=	Acetic acid originally present (moles, or moles per liter).
B	=	Ethanol originally present (same units as A).
C	=	Catalyst concentration, weight percent of sulphuric acid.
a	=	AB
b	=	(A + B + W/K)
c	=	1 - 1/K
E	=	Activation energy of the reaction, Cal/gm mole.
e	=	equilibrium point
k, k ₁	=	reaction rate constants, litres moles ⁻¹ minute ⁻¹
k ₂	=	reverse reaction rate constant
K	=	equilibrium constant = k ₁ /k ₂
M	=	Mole ratio, $\frac{B}{A}$, dimensionless
q	=	$4ac - b^2$, where $b^2 > 4ac$
R	=	Ideal gas law constant, Cal/gm mole °K
t	=	Time, minutes
T	=	Temperature °K.
W	=	Water originally present (same units as A).
X	=	Amount of acetic acid converted, (same units as A).

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APPENDIX ADeduction of equation 4.2

For the reversible reaction -

$$\begin{aligned} \frac{dX}{dt} &= k_1(A-X)(B-X) - k_2 X(W+X) \\ &= k_1(AB - AX - BX + X^2) - k_2 WX - k_2 X^2 \\ &= k_1 AB + (-Ak_1 - Bk_1 - k_2 W) X + (k_1 - k_2) X^2 \\ &= k_1 AB + \left(-A - B - \frac{k_2}{k_1} W\right) X + \left(1 - \frac{k_2}{k_1}\right) X^2 \end{aligned}$$

$$\text{Let, } a = AB$$

$$b = -(A+B+W/K)$$

$$b = -(A+B+W/K)$$

$$K = k_1/k_2$$

$$c = 1 - \frac{k_2}{k_1} = 1 - \frac{1}{K}$$

$$\frac{dX}{dt} = k(a+bX+cX^2), \text{ This integrates into}$$

$$\int_0^X \frac{dX}{cX^2 + bX + a} = \int k dt$$

$$\text{or, } \frac{1}{c} \int_0^X \frac{dX}{X^2 + \frac{b}{c} X + \frac{a}{c}} = kt$$

$$\text{or, } \frac{1}{c} \frac{dx}{\left(X + \frac{b}{2c}\right)^2 + \frac{4ac-b^2}{4c^2}}$$

$$\text{Putting } X + \frac{b}{2c} = z \quad \text{and} \quad \sqrt{\frac{4ac-b^2}{4c^2}} = m$$

when $b^2 > 4ac$, this reduces to the form

$$\frac{1}{c} \int_0^x \frac{dx}{z^2 - m^2} = kt,$$

$$\text{or, } \left[\frac{1}{2cm} \ln \frac{z-m}{z+m} \right]_{\frac{b}{2c}}^{x + \frac{b}{2c}} = kt$$

$$\text{or, } \frac{1}{2c \sqrt{\frac{4ac-b^2}{4c^2}}} \ln \frac{x + \frac{b}{2c} - \sqrt{\frac{4ac-b^2}{4c^2}}}{x + \frac{b}{2c} + \sqrt{\frac{4ac-b^2}{4c^2}}} - \frac{1}{2c \sqrt{\frac{4ac-b^2}{4c^2}}} \ln \frac{\frac{b}{2c} - \sqrt{\frac{4ac-b^2}{4c^2}}}{\frac{b}{2c} + \sqrt{\frac{4ac-b^2}{4c^2}}} = kt$$

Let $q = 4ac - b^2$, where $b^2 > 4ac$

$$\frac{1}{\sqrt{-q}} \ln \frac{2cX + b + \sqrt{-q}}{2cX + b + \sqrt{-q}} - \frac{1}{\sqrt{-q}} \ln \frac{b - \sqrt{-q}}{b + \sqrt{-q}} = kt$$

APPENDIX BCalculation for equilibrium constantsCONSTANT MOLE RATIO :

$$\text{Mole ratio} = \frac{\text{Ethanol}}{\text{Acid}} = 7.59$$

RUNS	C_{A0} m/l	C_{B0} m/l	Unreacted acid C_A m/l	Acetic acid converted $C_{A0} - C_A$ m/l	Water Produced m/l	Ester Produced m/l	$K = \frac{[\text{ester}][\text{water}]}{[\text{ethanol}][\text{acetic acid}]}$
K	2.000	15.180	0.511	1.489	1.489	1.489	0.0730
L	2.000	15.180	0.217	1.783	1.783	1.783	0.1047
M	2.000	15.180	0.158	1.842	1.842	1.842	0.1117
N	2.000	15.180	0.148	1.852	1.852	1.852	0.1130

CONSTANT CATALYST CONCENTRATION:

Catalyst concentration = 0.0845% by weight.

RUNS	Mole Ratio	C_{A0} m/l	C_{B0} m/l	Unreacted acid m/l	Acetic acid converted m/l	Water Produced m/l	Ester Produced m/l	$K = \frac{[\text{ester}][\text{water}]}{[\text{ethanol}][\text{acetic acid}]}$
O	1	8.701	8.700	2.794	5.907	5.907	5.907	0.461
P	3.32	4.000	10.19	1.068	2.932	2.932	2.932	0.2110
Q	6.00	2.460	14.760	0.539	1.921	1.921	1.921	0.1017
R	15.00	1.074	16.110	0.194	0.880	0.880	0.880	0.0448

APPENDIX C

EXPERIMENTAL DATA

Time HR	Free Acidity $C_A + c$ m/l	Catalyst Correction m/l	C_c	Actual Acetic Acid $C_A = C_{A+c} - C_c$ m/l	$\frac{C_A}{C_{A_0}}$	Acetic Acid Converted $X_A = 1 - \frac{C_A}{C_{A_0}}$
RUN K	$H_2SO_4 = 0.0464\%$ by wt.			$63^\circ C$	$B/A = 7.6$	$A_0 = 2.00$ m/l
0	2.000	-		2.000	1	0
1	1.4319	0.0039		1.428	0.714	0.286
2	1.1008	0.0039		1.097	0.549	0.451
3	0.860	0.0039		0.856	0.428	0.572
4	0.6512	0.0039		0.647	0.324	0.676
5	0.5819	0.0039		0.578	0.289	0.711
6	0.5478	0.0039		0.544	0.272	0.728
7	0.5346	0.0039		0.531	0.265	0.735
8	0.5148	0.0039		0.511	0.255	0.745

RUN L	$H_2SO_4 = 0.0830\%$ by wt.		$63^\circ C$	$B/A = 7.6$	$A_0 = 2.000$ m/l
0	2.000	-	2.000	1.000	0
1	1.1808	0.0035	1.177	0.589	0.411
2	0.861	0.0035	0.858	0.429	0.571
3	0.5561	0.0035	0.5492	0.2746	0.7254
4	0.415	0.0035	0.4081	0.2041	0.7959
5	0.332	0.0035	0.325	0.1626	0.8374
6	0.2609	0.0035	0.2540	0.1270	0.873
7	0.2324	0.0035	0.2255	0.1128	0.8872
8	0.2241	0.0035	0.2172	0.1086	0.8914

Time HR	Free Acidity $C_A + c$ m/l	Catalyst Concentra- tion C_c m/l	Actual Acetic Acid $C_A = C_A + c - C_c$ m/l	$\frac{C_A}{C_{A0}}$	Acetic Acid Converted $X_A = 1 - \frac{C_A}{C_{A0}}$
RUN M	$H_2SO_4 = 0.19\%$ by wt.		$63^{\circ}C$	$B/A = 7.6$	$A_0 = 2.000$ m/l
0	2.000	-	2.000	1.000	0
1	0.880	0.0159	0.8641	0.432	0.568
2	0.490	0.0159	0.4741	0.237	0.763
3	0.2822	0.0159	0.2663	0.1332	0.8669
4	0.2081	0.0159	0.1922	0.0961	0.9039
5	0.1951	0.0159	0.1792	0.0896	0.9104
6	0.1789	0.0159	0.1630	0.0815	0.9185
7	0.1743	0.0159	0.1584	0.0792	0.9208
8	0.1743	0.0159	0.1584	0.0792	0.9208

Time HR	Free Acidity $C_A + c$ m/l	Catalyst Correction C_c m/l	Actual Acetic Acid $C_A = C_A + c - C_c$ m/l	$\frac{C_A}{C_{A0}}$	Acetic Acid Converted $X_A = 1 - \frac{C_A}{C_{A0}}$
RUN N	$H_2SO_4 = 0.3\%$ by wt.		$63^{\circ}C$	$B/A = 7.6$	$A_0 = 2.000$ m/l
0	2.000	-	2.000	1.000	0
1	0.7134	0.02508	0.688	0.344	0.656
2	0.4141	0.02508	0.389	0.195	0.805
3	0.2484	0.02508	0.223	0.112	0.888
4	0.2064	0.02508	0.181	0.091	0.909
5	0.19608	0.02508	0.171	0.086	0.914
6	0.18708	0.02508	0.162	0.081	0.919
7	0.17544	0.02508	0.150	0.075	0.925
8	0.17286	0.02508	0.148	0.074	0.926

Time HR	Free Acidity $C_A + c$ m/l	Catalyst Concentration C_c m/l	Actual Acetic Acid $C_A = C_{A+c} - C_c$ m/l	$\frac{C_A}{C_{A0}}$	Acetic Acid Converted $X_A = 1 - \frac{C_A}{C_{A0}}$
RUN O	$H_2SO_4 = 0.0845\%$ by wt.		$63^\circ C$	$B/A = 1$	$A_0 = 8.7014$ m/l
0	8.7014	-	8.7014	1.000	0
1	6.4232	0.00795	6.415	0.737	0.263
2	5.1929	0.00795	5.185	0.596	0.404
3	4.2281	0.00795	4.220	0.485	0.515
4	3.6190	0.00795	3.6111	0.415	0.585
5	3.28925	0.00795	3.28129	0.3771	0.6229
6	3.0561	0.00795	3.0481	0.3503	0.6497
7	2.9490	0.00795	2.9411	0.338	0.662
8	2.80197	0.00795	2.7940	0.3211	0.6789

RUN P	$H_2SO_4 = 0.0845\%$ by wt.		$63^\circ C$	$B/A = 3.32$	$A_0 = 4.000$ m/l
0	4.000	-	4.000	1.000	0
1	2.6853	0.00734	2.678	0.670	0.330
2	1.9960	0.00734	1.989	0.497	0.503
3	1.6797	0.00734	1.6724	0.4181	0.5819
4	1.30414	0.00734	1.2968	0.3242	0.6758
5	1.20142	0.00734	1.19408	0.2985	0.70148
6	1.1457	0.00734	1.1384	0.2846	0.7154
7	1.1077	0.00734	1.1004	0.2751	0.7249
8	1.07534	0.00734	1.0680	0.2670	0.733

Time HR	Free Acidity C_{A+c} m/l	Catalyst Concentration m/l	Actual Acetic Acid $C_A = C_{A+c} - C_c$ m/l	$\frac{C_A}{C_{A0}}$	Acetic Acid Converted $X_A = 1 - \frac{C_A}{C_{A0}}$
RUN Q $H_2SO_4 = 0.0845\%$ by wt.			$63^\circ C$	$B/A = 6.00$	$A_0 = 2.4604$ m/l
0	2.4604	-	2.4604	1.000	0
1	1.5424	0.00714	1.5353	0.624	0.376
2	1.05774	0.00714	1.0506	0.427	0.573
3	0.86311	0.00714	0.8559	0.3479	0.6521
4	0.7062	0.00714	0.6991	0.284	0.716
5	0.6468	0.00714	0.6397	0.260	0.740
6	0.6099	0.00714	0.6028	0.245	0.755
7	0.57303	0.00714	0.56589	0.2299	0.770
8	0.5457	0.00714	0.5390	0.2191	0.7809

RUN R $H_2SO_4 = 0.0845\%$ by wt.			$63^\circ C$	$B/A = 15$	$A_0 = 1.0742$ m/l
0	1.0742	-	1.0742	1.000	0
1	0.5397	0.00693	0.533	0.496	0
2	0.3337	0.00693	0.327	0.304	0.696
3	0.261	0.00693	0.254	0.236	0.764
4	0.230	0.00693	0.223	0.208	0.792
5	0.212	0.00693	0.205	0.191	0.809
6	0.20673	0.00693	0.1998	0.186	0.814
7	0.204	0.00693	0.197	0.183	0.817
8	0.201	0.00693	0.194	0.181	0.819

APPENDIX D

Reproducibility data for run L

Condition: $T = 63^{\circ}\text{C}$ catalyst concentration = 0.0830% by wt.

Mole ratio = 7.6, Initial conc. of acid $C_{A0} = 2.00$ m/l

Time HR	0	1	2	3	4	5	6	7	8
Acid concentration C_A m/l	2.00	1.201	0.863	0.551	0.398	0.332	0.255	0.223	0.206
C_A/C_{A0}	1.00	0.601	0.432	0.276	0.199	0.166	0.128	0.112	0.103

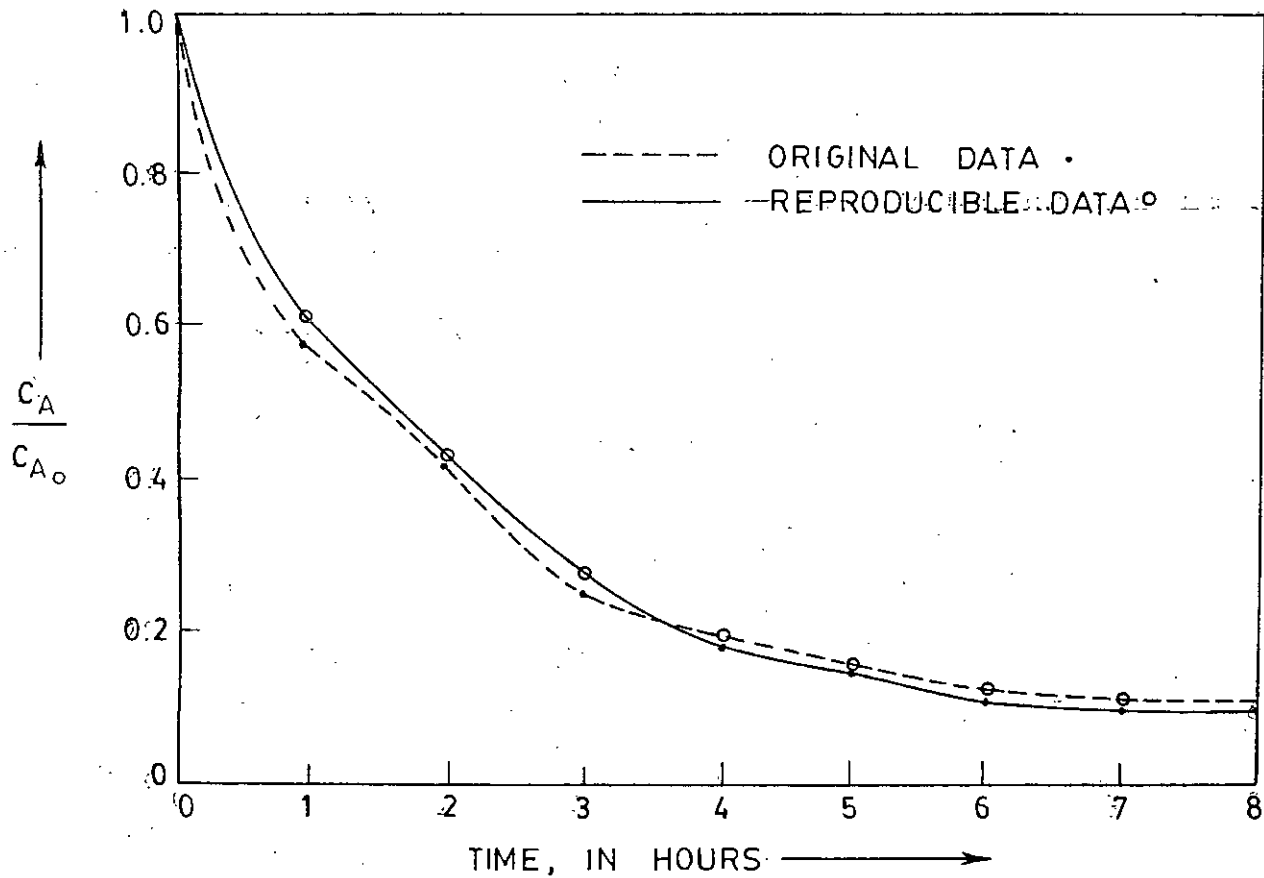


FIGURE D1 REPRODUCIBILITY FOR RUN L

APPENDIX ESample calculations for run L

Conditions: $T = 63^{\circ}\text{C}$, catalyst concentration $C = 0.0830\%$ by wt.

Mole ratio $\frac{B}{A} = 7.6$, Initial conc. of acid $C_{A0} = 2.00 \text{ m/l}$, $X_{Ae} = 0.891$.

Acetic acid A = 1 mole = 57.2 c.c.

Ethyl alcohol B = 7.6 mole = 443.2 c.c

Equilibrium constant K

C_{A0}	C_{B0}	Unreacted Acid C_A	Acetic acid converted $C_{A0} - C_A$	Water produced	Ester produced	$K = \frac{[\text{ester}][\text{water}]}{[\text{ethanol}][\text{acetic acid}]}$
m/l	m/l	m/l	m/l			
2.000	15.180	0.217	1.783	1.783	1.783	0.1047

Estimation of k

$$\text{where, } k = 0.0066 - 0.00592 C + 0.00683 \frac{B}{A} C$$

$$= 0.01041$$

Calculation of k

$$\text{where, } k = -\ln \left(1 - \frac{X_A}{X_{Ae}} \right) \left(\frac{M+X_{Ae}}{M+1} \right) (1/t)$$

$$= -\ln(0.186) \left[\frac{7.6 + 0.891}{7.6 + 1} \right] \left[\frac{1}{180} \right]$$

$$= 0.00922$$

Data for curve plotting

Time HR	X_A m/l	$1 - \frac{X_A}{X_{Ae}}$	$\frac{X}{A-x}$
0	0	1.000	0
1	0.411	0.539	0.259
2	0.571	0.359	0.4000
3	0.725	0.186	0.569
4	0.796	0.107	0.661
5	0.837	0.061	0.720
6	0.873	0.021	0.775
7	0.887	0.005	0.797
8	0.891	0	0.803

