SYNTHESIS OF IMMOBILIZED MOLYBDENUM CATALYST FOR OXIDATION PROCESSES

by

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A Thesis Submitted to
The Postgraduate School
Ahmadu Bello University.

In Partial Fulfillment of the
Requirement for the Degree of
M.Sc. Chemical Engineering
In Department of Chemical.Engineering,
faculty of Engineering
Ahmadu Bello University,
ZARIA

JUNE, 1994

CERTIFICATION

This research report entitled 'SYNTHESIS OF IMMOBILIZED MOLYBDENUM CATALYST FOR OXIDATION PROCESSES", by IYUKE, Sunny Esayegbemu meets the regulations governing the award of the degree of Master of Science (Chemical Engineering) of Ahmadu Bello University, Zaria, and is approved for its contribution to knowledge and literary presentation.

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I hereby declare that this thesis has been designed and composed by myself and it is a record of my own research work. That it has not been presented in any previous application for a higher degree. All sources of information are specifically acknowledged by means of references.

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JUNE, 1994.

DEDICATION

This work is dedicated to my Father in heaven and my father on earth; viz:

The LORD and His Glory, and

IYUKE, JOSIAH EFEYEDIA.

ACKNOWLEDGEMENT

"Be your brother's keeper", has become the driving force in obtaining assistance from various sources which have made this work successful.

My whole-hearted regard and gratitude to my supervisor, Dr. J.O. Oludipe, whose bright ideas, professional advice and constant attention in criticism have made this research a success.

My special thanks and respect go to the head of the Chemical Engineering Department, Prof. R.O. Ebewele and Prof. S.S. Adefila, for their fatherly advice, directive and rich encouragement throughout the length of my M.Sc degree programme. I also wish to acknowledge the special roles played by Dr. Ir. P. B. Onaji, Dr. J.O. Bello, Mr. Aderemi and every other lecturer of the Chemical Engineering department in giving me the scientific and engineering concepts I possess today. Also my thanks go to the entire non-academic staff-members of this department for their helps and contributions to the success of this work.

I remain grateful to my senior sisters Mrs Victoria J. Emakpo, Mrs. Vero J. Akpojotor, my younger sisters and brothers and the entire Iyuke family.

Also, I wish to express my concern and satisfaction for Flora Agba in her patience, Kate Onochie for her care, Mr.

Isaac Agbamisa, Miss Mercy Waje, Mr. Solomon Agidi, Abednigo Idibie for his brotherhood, and the lots of others I could not mention at this moment.

ABSTRACT

This research work reports a general concept in liquid phase oxidative catalysis which combined the advantages of homogeneous and heterogeneous catalysis, by the use of a resin immobilized molybdenum catalyst.

The immobilized molybdenum catalyst is prepared by a sorption process, whereby the molybdenum ions are anchored on the active sites of a polymer resin (Amberlite IRA-400 in CI form). Experimental observations suggest that the polymer resin probably has two active sites for sorption, and this led to the development of a model equation for two parallel first-order reactions with a common product for the sorption process as:

$$[Mo] = 3.47 \times iO^{-5}(0.45e^{-0.081t} + (1 - 0.45)e^{-0.026t})$$

For comparison of the polymer immobilised catalyst versus the unsupported (homogeneous) catalyst, maleic acid ($pK_{.} = 1,83$, $pK_{,} = 6.50$) was selected as the model substrate, because it can be smoothly oxidized to cis-epoxysuccinic acid ($pK_{1,} = 1.98$, $pK_{2.,} = 3.92$), using hydrogen peroxide in concert with ammonium molybdate. The rate of the epoxidation reactions was monitored by analysing the concentrations of maleic acid, hydrogen peroxide, and the volume of oxygen evolved due to the inevitable decomposition of hydrogen peroxide in aqueous solutions. A maximum obtainable yield of the epoxide was 84% at the conversion of 97% and selectivity

of 87% based on $H._2O_2$ consumed with the immobilized catalyst, while the corresponding values with homogeneous catalyst was 56% at the conversion of 76% and selectivity of 74%.

A detailed exploitation of the immobilized catalyst (in pseudo-homogeneous system) resulted in the proposition of a mathematical expression for the rate of epoxidation (based on H_2O_2 consumed).

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LIST OF SYMBOLS

Symbol	Description	Dimension
E	Activation energy	J
k	Reaction rate constant	$(mol/mi)^{1-n}$
K	Equilibrium constant.	dimensionless
L	litre, length	m
m	mass	g
M	Mole	mole
n	order or reaction	dimensionless
o(subscript)	initial condition	dimensionless
r	rate	mole/min
R	Gas constant	J/gm mol ^{0}k
t	time	min
T	Temperature	^{0}C
V	Volume	ml
W	Weight	gm
X	conversion	dimensionless
a	effective rate constant	dimensionless
θ	Fraction of sorbed molecules by the active site.	dimensionless
[ ]	Analytical concentration	mole/l

Abbreviations:

Cat.	Catalyst
im	immobilized
M.A.	maleic acid
sorp.	sorption
Vs	Versus

CHAPTER ONE

1. INTRODUCTION

The utility of materials such as metallic oxides of transition metals, as soluble oxidation catalyst, is often impaired by the practical and economic difficulties of using high catalyst concentrations without obtaining contaminated products. These problems had led to the development of the fact that, a number of advantages exist in depositing catalytically active metals on a support such as alumina, charcoal, silica or polymer.

In this study, special interest is given to the polymer support known as the ion exchange resin. The metal can be highly dispersed, perhaps as small crystallites throughout the pore system of the support. As a result, a large active metal surface is produced relative to the weight of metal used, and this is especially advantageous with precious metals. In a suitable pellet, granular or other physical form, a supported metal catalyst provides for flow of gases through the reactor and then diffusion of reactants through the pores to the active metal. The support can also improve dissipation of reaction heat, retard the sintering of metal crys tallites with resultant loss of active surface, and increase poison resistance, thus promoting a longer working life for the catalyst. Hence, supported metal catalysts are widely used in chemical processing.

In this research work therefore, a general concept in liquid-phase oxidation catalysis which circumvent these problems by the use of a reusable insoluble and inert macromolecule (Resin) containing the catalyst (Molybdenum) element as an integral part. Thus, an insoluble polymeric molybdenum derivative like its soluble monomeric molybdenum counter part is capable of functioning as an oxidative catalyst. For comparison of the polymer immobilized

(supported) catalyst versus the unsupported catalyst, maleic acid [pK_1 = 1.83 pk_2 = 6.50, (Handbooks of chemistry and physics, 46th edition)] was selected as the model substrate because it can be smoothly oxidized to cis-epoxysuccinic acid [pK_1 = 1.98, pk_2 = 3.92. (Wasserman, 1930)], using hydrogen peroxide in concert with Ammonium molybdate in a batch reactor. The degree of conversion X at time t can be conveniently determined by the iodine number determination of the olefinic unsaturation of maleic acid using N-Bromosuccinimide method (Mathur and Narang, 1975); iodometric titration for the hydrogen peroxide, and the concentration of oxygen evolved from the decomposition of hydrogen peroxide in aqueous solution.

The solid catalyst was prepared by treatment of a quarternary ammonium ion exchange resin (Amberlite IRA-400, Rohm and Haas Co.) in the chloride form with a solution of ammonium molybdate at about pH = 5. The chloride form of anion exchange resin is chosen because, the hydroxide form is a somewhat weaker base than the chloride form, giving the latter certain advantages for commercial water purification and it is generally used in analysis (Louis, M. 1963).

The primary objectives of this research are to synthesis polymer resin immobilized molybdenum catalyst for application in liquid-phase oxidation reactions in a batch reactor system and to establish its advantages over purely homogeneous molybdenum catalysts in terms of such parameters as stability, activity, selectivity, yield, ease of separation from reaction mixture, longer life span, more industrial and economic viability. The epoxidation/hydroxylation reaction of maleic acid with hydrogen peroxide was employed as the model reaction for the purpose of parameters evaluation.

CHAPTER TWO

2. LITERATURE REVIEW

There has been a growing interest in the scientific world concerning catalysis by supported complexes since about 1970. The starting goal was the following: when one anchors an homogeneous catalyst to a support it should be possible to accumulate the advantages of homogeneous catalysis, namely activity and selectivity and the advantages of heterogeneous catalysis, namely the easy separation and reuse of the costly catalyst. Besides these starting goals which have been reached in many cases, the subject of catalysis by supported complexes which overlaps homogeneous and heterogeneous catalysis has been the origin of new ideas, new synthesis, new concepts and unexpected results in both fields. Recently neither homogeneous nor heterogeneous catalysis can ignore the real possibilities of these new types of catalysts which are already recognised as the third generation of catalyst (Basset and Smith, 1977.)

In the last twenty six years, many developments have taken place in the field of catalysis by supported complexes. This has led to continued interest in this field of study.

The first approach in this field consisted of anchoring a homogeneous catalyst onto a support and trying as a primary goal to keep its molecular nature in order to preserve its activity and selectivity. In this effect, two methods have been developed:

(1) anchoring the complex on a polymer support which is not soluble in the mixture.

(2) anchoring the complex on an insoluble inorganic oxide.

The second approach is concerned with the anchoring of homogeneous catalyst on a support and trying as a primary goal to attain as high as possible activity and selectivity without any care about the fact that the molecular nature of

the catalyst is kept or not. In this case, most of the works have dealt with in organic oxides as supports and two main approaches have been tried:

(1) direct interaction of a homogeneous catalyst with a support,

(2) reaction of an organometallic with the functional groups of a support with at least a partial loss of its molecular nature.

2.1 MOLECULAR NATURE OF THE CATALYST

2.1.1 The Polymer as a Support

This field has certainly been the most intensively studied from a fundamental point of view. A great deal of work has been carried out by Grubbs et al (1973). Using Polystyrene-divinyl benzene cross linked polymers, the most common technique used is to link a phenyl phosphine group to a benzene ring of the polymer.

An interesting feature of these supported complexes is related to the possibility of multi-functionality obtained by anchoring on the same polymer two different catalysts able to carry two different reactions in a two step process. A typical example is the reaction of cyclo-oligomerization of butadiene on a nickel complex and then the subsequent hydrogenation of the cyclic dimers and trimmers to the saturated hydrocarbons with the WILKINSON catalyst. In the same way the cyclic dimers or trimmers can be selectively hydrogenated with a rhodium, carbonyl hydride complex into linear and branched aldehyde. This multi-functional process represents certainly an interesting approach of catalysis by supported complex but it should be pointed out also that the performances obtained certainly do not overcome what should be expected with a two stages process with two grafted catalysts.

It appears that kinetic problems related to comparison between homogeneous catalysis and catalysis by supported complexes are very complicated and many parameters are playing

a role simultaneously or separately. Among these parameters, diffusion of the substrate into the polymer "porous" system is certainly one of the most important. It appears now that this diffusion can be related to the size of the substrate as it occurs also in the frame work of a Zeolite support. This might be purely a kinetic effect of diffusion. This size effect has been mainly studied by Grubbs et al (1973). Diffusion of the substrate in to the polymer is also related to the chemical affinity of the substrate towards the support. This effect is clearly demonstrated in the catalytic hydrogenation of amino acid precursors (Minoru et al, (1977). Whereas, the WILKINSON catalyst grafted on a polystyrene-divinylbenzene support does not result in the slightest activity for the phenyl-alanine hydrogenation, the presence of dimethyl amino groups on some phenyl ring of the polymer result in a good supported catalyst.

2.1.2 Inorganic Oxides as a Support

A great deal of work (Howell, 1975) has been carried out by British petroleum which has intensively used silica as a support for many complexes and has investigated a wide range of catalytic reactions. The most interesting aspect of their work is related to the development of new methods for anchoring many homogeneous catalysts on silica.

2.2 THE NATURE OF ION-EXCHANGE RESIN

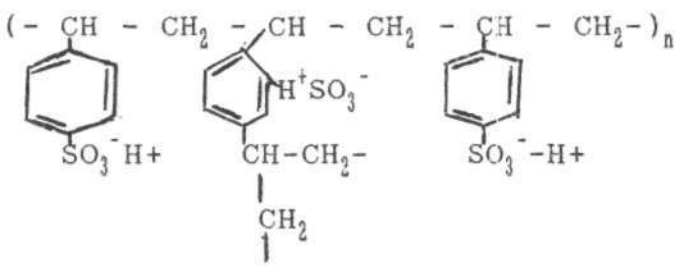
Ion exchange ranks with solvent extraction, precipitation, and distillation as a routine method of analytical separation. Its primary use is in organic and biochemistry. There it complements vapour-phase chromatography, being most useful in those cases where vapour-phase chromatography is difficult or impossible.

A solid ion exchanger is essentially a poly-electrolyte with ions of one charge anchored to an insoluble but permeable matrix, the ions of opposite charge being small and mobile and

therefore exchangeable with other ions.

Naturally occurring ion exchangers such as clay minerals, and many more have little or no application in chemical analysis. Most analytical work is done with the ion- exchange resins. The most useful ion-exchange resins are those based on cross-linked polystyrene (Louis Meites, 1963). The two major ion-exchange resins are:

(a) Cation Exchanger, for example, polystyrene-sulphonic acid with the structural formula as:



The middle ring in this formula is introduced into the polymer as a molecule of divinylbenzene. The liquids styrene and divinylbenzene are copolymerized by "bead polymerization" yielding solid transparent beads that are then treated with fuming sulphuric acid. Of course the sulphuric acid groups do not necessarily go into the p-position as indicated in the formula. The sulphunic acid groups are fully ionized in water, and the hydrogen ions can be exchanged for any cations desired. The resulting resin is called a cation exchanger.

(b) Anion Exchanger

To make an " anion exchanger" one may start with the same styrene divinylbenzene copolymer, and by treatment with chloromethyl ether and a tertiary amine one introduces

functional groups such as

$$- CH_2 - N(CH_3)_3^+ \; CL^- \quad \text{or} \quad - CH_2 - N(CH_3)_2 \; CH_2 \; CH_2 \; OH^+ \; CL^-$$

Type I Type II

Here the chloride ions can be exchanged for any desired anions, including hydroxide ions, and the corresponding hydroxides are strong bases. The hydroxide form of a type II resin is a some what weaker base than that of type I, giving it certain advantages for commercial water purification, but otherwise the two types of resin are very similar. Type I resin are generally used in analysis. The resulting resin contains strongly basic quaternary ammonium groups known as strongly basic anion exchange resins.

All these resins are available with different degrees of cross-linking. The cross-linking is expressed as the proportion of divinylbenzene used to make the original copolymer, and ranges up to 20 to 24 percent by weight. The greater the cross-linking, the less the resin swells in water and the more ions it holds per unit volume, but diffusion in high cross-linked resins is very slow and large ions can not enter. For most purposes a cross-linking of 8 percent is used, though in biochemical and organic applications a lower cross-linking, such as 4 or 2 percent, may be preferred.

In this work the polymer used as the support, is the anion exchange resins, strongly basic active group, quaternary ammonium type with cross-linking of 8 percent, known as the "Amberlite IRA-400" in the chloride form

[Laboratory chemicals & biochemical, BDH, 1984-1985). This choice is also buttressed by the fact that, most effective tool for separating metals by ion exchange is not cation exchange, but anion exchange of chloride complexes, most metals are taken up by anion-exchange resins from hydrochloric acid solutions (Louis and Meites, 1963). List of some typical polymer resins is shown in table 2-1.

TABLE 2-1: ION EXCHANGE RESINS

CATION EXCHANGE RESINS, STRONGLY ACIDIC, ACTIVE GROUP:- SO_3^-
Cross-linked polystyrene-divinylbenzene
Typical applications: Water softening and deionisation; separation of rare earths; separation of peptides and amino acids; inorganic separations; esterification catalysis; wine stabilisations, etc.

Resin	Grade	Form supplied	Mesh size B.S.S. (as supplied)	Moisture content %	Wet density (apparent) g per ml	Exchange capacity	Cross linking %	Max Operating temp °C	pH range
5009 Amberite IR-120	Standard	Na^+	14-52	44-48	0.84	Wet 1.9 meq/ml Dry: 5.0 meq/g	8	120	1-14
5001 Amberite IR-120	Analytical	H^+	14-52	49-55	0.77	Wet 1.9meq/ml Dry: 5.0 meq/g	8	120	1-14
'Amberlite CG-120(Na)	Chromatographic	Na^+	*U.S Standard Screens	10max	about 0.0 on rehydration	Wet 1.9meq/ml Dry: 5.0meq/g	8	120	1-14
55036 Dowex' 50-X8	Standard	Na^+	18-52	45	0.85	Wet 1.9meq/ml	8	120	1-14
55038 Dowex' 50W-X8	Standard	H^+	16-40	53	0.80	Wet 1.7meq/ml Dry: 4.8 meq/g	8	120	1-14

Table 2-1 (Cont'd)

ANION EXCHANGE RESINS, STRONGLY BASIC ACTIVE GROUP; QUATERNARY AMMONIUM
Cross-linked polystyrene-divinylbenzene matrix (except 'Amberlite' IRA-458)
Typical applications: Water conditioning; removal or recovery of high molecular weight anions; fractional separation of organic acids:

Separation of Amino acids; separation of metals as anionic complexes, etc.

Resin	Grade	Form supplied	Mesh size B.S.S. (as supplied)	Moisture content %	Wet density (apparent) g per ml	Exchange capacity	Cross linking %	Max Operating temp °C	pH range
50011 Amberite IR-400	Standard	Cl^-	14-52	42-48	0.70	Wet 1.4meq/ml Dry: 3.5meq/g	8	77 (Cl-form) 60 (OH-form)	1-12
5012 Amberite IR-120	Standard	Cl^-	14-52	59-65	0.69	Wet 1.0meq/ml Dry: 4.3meq/g	4	77 (Cl-form) 60 (OH-form)	1-12
5013 'Amberlite IRA-401 Intermediate high porosity High capacity grade	Standard	Cl^-	14-52	53-60	0.68	Wet: 1.25 meq/ml Dry: 4.3 meq/g	6	77 (Cl^-form) 60 (OH-form)	1-12
55014 'Amberlite IRA-410 regeneration efficiency for water conditioning	Standard	Cl^-	14-52	40-45	0.70	Wet 1.40meq/ml Dry 3.7 meq/g	8	77 (Cl-form) 40 (OH-form)	1-12
5505 'Amberlite IRA-400(Cl) Minimum Limits of Impurities	Analytical	Cl^-	14-52	42-48	0.70	Wet 1.4meq/ml Dry: 3.8meq/ml	8	77 (Cl-form) 60 (OH-form)	1-12
5506 'Amberlite IRA-400(Cl) High porosity	Analytical	Cl^-	14-52	59-65	0.69	Wet: 1.0meq/ml Dry: 4.3 meq/ml	4	77 (Cl-form) 60 (OH-form)	1-12

2.3 THE SWELLING OF ION-EXCHANGE RESINS

A very important factor which determine the rates of diffusion in resins is the extent which they swell when immersed in a solution. The degree of swelling is determined by the chemical nature of the polymer, the degree of cross-linking and the details of the network structure, the concentration of ionizable groups in the resin, the nature of the ions released by these groups, the concentration of the surrounding solution and the temperature.

Any cross-linked polymer swells to some extent when it is immersed in a solvent. Swelling is encouraged by the entropy of mixing of the polymer and the solvent. It may be either encouraged or discouraged by the heat of mixing of the polymer and the solvent depending upon whether this heat is negative or positive. It is resisted by the tension which is set up in the polymer sub-chains (that is the chain sections between network junctions) when their configurations are disturbed by the distension of the network. The first and third effects are concerned principally with the configurational entropy and contribute to the free energy of the system in direct proportion to the absolute temperature. The second effect is, to a first approximation, independent of temperature.

Most organic polymers are only slightly swollen by water as the heat of mixing is large and positive. Polymers which contain polar groups, such as hydroxyl and carbonyl, absorb more water than do hydrocarbon polymers. Thus, phenol-

formaldehyde resins would tend to swell more than those derived from polystyrene if they could be compared under swelling of an ion-exchange resin in water, far greater than could be accounted for by the entropy of mixing of the polymer and solvent. The initial rate of swelling is also very high and may cause the beads of a dry resin to shatter before the center of the bead has been plasticized by the in coming water. The first water molecules to enter hydrate the ions. This is strongly exothermic and far outweighs the endothermic interactions between organic parts of the polymer chains and water. Hydrating the ions loosens the exchangeable or counter ions from the oppositely charged ions which remain bound to the polymer chains. The counter ions can then move around more or less independently inside the resin. The ultimate extent of swelling depends some what upon the nature of the counter-ions. It tends to be greater with highly hydrated ions, such as magnesium, than with relatively non-hydrated ions, such as caesium and in general, it is greater in a cation than in a comparable anion exchanger. The release of counter-ions greatly enhances the increase in entropy which occurs when more solvent enters the resin. This effect increases the tendency to swell.

Apart from a boundary space charge which involves a trivial number of ions, the resin remains electrically neutral and the counter-ion therefore, remain within the volume occupied by the polymer network. Each resin particle may thus

be imagined as surrounded by a skin which is permeable to water but impermeable to the counter-ions. The driving force of swelling is therefore, akin to an osmotic pressure driving solvent in to dilute the ionic solution inside. Clearly the greater the concentration of ionizable groups per unit volume of resin, the grater the osmotic pressure and, hence, the greater the swelling. Thus, when a resin is immersed in a salt solution instead of in pure water, the osmotic pressure difference between the external medium and the inside of the resin is reduced by the osmotic pressure of the external solution. Consequently, the ultimate swelling of the resin is less than in pure water.

2.4 CATALYSIS BY ION EXCHANGE RESINS

Many chemical reactions, both inorganic and organic, can be catalyzed by ion exchangers for reactions of gases and liquids and solutes.

2.4.1 Reactions of Liquids and Solutes

A large number of reactions of liquids and solutes are subject to homogeneous catalysis by dissolved electrolytes. In many cases, the electrolyte is an acid or a base, where the catalytically active species are the H^+ ion or the OH^- ion. Other ions may be catalytically active such as Hg^{2+} which catalyzes the hydration of acetylene derivatives, and CN^- catalyzes benzoic condensation.

It has been found that the dissolved electrolyte can be replaced by an ion exchanger which contains the catalytically active ion as the counter ion. The reaction now occurs in the pores of the ion exchanger where the active specie is present. The ability of ion exchanger to catalyze liquid-phase reactions was first observed by Tacke and Suchting (1911), who found that sucrose in aqueous solution is inverted by acidic Zeolites. Practical applications and plant-scale processes were first developed by Farbenindustrie (1953) during World War II.

The use of solid ion exchangers has the following advantages over homogeneous catalysis by dissolved electrolytes:

1) the catalyst is readily removed from the reaction products by, say, decantation or filtration.
2) Continuous operation in columns is possible (Far benindustie, 1953).
3) Often the purity of the products is superior since side reactions are less significant (Lanrange *et, al.*, 1953).
4) The possibility of isolating reaction intermediates which can not be obtained by homogenous catalysis (Wadman, 1952).
5) There is greater selectivity of the ion-exchanger catalyst (Deuel *et. al.*, 1951).

On the other hand, the applicability of the method is restricted by the chemical and thermal stability of the ion exchangers. Also, ion-exchanger catalysts are much more expensive than dissolved electrolytes.

As a rule, organic ion-exchanger resins rather than other ion-exchanger materials are used for catalysis of liquid-phase reactions. The resins are superior to the inorganic ion exchangers because of the higher mobilities of the reactants and products in the pores of the (swollen) catalyst. Also, the chemical stability of the resins, particularly against acids, is usually higher. Serious disadvantages of the organic resins are their limited thermal stability and, in reactions involving strong oxidation agents, their insufficient resistance to oxidative decrosslinking. For reactions at higher temperatures (above 100°C) and in the presence of oxidation agents such as H_2O_2, the inorganic ion-exchange gels are likely to be more satisfactory (Austerweil (1958).

(a) Mechanism of reaction within the pores

The pores of an ion-exchanger which is in contact with a solution, contains solvent, solutes, and the counter ions. The counter ions are mobile and solvated and thus in a condition which is, in principle, not different from that in a corresponding homogenous solution. It can therefore be expected that counter ions display catalytic activity in the

pores of a resin, and that the reaction mechanism in homogeneous catalysis by a dissolved electrolyte and heterogeneous catalysis by a resin is essentially the same. These conclusions are reasonably well confirmed by experimental observations which show that the order of the actual chemical reaction is the same in both cases and that the activation energy is similar (but not necessarily true for the observed overall process which may be diffusion-limited). Catalysis of liquid phase reactions by ion-exchange resins is not a true case of heterogeneous catalysis, but may be described more adequately as homogeneous catalysis in the pore liquid (Helfferich, 1954). The principal differences between catalysis by dissolved electrolytes and by resins are, first, with resins as catalysts the reaction occurs in the pore liquid only so that the reactants must diffuse into the reaction zone and the products must diffuse out, and, second, the matrix and the fixed ionic groups may affect the reaction.

(b) Catalyst Selectivity

Almost every chemical reaction is accompanied to a greater or lesser degree by side reactions. Many reactions proceed in consecutive steps. In some cases, a reaction mixture may undergo different reactions which lead to different products. All this, of course, is true for catalytic as well as for other reactions. An ion-exchanger catalyst may produce other results than a dissolved

electrolyte. As a rule, the ion exchanger is more selective, that is, it distinguishes more sharply between the various reactant molecules. One might say that ion exchanger as catalysts lie half-way between the nonselective dissolved electrolytes and the extremely selective enzymes. The selectivity of the ion exchangers catalyst can be explained in terms of molecular sizes of the reactants and products, and sieve action of the pores of the ion exchanger; and also with differences in sorption of the various reactants.

The selectivity of ion-exchanger catalysts often leads to yields which are considerably higher than those obtained with catalysis by dissolved electrolytes. Also, the case with which the catalyst can be separated from the liquid reaction mixture facilitates the isolation of reaction intermediates and helps avoid yield losses by the subsequent reactions of the products, particularly if the desired products are not very stable in the presence of the catalyst.

2.4.2 Selection of Catalysts and Operating Conditions

In most practical applications, it is desirable to obtain the highest possible reaction rate with a given amount of catalyst. This can be achieved by proper choice of the catalyst material and the operating conditions.

First of all, suitable resin type and solvent should be selected in such a way that the resin is chemically stable and swells substantially in the solvent, and that equilibrium

sorption of the reactants is high. Under such conditions a high catalyst efficiency and high mobilities of reactants and product in the resin can be expected. The ion-exchange capacity of the resin should be as high as possible since the reaction rate is proportional to the amount of counter ions in the resin.

An increase in temperature enhances the rates of both the chemical reaction and diffusion and thus gives a higher overall rate. However, the operating temperature is usually limited by the thermal stabilities of the resin or the compounds involved.

2.5 CATALYTIC OXIDATION IN THE HOMOGENEOUS LIQUID PHASE

The liquid-phase oxidation of organic substrates using metal complexes as catalyst has become a profitable means of obtaining industrially important chemicals. These reactions depend on some conditions.

(1) Catalysts

Catalytic activity for epoxidation by hydroperoxides has been claimed for compounds of a great number of metals including chromium, molybdenum, niobium, nickel, rhenium, selenium, tantalum, titanium, vanadium, tungsten, and zirconium. Comparative studies (Indictor, 1965) have demonstrated that many, if not all, of these provide a higher yield of epoxide than uncatalysed reactions. Molybdenum compounds

appear to be the best catalysts (Sheng and Zajacek, 1968).

Tungsten compounds, though the best catalysts in combination with hydrogen peroxide (Mugden et al., 1949) rank far below both molybdenum and vanadium in general use and usually in yields.

(2) Concentration of reactants and Solvents.

In most instances, an excess of Olefin to hydroperoxide of at least 2:1 or 3:1, with the olefin frequently serving as solvent, is recommended (Augustin et al, 1971). Published reports to date, have concentrated solely on maximizing the yield based on hydroperoxide consumption.

The concentrations of catalyst employed have varied from 0.1 to 1% by weight of hydroperoxide for soluble materials to 1 to 10% for insoluble or slightly soluble substances (Augustine et al., 1971).

(3) Temperature

In general, the lower the temperature, the less hydroperoxide decomposes by other routes. Sheng and zajacek (1968), have provided a systematic study for molybdenum catalysis showing that yields (based on hydroperoxide conversion) which may be as high as 98% at 100°C fall to 75 - 80 at 130°C.

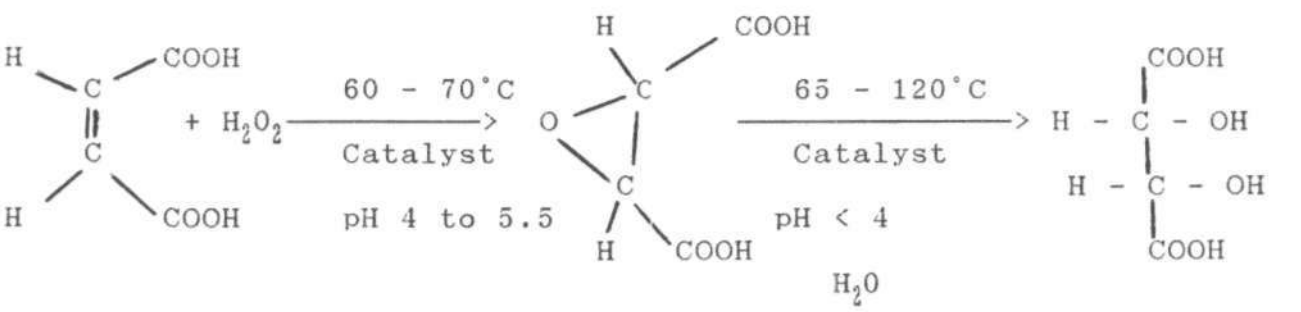
2.6 AMMONIUM MOLYBDATE CATALYZED OXIDATION OF MALEIC ACID WITH HYDROGEN PEROXIDE

Maleic Acid, also known as 2-butadiene dicarboxylic acid can be oxidized by hydrogen peroxide in the presence of catalysts, such as compounds of molybdenum, tungsten and Vanadium to produce cis-epoxysuccinic acid and tartaric acid in series. These reactions take place in two steps.

(1) Epoxidation of Maleic acid to cis-epoxy succinic acid

(2) hydrolysis of the epoxide to tartaric acid.

The maleic acid reacts with hydrogen peroxide at a temperature range of between 60°C to 70°C in a pH controlled medium (pH 4 to 5.5), in the presence of these catalysts to yield the epoxysuccinic acid. At still wider temperature ranges of say between 65 to 120°C, and at lower pH values than 4 at the presence of the same catalyst as above, and in the absence of sodium hydroxide, the reaction continues to yield a second product called tartaric acid.



I II III

...(i)

where the compounds I represents Maleic Acid; II represents cis-epoxysuccinic acid, and III represent tartaric acid, which is in dl and meso-form. The dl form could as well reacts with the catalyst to produce complex.

The best yield of hydroxylation of maleic acid is generally obtained in batch reactor systems between the temperature range of 80 to 100°C with mole ratios of hydrogen peroxide to maleic acid of 1:1.5 and 0.5% catalyst concentration for approximately 10 hours. Continuous addition of hydrogen peroxide to force the reaction to completion gives a final yield of 61%. But with filtration and recycle (synthetic production methods), yield of about 98% can be obtained (Graham, *et al.*, 1969).

Thus, in regard to this study the production of II, (epoxysuccinic acid) can be maximized if the first step of the oxidation reaction is encouraged and the second step discouraged, by restricting the reaction within the conditions of the first step alone. This is because the tartaric acid is known to deactivates the catalyst by forming inactive complexes with it.

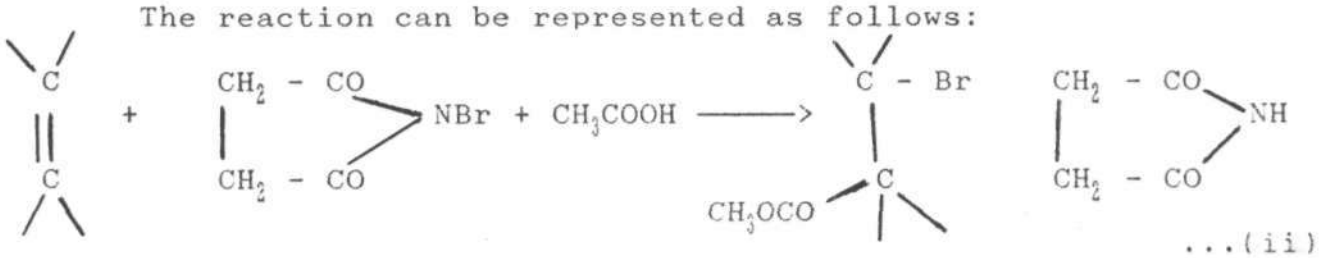
2.7 ANALYTICAL PROCEDURES

2.7.1 Determination of Iodine Number of Olefinic Unsaturation Using N-Bromo-succinimide

Since the bromine atom in N-Bromosuccinimide is in the +1 oxidation state, in glacial acetic acid medium, coupled

addition of bromine and acetoxy groups takes place along a double bond (Iovchev, 1965).

The reaction can be represented as follows:



...(ii)

The reaction has been referred to as bromoacetoxylation of the alkene bond. The addition reaction involves 1 mole N-bromosuccinimide per alkene bond which is equivalent to the addition of two equivalent of iodine. Since the N-bromosuccinimide consumed in the above reaction can be determined iodometrically, this offers a method for the determination of iodine number of the sample. This method involves the addition of potassium iodide to the bromoacetocylate, at equation (ii), and the iodine liberated is titrated with standard sodium thiosulphate solution. From the difference in the volumes of sodium thiosulphate solutions consumed, the iodine value can be calculated from the equation (Mathur *et. al.*, 1975):

1 ml of 0.1N sodium thiosulphate solution

= 12.69 mg of iodine.

$$\text{Iodine number} = \frac{(B - S) * 12.69 \times 100}{W}$$

where B = volume (ml) of sodium thiosulphate solution used in blank titration

S = volume (ml) of sodium thiosulphate solution used in the sample titration.

W = Weight (mg) of the sample.

The method has been used successfully for the determination of iodine number of fatty acids, for example, Oleic acid, elaidic acid, erucic acid, brassidic and eleostearic acids. An accuracy of ±0.8% is generally achieved, which is comparable with other standard methods (Mathur and Narang, 1975).

2.7.2 Determination of Hydrogen peroxide by Iodometric Titration

The reaction of acetic acid and potassium iodide gives hydrogen iodide and potassium acetate. Hydrogen peroxide can then react with the hydrogen iodide to form iodine and water. This iodine can be reacted with sodium thiosulphate to form sodium iodide and thiosulphate ion of sodium.

The presence of iodine in the reaction mixture due to its production, causes brown coloration of the solution, but when this solution is titrated with sodium thiosulphate, the colour disappears, indicating the end of the reaction and the end-point of the reaction.

In excess hydrogen iodide, hydrogen peroxide can only generate certain moles of iodine in accordance with the stoichiometry of the reaction, whence the amount of iodine generated can be obtained from the titration of sodium thiosulphate with iodine; and comparing molar ratios, the amount of hydrogen peroxide used in the reaction can be determined by the formula:

$$[H_2O_2] = \frac{(V - V_o) * M_{Na_2S_2O_3}}{2 * V_{sample}} \quad \ldots(2\text{-}1)$$

where

V_{sample} = volume of sample

V = volume of $Na_2S_2O_3$ consumed on titration of sample.

V_o = Volume of $Na_2S_2O_3$ consumed on titration of blank solution.

$M_{Na_2S_2O_3}$ = Molarity of $Na_2S_2O_3$ solution

Conversion of hydrogen peroxide is evaluated by,

$$X_{H_2O_2} = 1 - \frac{[H_2O_2]}{[H_2O_2]o} \quad \ldots(2\text{-}2)$$

where $[H_2O_2]_0$ = Initial concentration of hydrogen peroxide

$[H_2O_2]_0 - [H_2O_2]^{O_2}$ = amount of hydrogen peroxide available for reaction .

$$\text{Selectivity} = \frac{[H_2O_2]_0 - [H_2O_2] - [H_2O_2]^{O_2}}{[H_2O_2]_0 - [H_2O_2]} \times 100 \quad \ldots(2\text{-}3)$$

where $[H_2O_2]^{O_2}$ = Amount of O_2 evolved during the reaction corrected to the equivalent hydrogen peroxide concentration.

The reactions involved in iodometric titration are:

$$CH_3COOH_{(aq)} + KI_{(aq)} = HI_{(aq)} + CH_3COOK_{(aq)}$$

$$H_2O_2 + 2HI = I_2 + 2H_2O$$

$$I + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

CHAPTER THREE

3 MATERIALS, INSTRUMENTATION AND METHOD

3.1 EQUIPMENT AND INSTRUMENTATION

(1) Experimental (Micro) reactor (50mL) - The reactor was designed and constructed in the chemistry department of Ahmadu Bello University, Zaria.

(2) Refrigerator the thermocool model

(3) Oven the Heracus model

(4) Cecil Instruments spectrophotometer

(5) Weighing Balance, the saluter model

(6) Titrimetric apparatus including separation funnels

(7) Oil/water bath thermostat

(8) Stop watch

(9) Gallenhamp magnetic stirrer regulator hot plate

(10) Condensers

(11) Thermometer

(12) Beakers, burettes, pipettes, separation funnels and glass flasks.

Reagents

(1) Stannous chloride, BDH Chemicals Ltd.

(2) Hydrochloric acid (conc.)

(3) Metallic Tin

(4) Isopropyl ether, BDH chemicals Ltd.

(5) Ferric sulphate solution (8%)

(6) Potassium thiocyanate (5%)

(7) Ammonium molybdate, BDH chemicals Ltd.

(8) Sulphuric acid (conc.)

(9) Amberlite Resin IRA - 400 (CL^-).

3.2 INSTRUMENTAL ANALYTICAL METHOD FOR THE DETERMINATION OF MOLYBDENUM CONCENTRATION

The advantages of calorimetric methods over gravimetric and titrimetic methods are in their simplicity, rapidity and sensitivity. The two calorimetric methods of outstanding importance for the determination of molybdenum are based on the use of thiocyanate and dithiol. In this study however, the thiocyanate is preferred because of its simplicity and availability of the reagents and materials needed.

Thiocyanate Method

Molybdenum forms orange-red complex with thiocyanate ions in mineral acid solution in the presence of a reducing agent (Sandell, 1950). Stannous chloride is the mostly used reducing agent in the thiocyanate method, but other reagents such as potassium iodide (Hope, 1957), and copper (ii) chloride (Grouthamel and Johnson, 1954) have also been used.

The coloured complex contains molybdenum (v), and is probably a molybdenyl thiocyanate. Maximum absorption occurs at about 470 nm (Elwell and Wood, 1971). The colour or rather,

the absorbance of the sample corresponds to the concentration of molybdenum present in the sample. To increase the sensitivity of the method and improve the stability of the colour, the complex can be extracted into an organic solvent such as isopropyl ether.

Procedure:

100ml of the standard molybdenum solution was taken into a 250ml separating funnel. Approximately 10ml of potassium thiocyanate solution (5%) was added, and was shaken for about 30 seconds. About 10ml of the stannous chloride solution (35%) was then added, and the content was vigorously shaken for about 1 minute. 50ml of the isopropyl ether was added, the funnel was stoppered, and then shaken vigorously for several minutes. The funnel is depressurized to avoid breakage of glass ware due to the increase of pressure as the extraction is taking place. The two layers were allowed to separate. The aqueous (lower) layers was run off into a beaker, and the organic layer was transferred to 100ml calibrated flask. The aqueous layer was returned to the separating funnel, and 40ml of Isopropyl ether was added, the funnel was stoppered and the shaking was repeated. The aqueous layer was run off and discarded. The organic layer was collected and allowed to stand for 3 minutes using spectrophotometer.

Some of the clear extract was transferred to 10-mm absorption cell and the absorbance was measured at a

wavelength of 470 nm.

A blank solution which did not contain any molybdenum concentration was prepared and its absorbance was measured by the same procedure, at the same wavelength.

3.3 PREPARATION OF IMMOBILIZED MOLYBDENUM CATALYST

Very special metal catalyst have been prepared by the interaction of ion-exchange Resin, Amberlite IRA-400 chloride form, with aqueous solutions of molybdenum which is a very strong oxidizing transition metal. The metal individually interacts with the active site (CL^- groups) to form complexes, and the metal ions are accordingly dispersed with the CL^- spacing in the ion-exchange resin.

3.3.1 EXPERIMENTAL DETAIL

(i) Stannous chloride solution (35%)

175g of stannous chloride was transferred to a beaker (400 mL), 100mL of hydrochloric acid (1+1) was added, warmed (60 to 70°C) until the stannous chloride has almost dissolved and then cooled. The solution was transferred to mark. A few pieces of metallic tin were added to stop further reaction, and the flask was loosely covered.

(ii) Isopropyl ether solution

This solution was immediately prepared before use as follows: 50mL of Isopropyl ether was shaken with 25mL of

ferric sulphate solution (8%), 10mL of potassium thiocyanate solution (5%) and 10mL of the stannous chloride solution (35%). This was run off and the aqueous lower layer was discarded.

(iii) Standard Molybdenum Solution

0.2523g of high purity ammonium molybdate was dissolved in 100mL of sulphuric acid (1%) and diluted to 1 litre. Such that,

1 mL = 0.2 mg of molybdenum.

The general method of catalyst preparation employed in this work is a modified form of that reported by Akamatsu et al (1961). A desired volume of standard solution of molybdenum was diluted to 100 mL with distilled water.

Exactly 0.4g of the ion-exchange was weighed. 30 mL of the diluted molybdenum solution was introduced into the experimental reactor, and the 0.4g resin was added. The mixture was heated at constant temperature with the aid of the thermostat for 1 hour with constant stirring, using a magnetic stirrer hot plate and reflux condenser. Operating temperature was 40°C. During the 1 hour of heating, sample (0.5mL) was taken every 10 minutes, and set for instrumental analysis, with the aid of spectrophotometer, to monitor the rate of sorption of molybdenum into the resin. At the end of the 1 hour, the ion-exchange resin-molybdenum raw catalyst was filtered from the hot solution and was placed in an oven and

air-dried at 75°C for 3 hours. The drying temperature was chosen such that it lies between the catalyst preparation temperature and the maximum operating temperature (77°C) of the resin to avoid destruction and malfunctioning. The 3 hour drying time was chosen to ensure complete dryness. Drying time and temperature were maintained constant for all preparations. The spectrophotometric curves were determined from the calibration curve, as discussed below. The 0.5ml aliquot was taken so that the effect of 6 such samples of total volume of 3 ml will be negligible compared to the total volume of 30mL of the reaction mixture.

3.3.2 OPTIMIZATION OF OPERATING CONDITIONS

(1) Weight of Resin

In this section, various amounts of the resin in the range of 0.3 to 0.8 gramme were weighed and used for the sorption process as detailed in sections (3.2) and (3.3.1). Consequently, curves of concentration against time with the corresponding weights of the resin were plotted (Fig. 3-1.a) at fixed temperature of 40°C and initial concentration of ammonium molybdate of 3.47×10^{-5}M.

(2) Initial Concentration of Ammonium Molybdate

Different solutions of ammonium molybdate in the range of 1.5 to 10.0×10^{-5}M at constant temperature of 40°C and fixed weight of resin, 0.4 gramme were prepared and the same

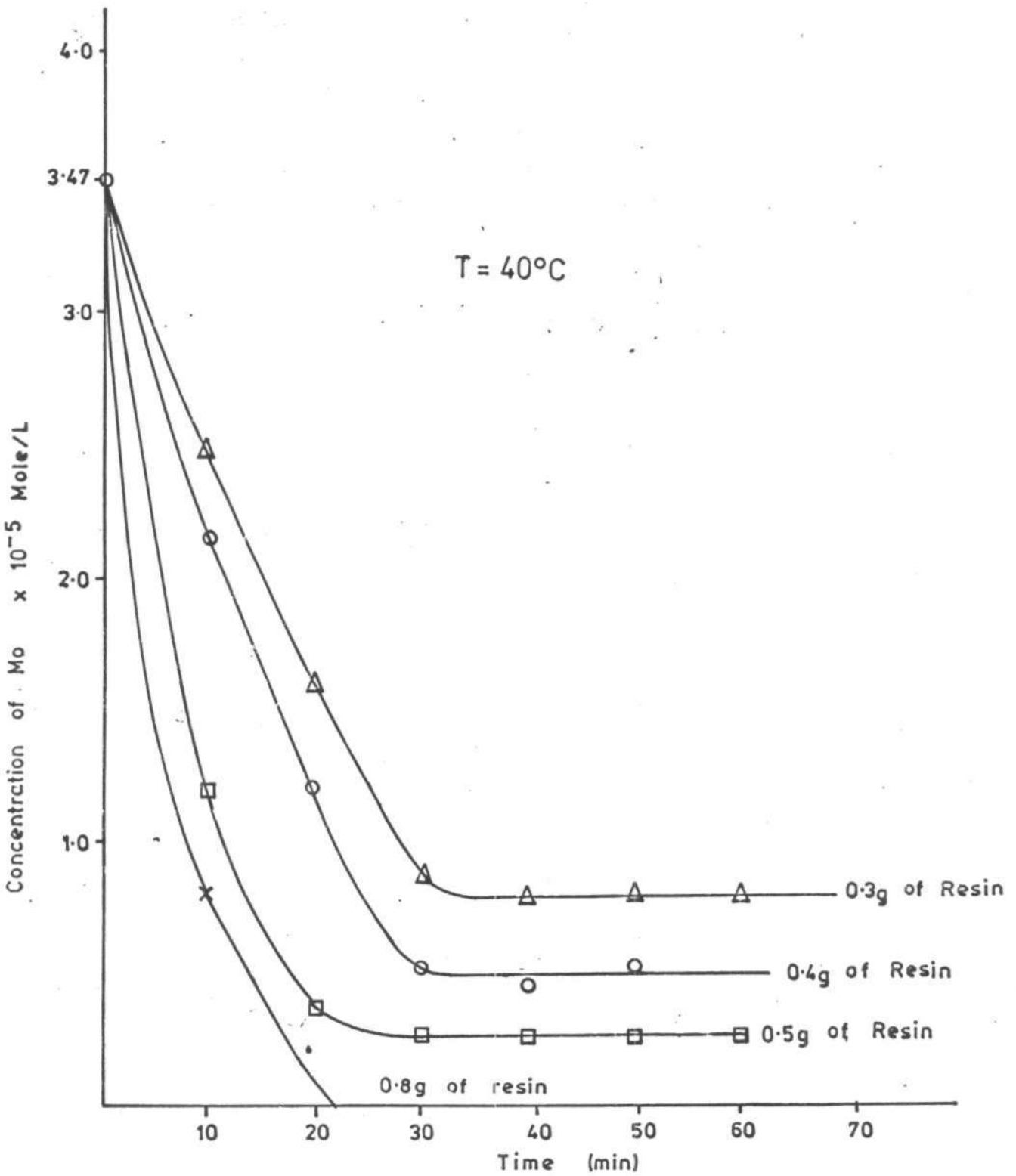


Fig.(3–1a) Typical Plot showing Concentration Vs Time in a series where the amount of Resin is varied

procedure as in (1) above were followed. The concentration-time curves were also plotted (Fig. 3-1.c).

(3) Operating Temperature

In trying to find the best operating (sorption) temperature, a fixed amount of resin, 0.4 gramme was taken, fixed initial concentration of ammonium molybdate was prepared. Under these conditions, at temperatures ranging from 30 to 70°C, the sorption process was also studied following the same procedures as is (1) above, then the concentration time curves were plotted (Fig 3-1.b).

Based on the analysis of the results obtained from the foregoing investigations, the following operating conditions were selected on polymer resin as support (as seen in figures (4-1) and (4-2):

Temperature = 40°C

Weight of resin = 0.4 gm

Aqueous molybdenum concentration = 3.47×10^{-5}M.

Consequently, these parameters would figure as standards in all further investigations involving the synthesis of the immobilized catalyst.

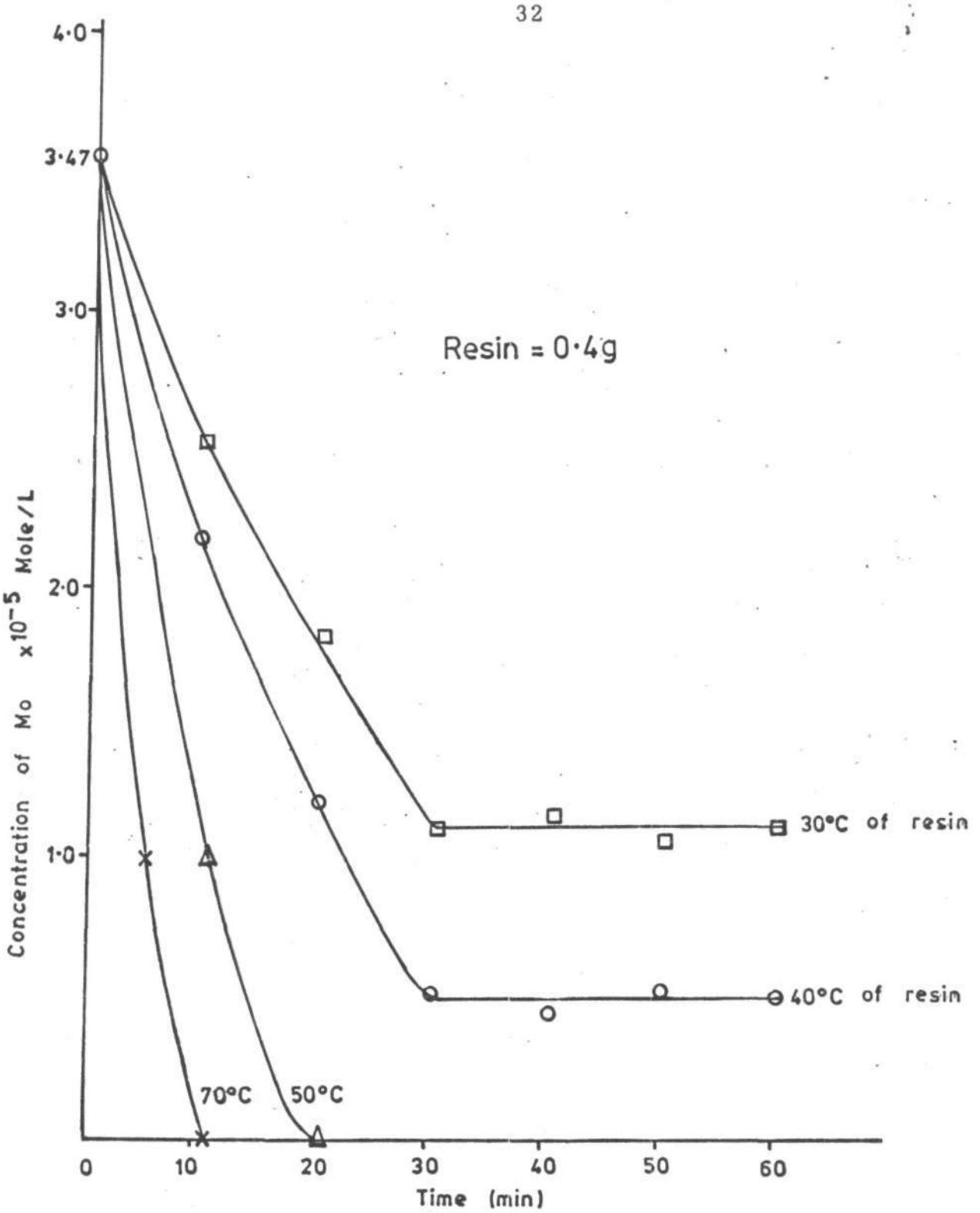


Fig. (3–1·b) Typical plot showing Concentration Vs Time in a series where the Adsorption Temperature is varied

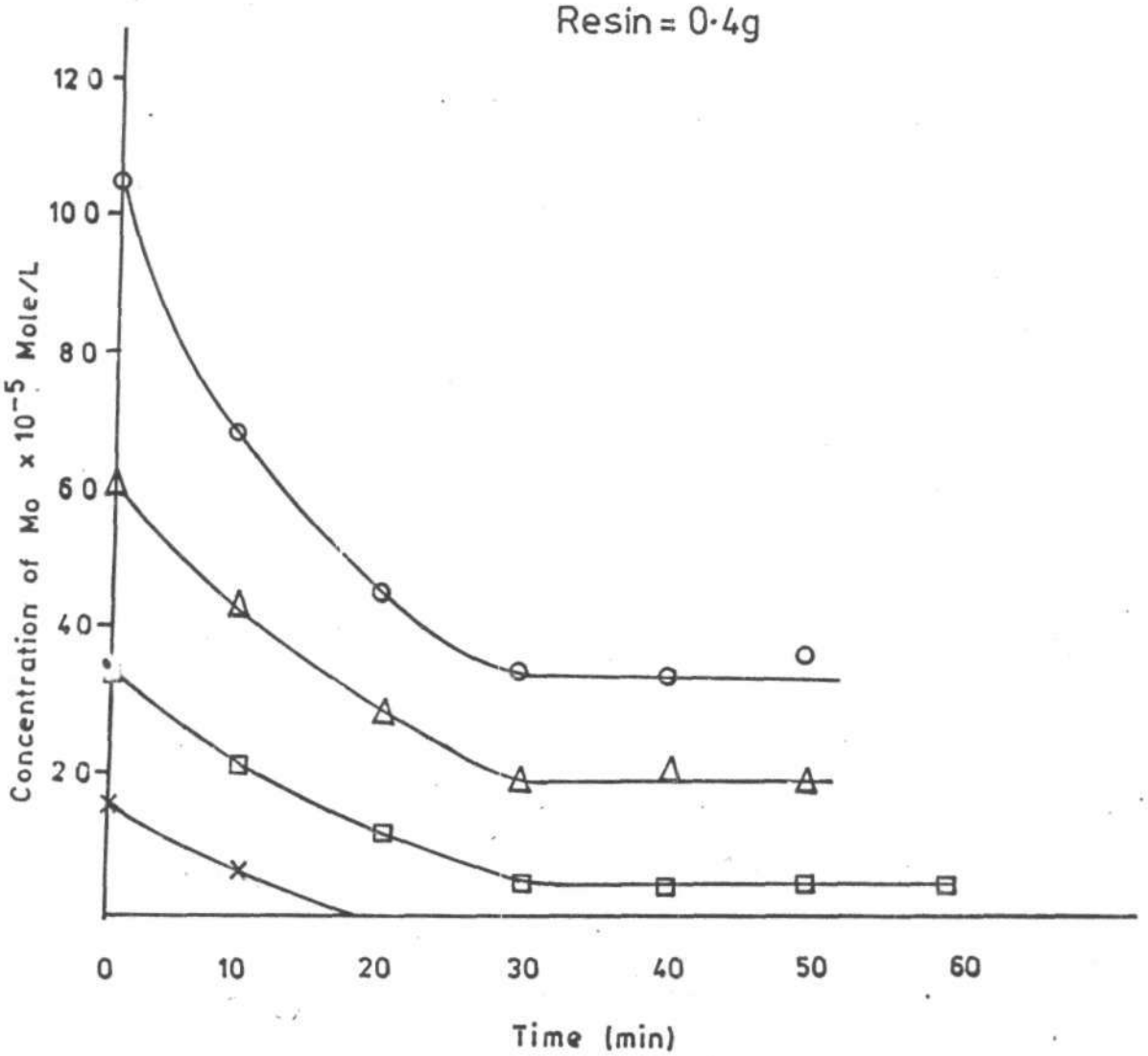


Fig.(3-1c) Plot of typical Kinetic Curves showing Concentration Vs Time in the Series where the Initial Concentration of Mo is varied

CHAPTER FOUR

4. RESULTS AND DISCUSSION OF SORPTION KINETICS

The wide potentialities of sorption methods for the concentration and separation of metal ions has stimulated the development of methods of synthesis and the study of new sorbents. Consequently, the significance of the idea and achievement of this research work can not be over emphasized. Thus ammonium molybdate have been chosen in this study as the molybdenum substrate because of its availability and it can be easily dissociated to produce molybdenum ions, which are then immobilized in the polymer resin.

4.1 SORPTION OF MOLYBDENUM FROM AQUEOUS SOLUTION INTO RESIN

Amberlite IRA-400 (CL^-) form of resin have been chosen for this study for reasons of comparative qualities as highlighted in section (2.2) and table (2-1).

However, the rate of sorption of molybdenum ion into resin depends on such factors as its concentration in solution, temperature of the system, sorption time, and amount of resin (equivalent to the amount of available active sites per unit surface area.) To this effect, the sorption process have been studied with different amount of resins, temperatures, and initial concentrations of molybdenum, as shown in fig (3-1.a), (3-1.b) and (3-1.c) respectively. Fig

(4-1) and (4-2) show adsorption curves at varying amount of resin and temperature respectively

4.2 KINETIC STUDY OF SORPTION

As can be seen from figures (3-1.a,b,c,), the rate of sorption depends on concentration of molybdenum, amount of resin and temperature of sorption process. Consequently, the effect of each of these factors on the sorption rate are studied by varying one parameter while keeping others constant.

(1) Order of Sorption with respect to molybdenum concentration:

Assuming the rate of sorption to be:

$$\mathbf{r}_{sorp.} = K_{sorp.}\,[Mo]^{n} \qquad \ldots\ (4\text{-}1)$$

where $\mathbf{r}$ = rate of sorption of molybdenum from the solution

$K_{sorp.}$ = sorption rate constant.

Taking the 'log' of both sides of Equation (4-1)

$$\log \mathbf{r}_{sorp.} = \log K_{sorp.} + n \log [Mo]$$

Hence, a plot of log of initial rate of sorption against log of initial concentration of molybdenum as shown in fig (4-3), gave the gradient (order of sorption),

$$n = 1.03 \approx 1.0.$$

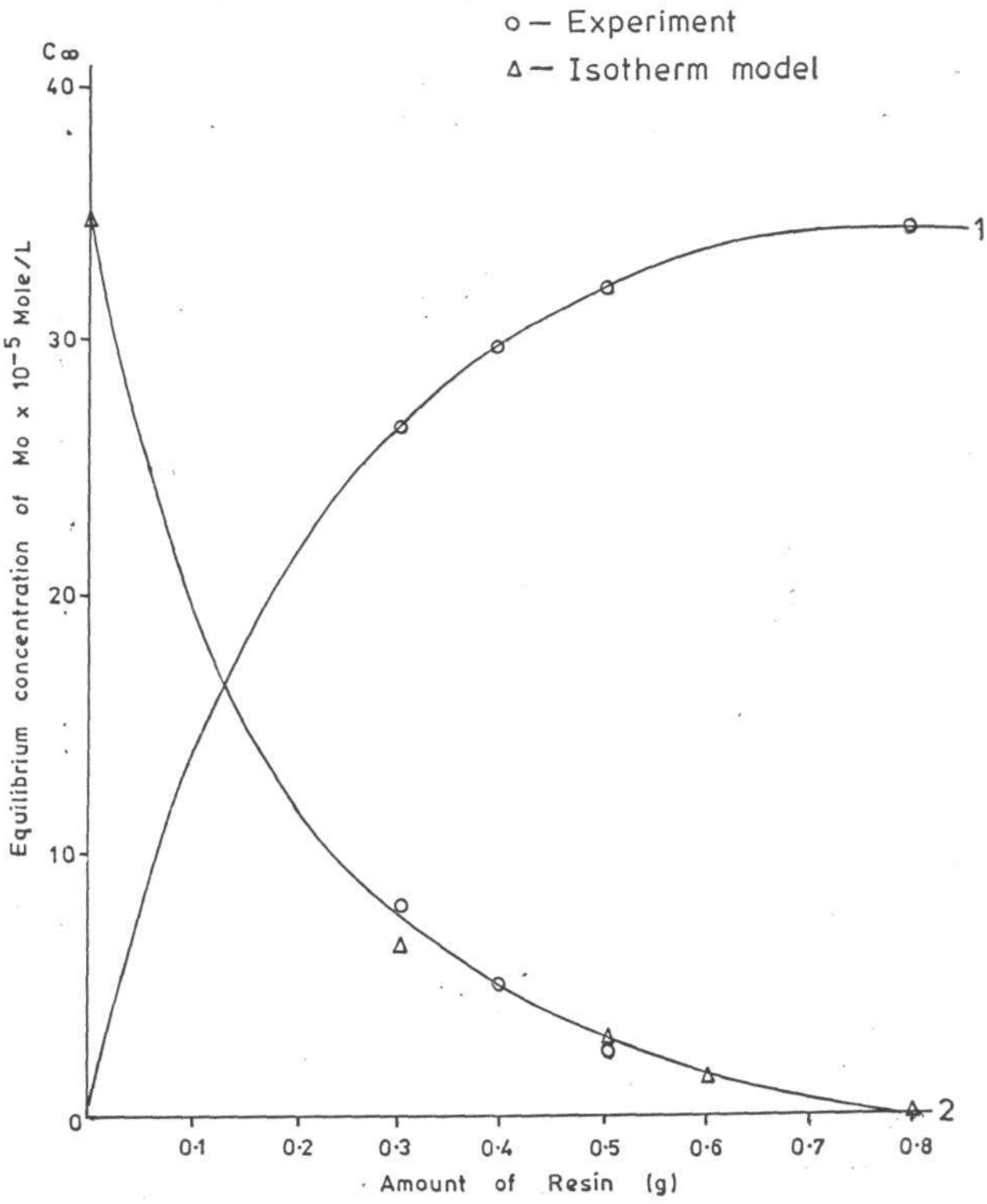


Fig. (4–1) Plot showing Adsorption Isotherm

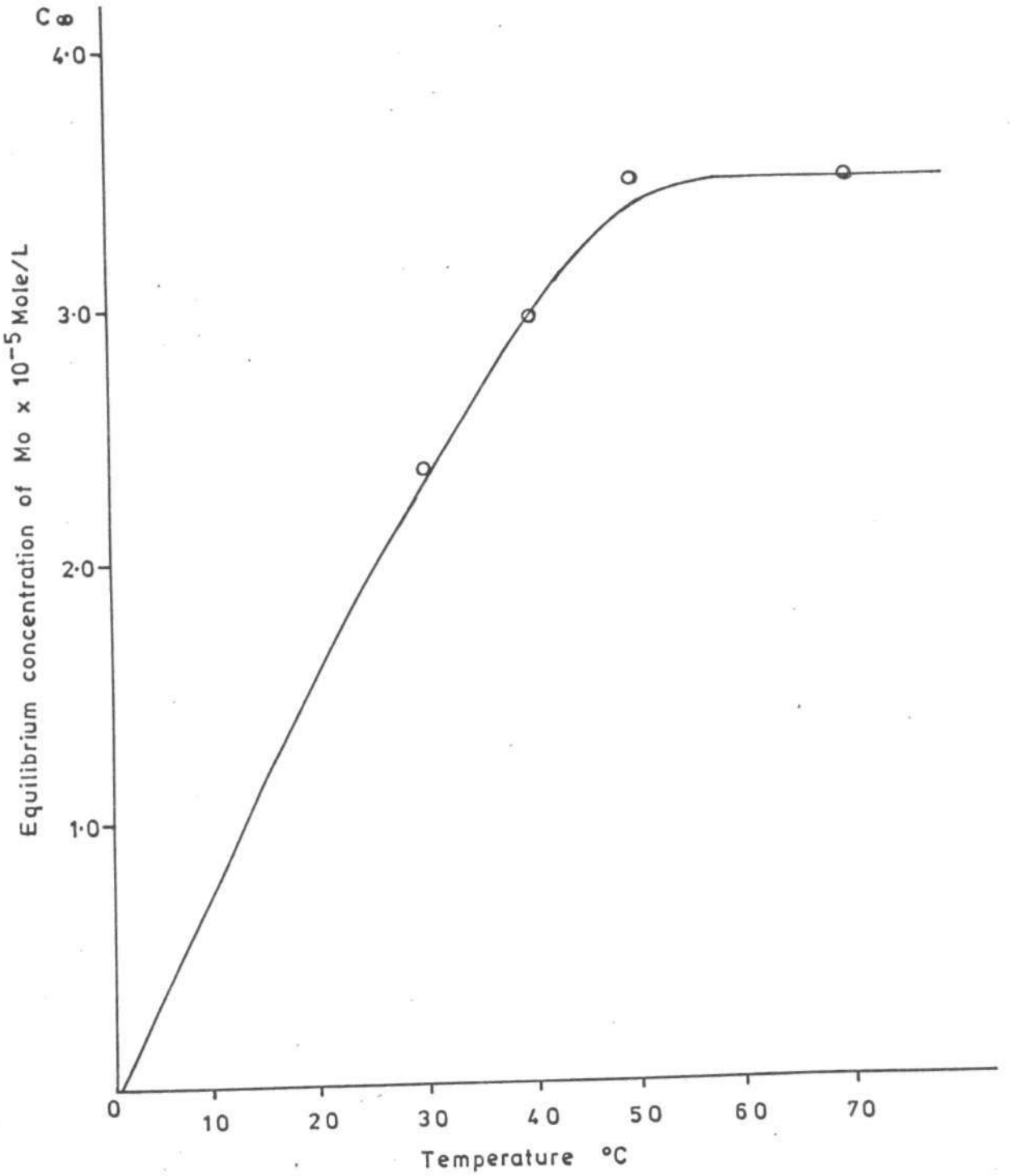


Fig. (4–2) Plot of equilibrium concentration vs temperature of sorption

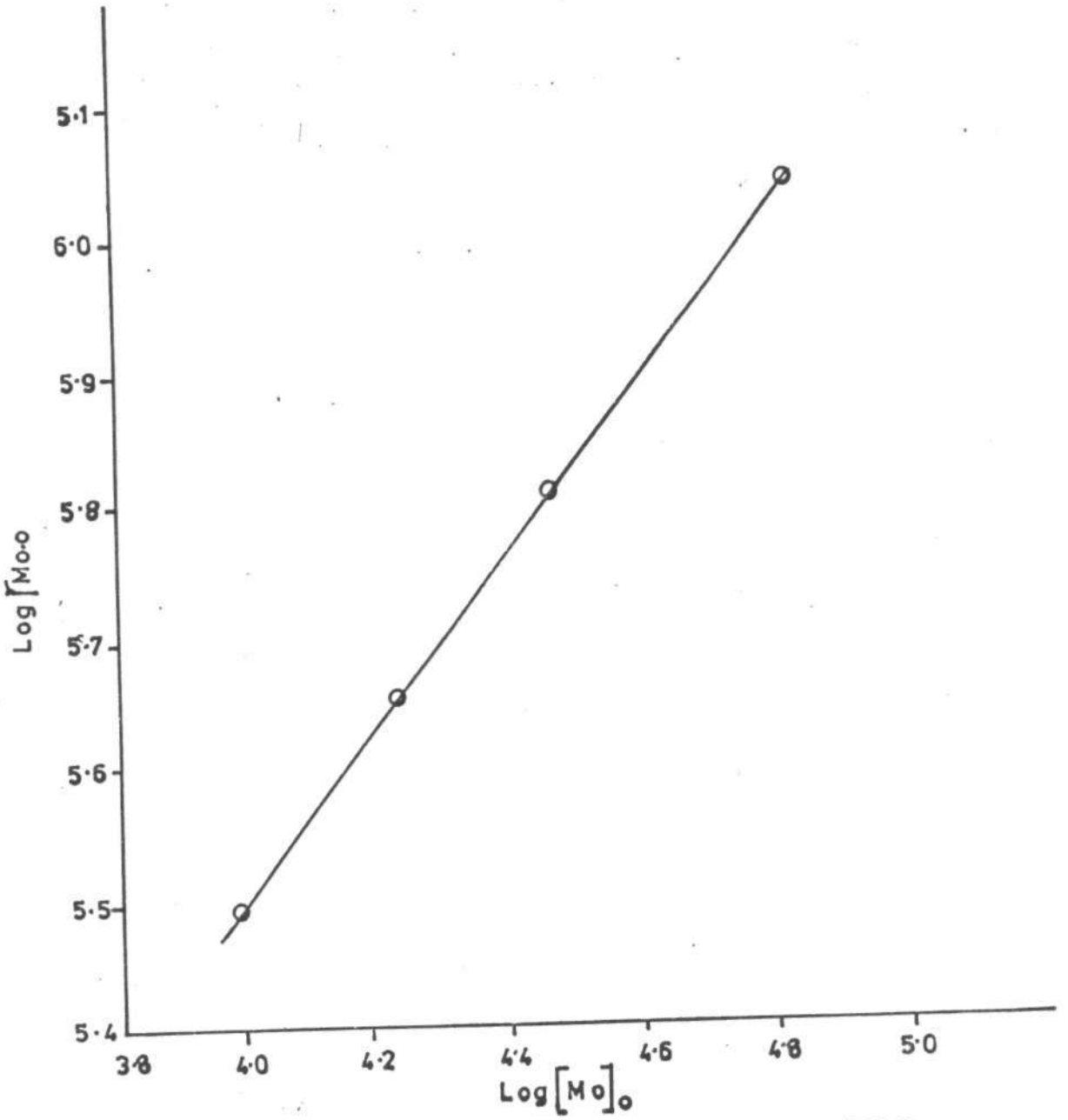


Fig. (4-3) Plot of Log [M.o.o Versus Log [Mo]o

Therefore, the order of sorption with respect to molybdenum concentration = 1.0

(2) Order of Sorption with respect to amount of resin:

As in (1) above, assuming the rate of sorption to be:

$$r_{sorp} = K_{sorp}. \times [Resin]^{n} \qquad \ldots (4\text{-}2)$$

where n = order of sorption

[Resin] = amount of resin (gm).

Taking 'log' both sides of Equation (4-2):

$$\text{Log } r_{sorp} = \log K_{sorp}. + n \log [Resin].$$

The plot of log r_{sorp} against log of amount of resin (fig. 4-4) gave the slope (n)

$(n) = 1.02 \approx 1.0$

Therefore, the order of sorption with respect to amount of resin = 1.0.

(3) Activation Energy of Sorption:

Using differential method on the curves of fig (3-1.b), a plot of $r_{sorp}.$ against [Mo] was made, as shown in fig (4-5), from which the values of K_{sorp} (slopes) at the corresponding temperature were evaluated, and the results are presented in Table (4-1).

Table (4-1) sorption rate constant at different temperature

Temp.T °C	T °K	K_{sorp} $(min)^{-1}$	In K_{sorp}.	K^{-1} 1/T
30	303	0.035	-3.35	$3.30x10^{-3}$
40	313	0.053	-2.94	$3.2x10^{-3}$
50	323	0.122	-2.10	$3.10x10^{-3}$
70	343	0.281	-1.27	$2.92x10^{-3}$

Applying Arrhenius temperature dependencies for sorption processes (Levenspiel, 0, 1986)

$$K_{sorp} = K_{sorpo} \exp. - [E_{sorp}./RT] \quad \ldots (4\text{-}3)$$

Taking (log) of both sides of Equation (4-3)

$$\text{In } K_{sorp} = \text{In}K_{sorpo}. - E_{sorp}/RT \quad \ldots (4\text{-}4)$$

Where R = rate gas constant = 8.314 J/gm mol °k.

Hence, a plot of In K_{sorp}. Versus I/T (fig. 4-6)

slope = E_{sorp}/R = - 1481.48

Therefore, E_{sorp} = 1481.48*8.314

= 12.317 KJ/gm mol

Rearranging Equation (4-4),

In K_{sorpo} = In K_{sorp} + I/T * slope

Taking the average from table (4-1)

$$\text{In } K_{sorpo} = \frac{\Sigma \text{ In } K_{sorp} + \Sigma(I/T * \text{slope})}{4}$$

$$= \frac{-9.66 + (0.0125 * 1481.48)}{4}$$

= 2.2220324

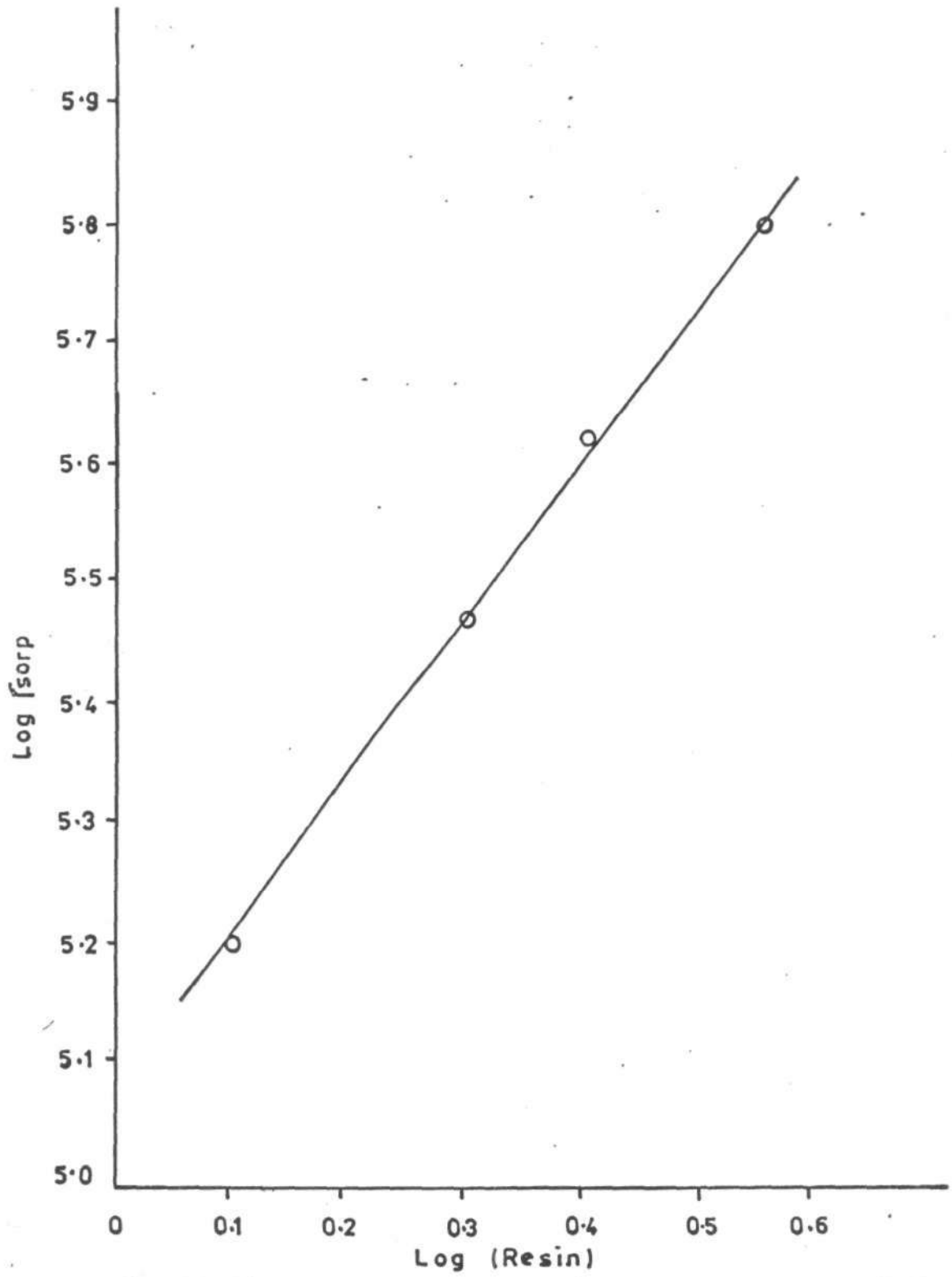


Fig. (4–4) Log–Log Plot of ʃsorp vs amount of Resin for determination of the dependency of rate on the amount of Resin

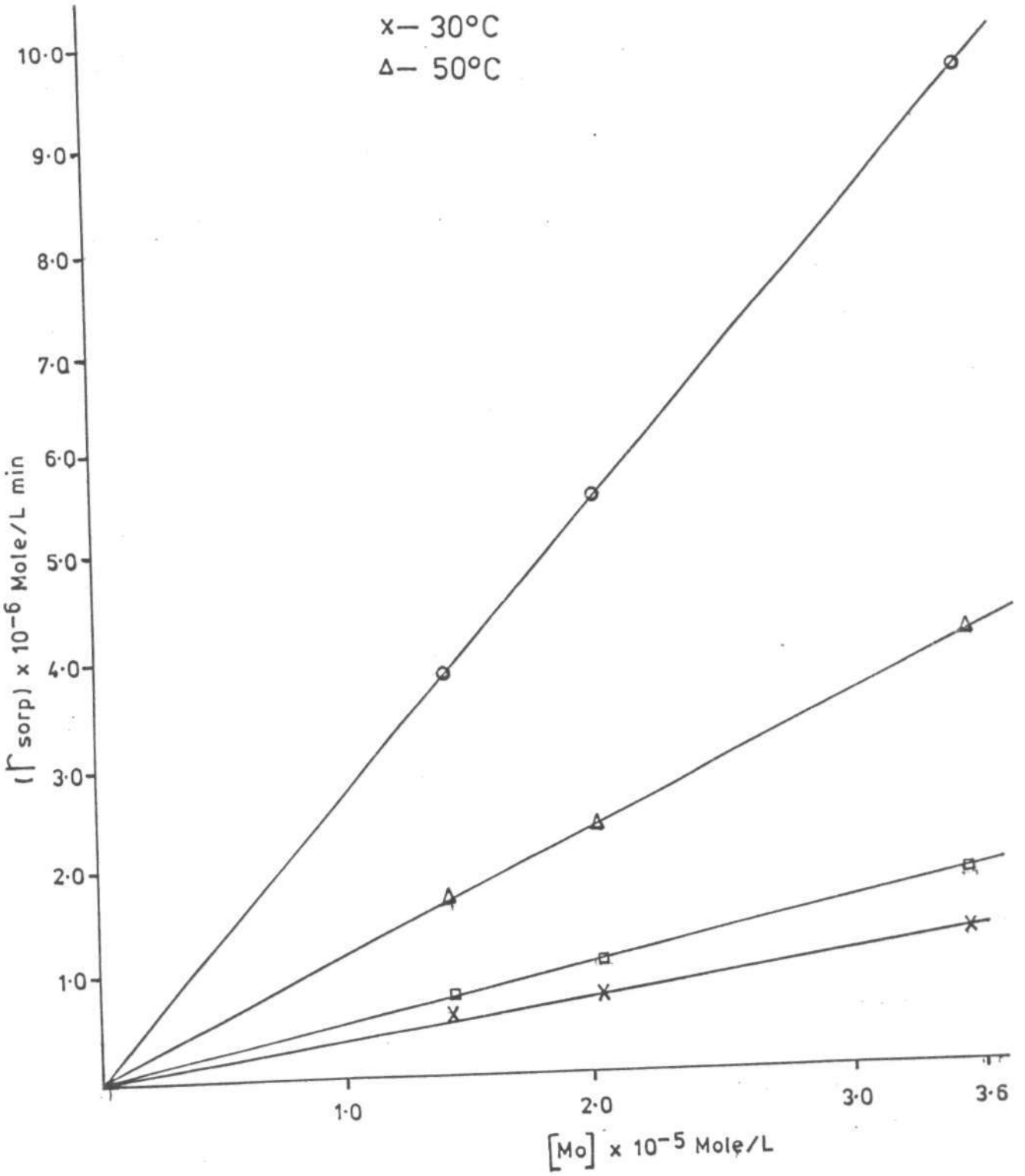


Fig. (4–5) Plot of Sorption rate (Γsorp Vs Molybdenum concentration [Mo] at different Temperatures

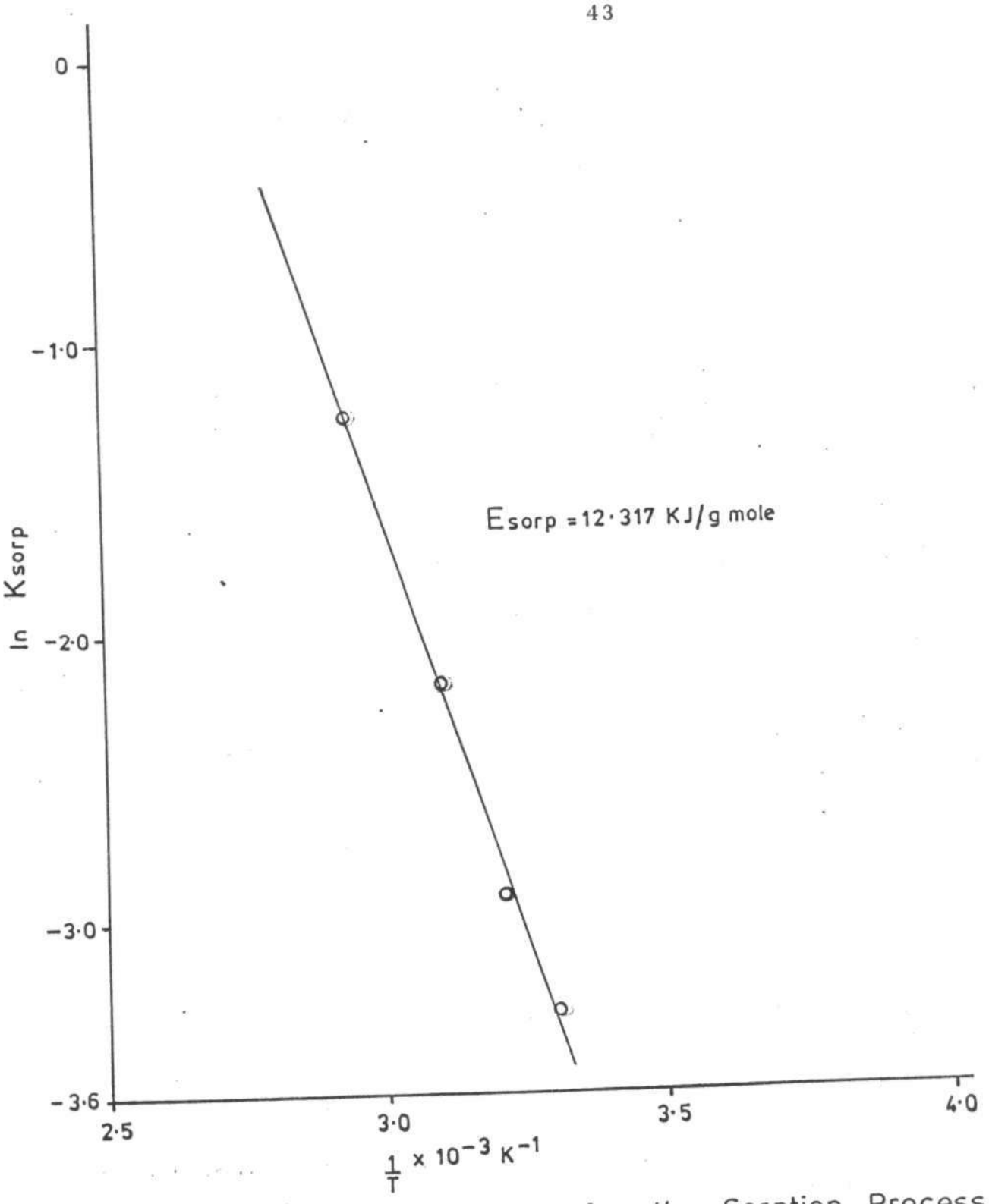


Fig. (4-6) Arrhenius Plot for the Sorption Process

Therefore, K_{sorpo} = 9.2261

Substituting these values into Equation (4-3),

K_{sorp}. = 0.081 $(min)^{-1}$

Therefore, the rate of sorption is:

$$\Gamma_{sorp}. = 0.081\ [Resin]\ [Mo] \qquad \ldots (4\text{-}5)$$

4.3 SORPTION RATE MODEL

The sorption rate equation (4-5) obtained above suggests that the resin is homogeneous in terms of the activity of the sorption site, that is, the resin has one site for sorption.

However analysis of fig (4-7) shows two distinct gradients which suggests that there may actually be two active sites on the resin where the sorption of molybdenum takes place in parallel. In order to test this assumption, a typical model equation for two parallel first-order reactions with a common product was proposed for the sorption process as follows:

$$[Mo] = [Mo]o\ (\theta e^{-k1t} + (1-\theta)e^{-k2t}) \qquad \ldots (4\text{-}6)$$

where θ = fraction of Mo sorbed by the first set of active sites with sorption rate constant, k_1

$(1-\theta)$ = fraction of Mo sorbed by the second set of active sites, with sorption rate constant, k_2

[Mo]o = Initial molybdenum concentration in solution

[Mo] = analytical concentration of molybdenum in solution at any time t.

The initial and final slopes (fig. 4-7) represent the respective sorption rate constants K_1 and K_2. The abscissa value of the point of intersection of the two slopes divides [Mo]o into [Mo_1]o and [Mo_2]o from where θ is evaluated. The estimated values of the parameters K_1, K_2 and θ are as follows:

$K_1 = 0.081$

$K_2 = 0.026$

$\theta = 0.45$

By substituting these values into equation (4-6) we can evaluate the analytical concentration of molybdenum in aqueous solution at any given time during the sorption process, that is

$$[Mo] = [Mo]o\ (0.45e^{-0.081t} + (1-0.45)\ e^{-0.026t}\ ) \quad \ldots (4-7)$$

By testing the parameters (k_1, K_2 and θ) in the model equation (4-7), it was observed that good agreement was obtained between the analytical molybdenum concentration values determined experimentally and those evaluated by the model as seen in fig (4-8). This makes our assumption of the existence of two active sites in the resin valid. On the contrary, a remarkable disagreement was observed between experiment and the model when one active site with a simple first-order sorption rate constant, that is,

$$[Mo] = [Mo]o\ e^{-kit} \quad \ldots (4-8)$$

was tested.

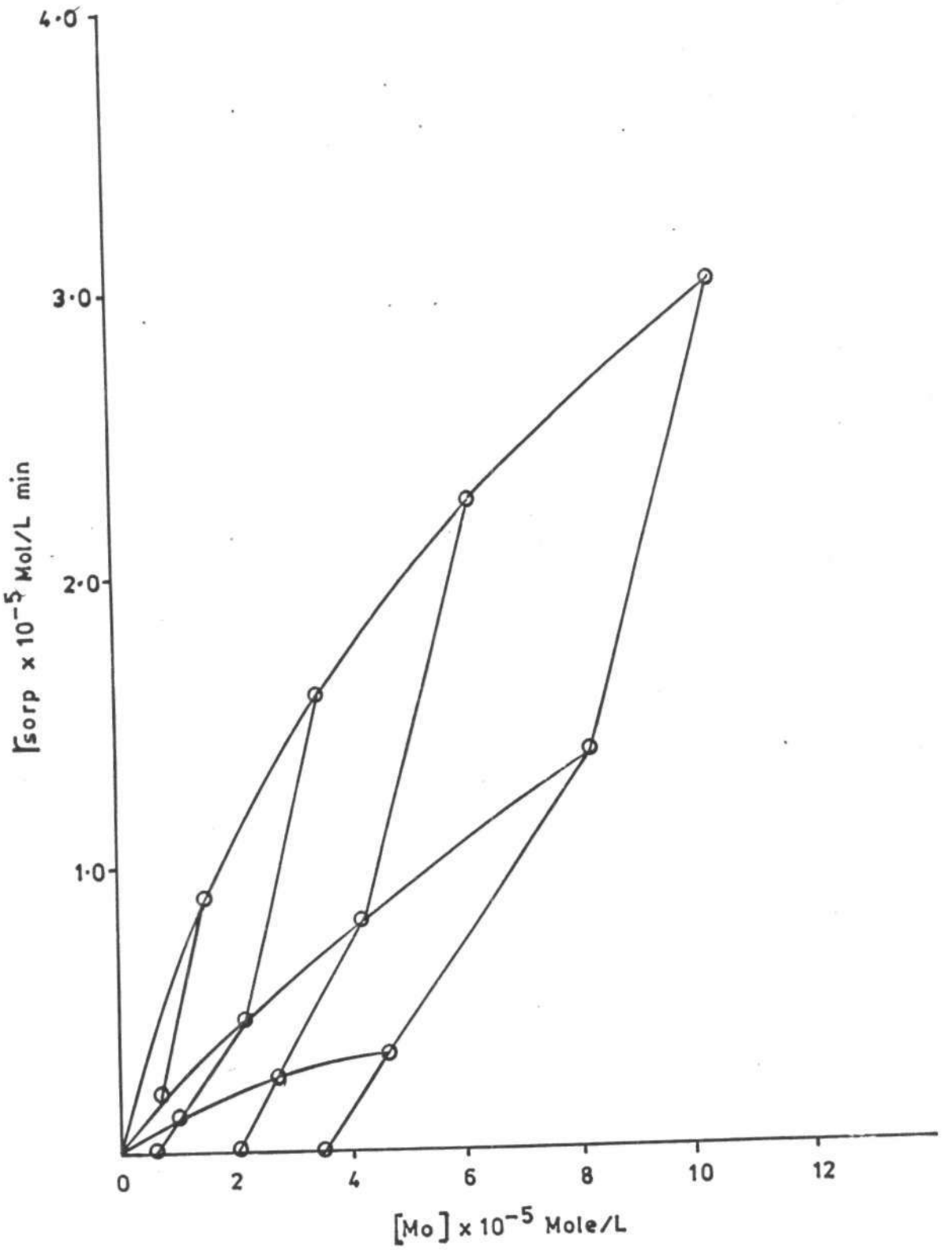


Fig. (4–7) Typical plot of Sorption rate Vs Mo concentration showing two active sites of Sorption

This is shown by curve 1 in fig. (4-8).

A further test of the parameters (k_1, K_2 and θ) in the model equation (4-7) on the entire experimental points of fig (3-1.c) shows good agreement also with those evaluated by the model as seen in fig. (4-9).

4.4 THERMODYNAMICS OF SORPTION

The rate of uptake of material by beads of Resin (ion exchanger) from an ambient solution and the transport of material from one solution to another across an ion-exchange membrane can only be understood when the conditions of equilibrium between the resin and the solution are known. Thus, the sorption of molybdenum from its aqueous solution into resin can be represented as:

$$Mo + Re \rightleftharpoons [Mo\text{-}Re]$$

The equilibrium constant is

$$K = \frac{[Mo\text{-}Re]}{[Mo]\,[Re]} \qquad \ldots (4\text{-}9)$$

where [Re] = molar concentration of molybdenum ions in resin based on the number of gramme corrected by the constant σ

$$= Re\,\sigma\,\frac{1000}{V} - [Mo\text{-}Re]$$

$Re\,\sigma\,\frac{1000}{V}$ = molar concentration of active sites in the resin.

Re = amount of resin (gm).

V = volume of reaction mixture (30ml).

[Mo-Re]= molybdenum concentration in the reaction mixture at equilibrium

Hence we propose an adsorption model as:

$$K = \frac{[Mo\text{-}Re]}{[Mo]\,(Re\,\sigma\,\frac{1000}{V} - [Mo\text{--}Re])} \qquad \ldots (4\text{-}10)$$

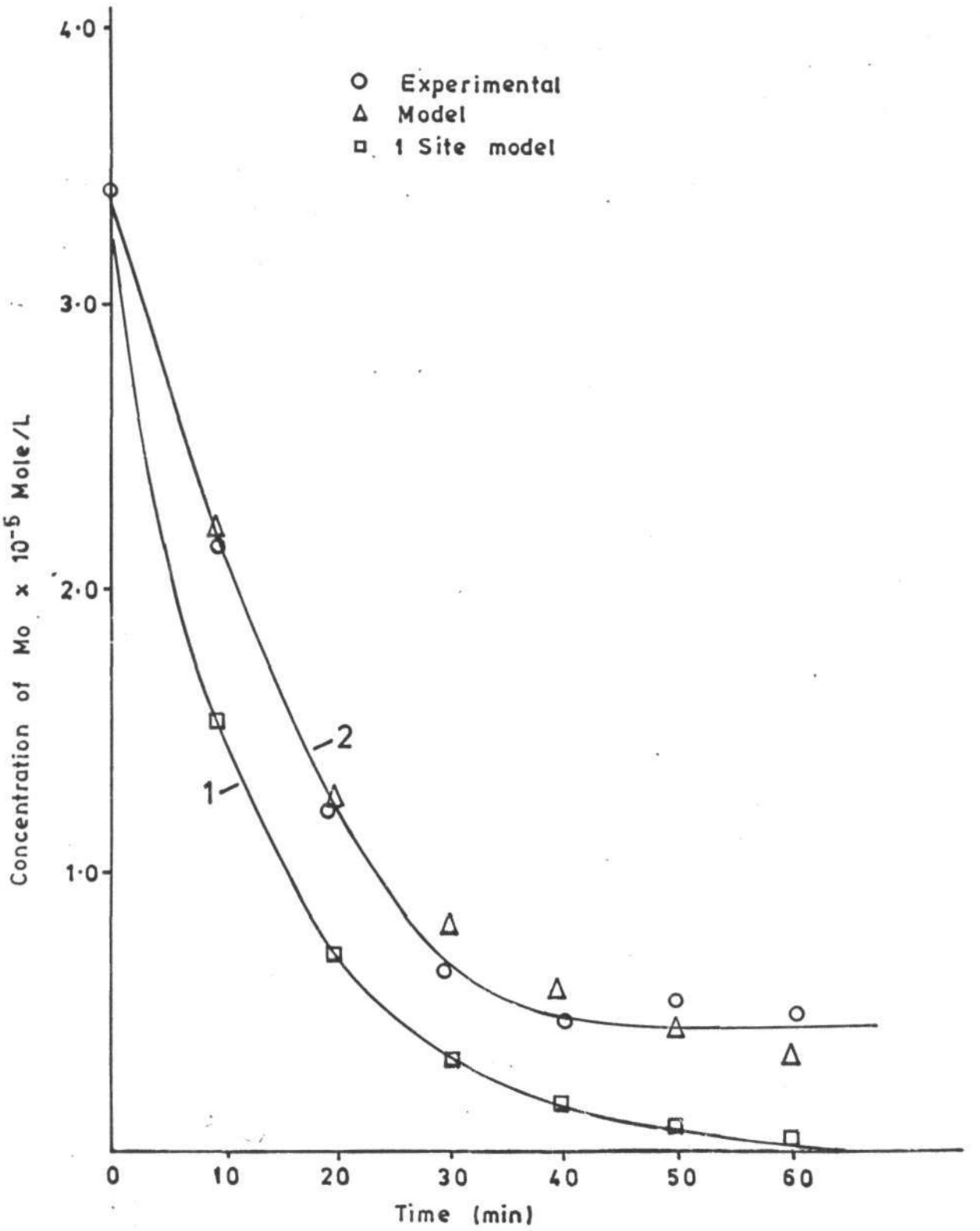


Fig. (4-8) Typical plot of [Mo] Vs Time showing Agreement between experimental and two active site model (2) but disagreement with one active model (1)

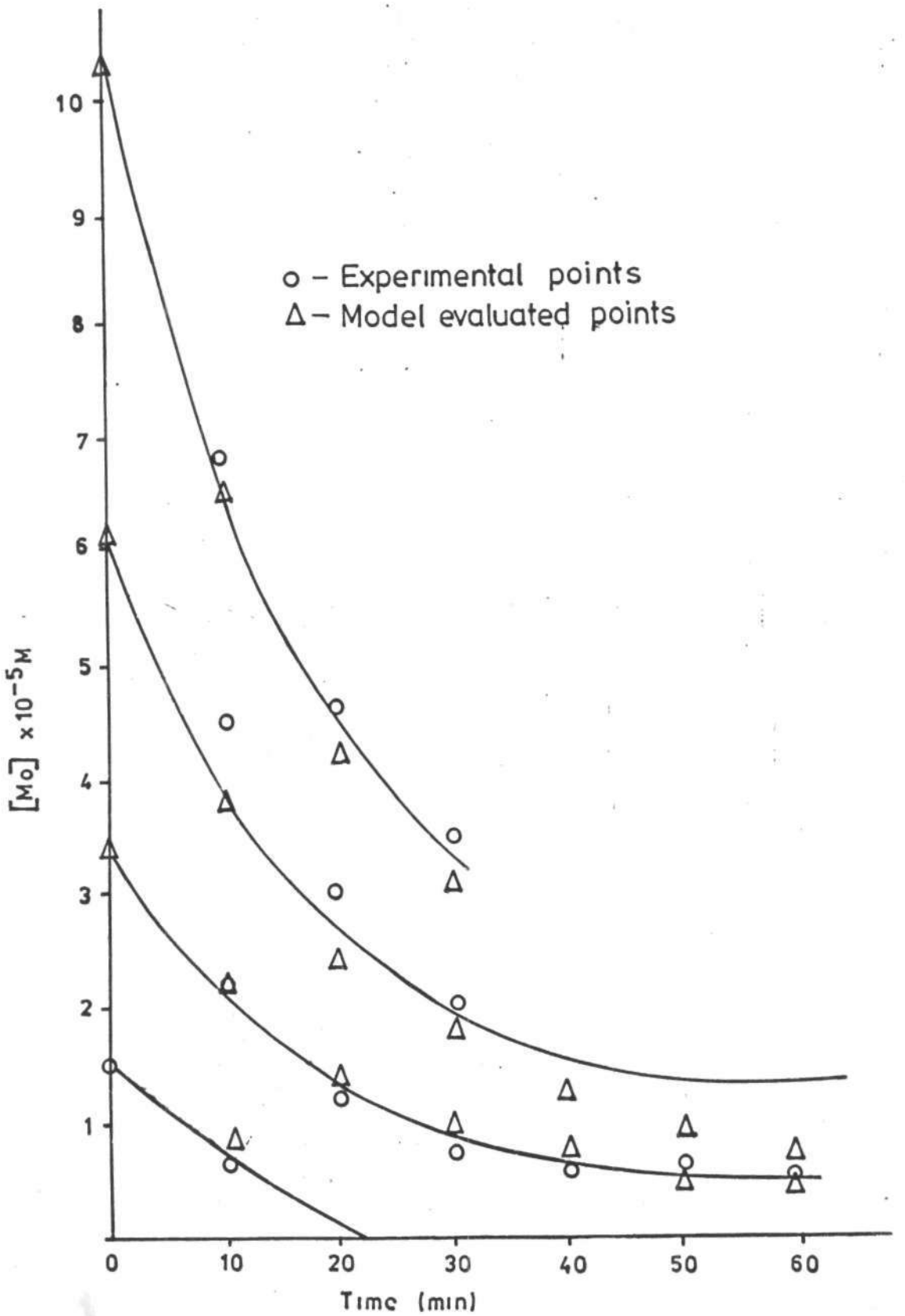


Fig (4-9) Typical Kinetic plots showing Agreement between Experimental Points (o) and Model evaluated points (Δ)

By rearranging equation (4-10) we have;

$$[\text{Mo-Re}] = \frac{K[\text{Mo}]\left(\text{Re}\,\sigma\,\frac{1000}{V}\right)}{1 + K[\text{Mo}]} \qquad \ldots (4\text{-}11)$$

By iteration using experimental points of curve (1) in fig (4-1) with equation (4-11), the values of the parameters (K and σ) are found to be

$$K = 612$$

$$\sigma = 1.24 \times 10^{-4}$$

By substituting these values into equation (4-11)
we can evaluate the equilibrium molybdenum concentration in aqueous solution at any given amount of resin during the sorption process;
that is,

$$[\text{Mo-Re}] = \frac{2.53\ \text{Re}\ [\text{Mo}]}{1 + 612[\text{Mo}]} \qquad \ldots (4\text{-}12)$$

When these parameters (K and σ) were tested in the adsorption isotherm equation (4-12), it was observed that good agreement was obtained between the analytical equilibrium molybdenum concentration values determined experimentally and those evaluated by the model equation as shown by curve (2) of fig. (4-1). This then confirms our proposed adsorption model (equation 4-10) with correction constant σ, valid.

The high value of K(612) implies that the sorption

process favours more of adsorption than desorption process. Hence the reaction equilibrium can be rewritten as :

$$Mo + Re \rightleftharpoons [Mo\text{-}Re]$$

Free Energy change of Sorption

Free energy change is given by:

$$\Delta G = -RT \ln K \qquad \ldots(4\text{-}13)$$

where R = 8.314 J/gm mol K (Gas constant).

T = 40 + 273 = 313K

K = 612

Therefore,

ΔG = - 8.314 x 313 (In612)

= - 16.7KJ.

This value indicates that the sorption of molybdenum in to the resin is spontaneous.

A detailed study of the sorption kinetics, thermodynamics, and the optimum operating conditions for the synthesis of molybdenum catalyst immobilized on polymer resin as support have been discussed in this chapter. It is now expedient that the behaviour of the synthesised catalyst during exploitation in chemical reaction proper be duly investigated. This is the subject matter of the following chapter (5).

CHAPTER FIVE

5. STUDIES ON OXIDATION REACTIONS USING POLYMER ANCHORED (IMMOBILIZED) CATALYST

The successful synthesis of the polymer immobilized molybdenum catalyst in chapter three, which was discussed in chapter four, has stimulated a number of applications for oxidation processes. These processes include ethylene oxide production from ethylene, maleic acid, and acyl chloride, production of petrochemicals in the petroleum industry, and other common oxidation reactions.

However, to establish the activity and usefulness of the immobilized catalyst, a typical oxidation reaction, of maleic acid by hydrogen peroxide as a model reaction was chosen due to the following reasons:

(1) Maleic acid can smoothly be oxidized to cis-epoxysuccinic acid.

(2) Oxidation of maleic acid with hydrogen peroxide is a simple process.

5.1 EXPERIMENTAL DETAIL FOR EPOXIDATION OF MALEIC ACID BY HYDROGEN PEROXIDE

Reagents

(1) Maleic acid (COOH. CHCH. COOH), BDH chemical ltd.

(2) Ammonium molybdate (NH_4) MoO_4 catalyst, BDH chemicals Ltd.

(3) Resin - supported catalyst (Synthesised).

(4) Sodium thiosulphate (Na_2 S_2 O_3). $5H_2O$, Baker grade, minimum assay 99.5%. BDH chemical ltd.

(5) Sodium hydroxide (NaOH). Assay = 99%

(6) Hydrogen peroxide (H_2O_2), BDH, chemicals ltd.

(7) Potassium iodide (KI), BDH, Minimum assay 99.5%.

(8) Acetic acid (CH_3 COOH, glacial, SCR. M.N = 60.05) minimum assay = 99.1%,BDH chemical ltd.

(9) Distilled water

(10) N-Bromosuccinimide

(11) Starch indicator, 1% (M/V) aqueous solution.

(i) N-Bromosuccinimide solution, was prepared by dissolving 18 gm of the reagent in litre glacial acetic acid.

(ii) Potassium iodide, 10%(W/V) aqueous solution.

(iii) Sodium thiosulfate, O.IN solution, standardised against standard copper sulphate solution.

Procedure

The epoxidation reactions were carried out in the jacketed micro - reactor (50ml) fitted with a condenser, thermometer and thermostat. 26ml of maleic acid (2.0 M) solution was introduced into the reactor and stirred with magnetic stirrer. The temperature was set at 65°C with the thermostat. To this solution 0.87ml of sodium hydroxide

(1.5M) was added. The heat of neutralization caused a rise in temperature, but the 65°C temperature was maintained by the thermostat. To the warm solution, 0.13ml of 2.97 x 10^{-5}M aqueous solution of molybdenum (homogeneous catalyst) or 0.4 gm of the synthesised (immobilized) catalyst, was added such that about 1% of the catalyst by volume of hydrogen peroxide was used. 13ml of 20% hydrogen peroxide (IM) was added in one portion. The amount of hydrogen peroxide to that of maleic acid in the reaction mixture was 1:1. 1 ml aliquot was taken every 10 minutes for one hour, and analysed, to monitor the rate of consumption of hydrogen peroxide or maleic acid as described in section (2.7). A total volume of 6ml of aliquot samples were taken, such that the effect of removal of 6ml from 40ml (the total volume of the reaction mixture) will be negligible.

To be able to evaluate selectivity of the catalyst, the volume of oxygen evolved (due to the inevitable decomposition of hydrogen peroxide into oxygen and water) was collected every 10 minutes in the course of the epoxidation reaction.

Furthermore, in order to evaluate the stability of the immobilized catalyst during exploitation in homogeneous oxidation reactions, the catalyst was reused 7 times, in turn for the epoxidation reaction. After each reaction, the catalyst was filtered, washed with distilled water, dried at 75°C for one hour and then reused . In the reuse reaction, 6.8 x 10^{-2}M hydrogen peroxide, and 6.0 x 10^{-2}M maleic acid were

chosen as the standard parameters because of the maximum yield and conversion obtained under these conditions.

5.2 KINETICS OF MALEIC ACID EPOXIDATION WITH HYDROGEN PEROXIDE USING IMMOBILIZED MOLYBDENUM CATALYST

5.2.1 Results of Preliminary investigation

It has been established in section (2.0) that chemical interaction exists between the metal (of the catalyst component) and the polymer resin through the functional groups of the resin. It is therefore expected that the kinetic regularities of reactions catalysed by the immobilized catalyst will be some what similar to that of the homogeneous catalysis. It is therefore important, first of all, to establish the superiority of catalysis by the immobilized catalyst over homogeneous catalyst in terms of such parameters as extent of reaction and yield.

To this end, a preliminary investigation was conducted by carrying out a typical maleic acid epoxidation reaction with hydrogen peroxide using molybdenum catalyst (supported) and in homogeneous solution (unsupported), in turn under the same set of condition: T = 65°C, [M.A] = 1.29×10^{-2} mole/litre, [cat.] = 2.97×10^{-5} mole/litre and $[H_2O_2]$ = 7.65×10^{-2} mole/litre. The result of this investigation is presented in fig (5-1). As seen in the figure, the extent of reaction is far higher with the supported catalyst than the unsupported one. For example, when both reactions have been run for one hour, conversion of

77% was achieved with the supported catalyst as against 46% with the unsupported catalyst. Table (5-1) shows the difference in the activities of the two catalyst systems which also favours the use of the supported catalyst.

Thus, having established the superiority of the immobilized over the homogeneous catalyst, coupled with the apparent advantages achievable with its use as earlier discussed in section (2.1.1), it is now reasonable to carry out a detailed investigation of a typical oxidation process (as stated above) with a view to establishing the kinetic characteristics of reactions catalysed by the immobilized (anchored or supported) catalyst, and also, to develop the necessary mathematical models that may be used for reactor design. For the purpose of easy comparative analysis, investigations involving homogeneous catalysis were also carried out.

As a rule, in order to establish the kinetic or mathematical laws guiding a chemical reaction, it is important to know how the rate of reaction varies with changes in the initial condition of reactant species under a given set of conditions. Usually, a unifactor experiment is carried out in which only one parameter is varied at a time while others are fixed.

Thus, one can easily evaluate the order of reaction with respect to the concentration (pressure) of that parameter whose initial conditions were varied in a particular experimental series.

Table (5-1): Time dependence of Activity of immobilized and homogeneous molybdenum catalyst.

Time min	% Activity	
	Homogeneous Catalyst	Immobilized catalyst
0	100	100
10	56	76
20	45	59
30	39	49
40	33	40
50	28	34
60	25	30

5.3 EFFECT OF HYDROGEN PEROXIDE CONCENTRATION

In order to determine the effect of changes in hydrogen peroxide concentration on the rate of the epoxidation reaction, a series of experiments were carried out in which the initial hydrogen peroxide concentrations were varied within the range of 5.72 $x10^{-2}$ to 8.97 $x10^{-2}$ mole/litre under the following conditions. T = 65°C, [M.A] = 5.2 x 10^{-2} mole/litre, [Cat] = 2.97 x 10^{-5} (immobilized on support-resin and also in homogeneous system), and NaOH = 1.5M.

Plots showing typical kinetic curves for maleic acid epoxidation with hydrogen peroxide are presented in fig. (5-2), (with —— immobilized catalyst) and (with----homogeneous catalyst). Figs. (5-3a) to fig (5 - 3.d) show typical products distribution during the course of the reaction under various initial hydrogen peroxide concentration (within the range stated above). Morealso, Fig. (5-4) shows typical selectivity-time curves, where the immobilized (resin supported) catalyst show a higher selectivity than the homogeneous (unsupported) catalyst. The values of selectivity were evaluated based on hydrogen peroxide consumption as described in section (5.1) taking into consideration loses occasioned by the inevitable decomposition of hydrogen peroxide.

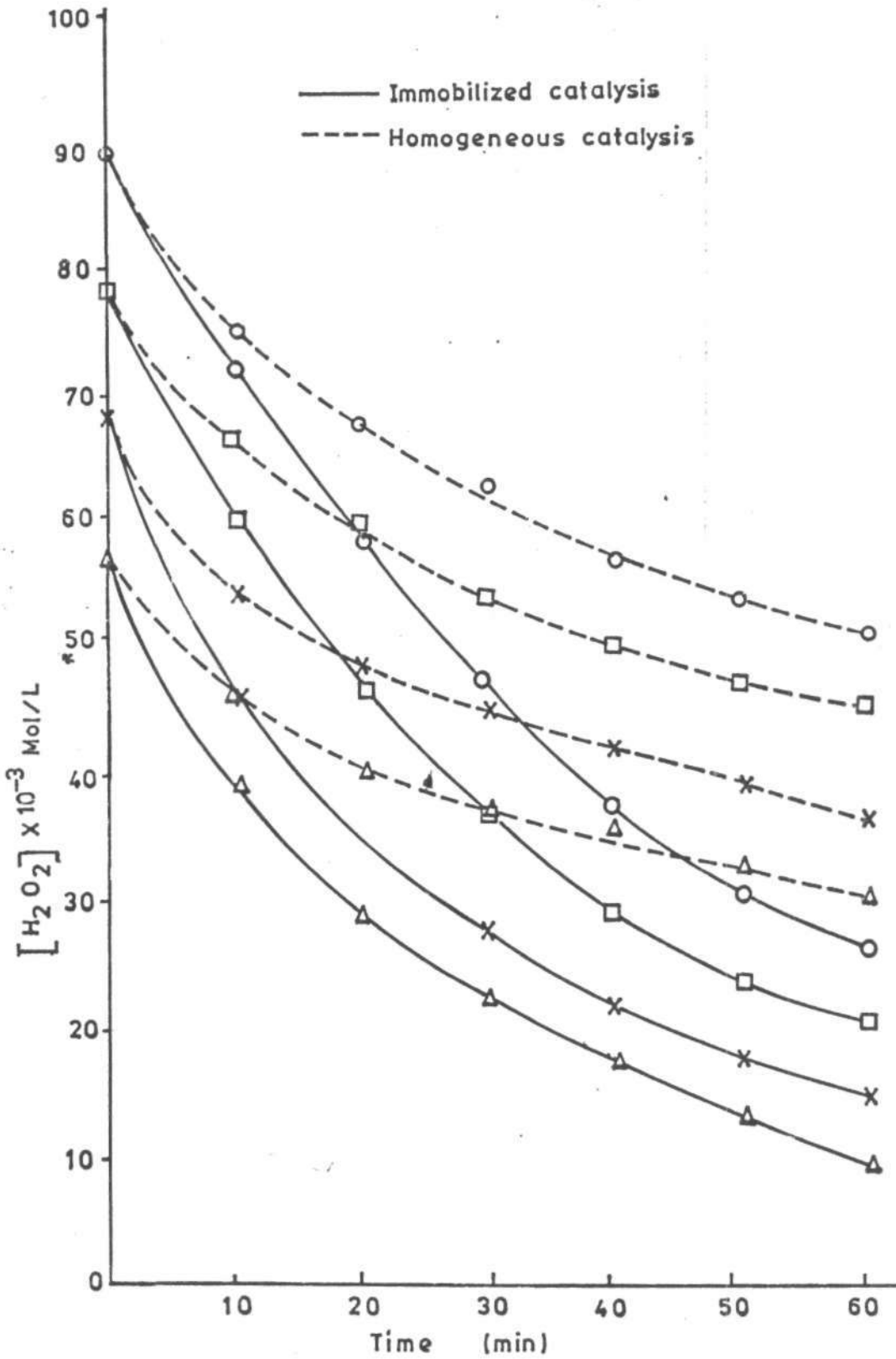


Fig. (5-2) Plot of Typical Kinetic curves of Maleic acid epoxidation as initial concentration of H_2O_2 is varied

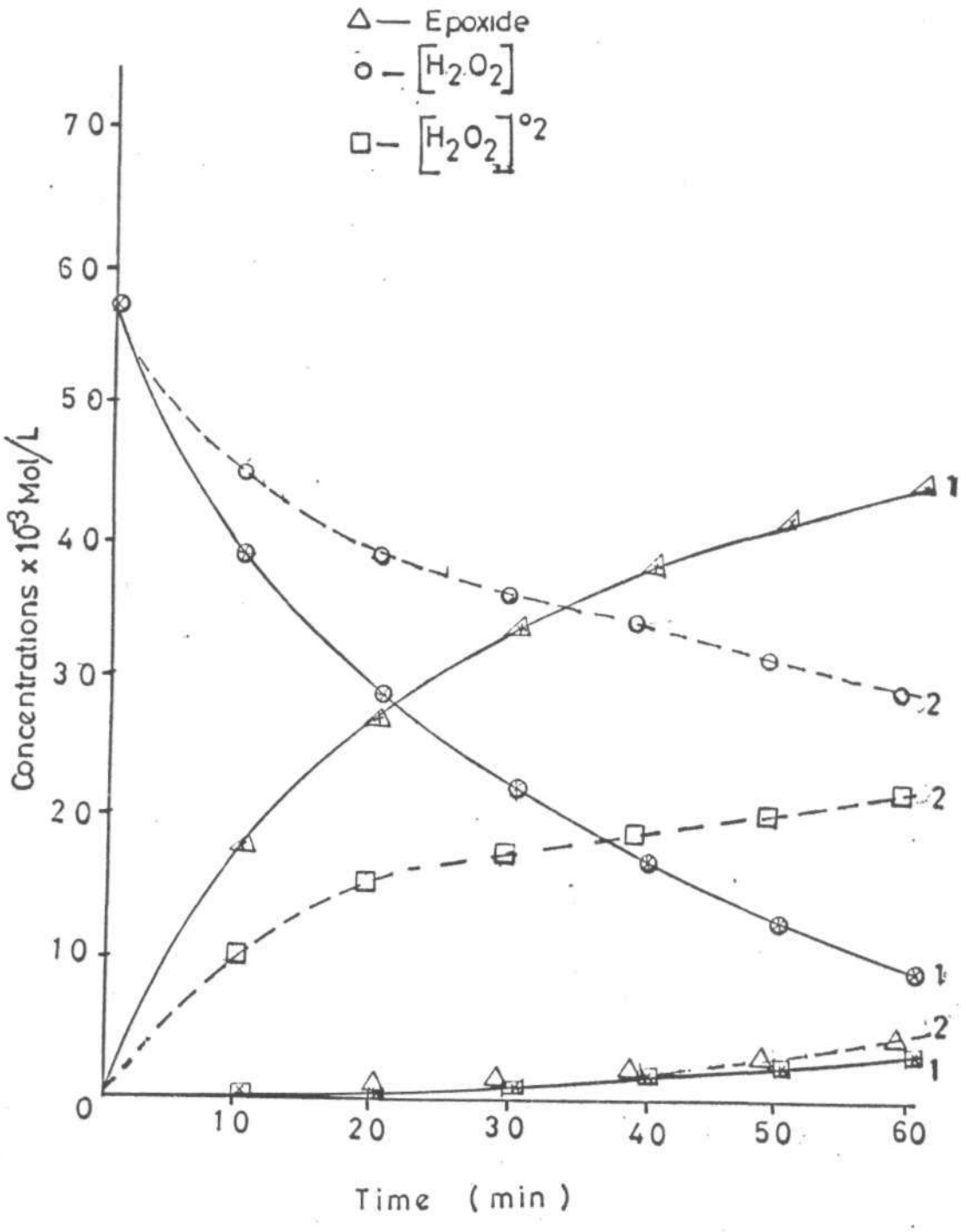


Fig (5-3a) Product distribution in the course of Maleic acid epoxidation using:- (1) immobilized, (2) homogeneous catalysts

$[H_2O_2]_o = 5.72 \times 10^{-2} M$

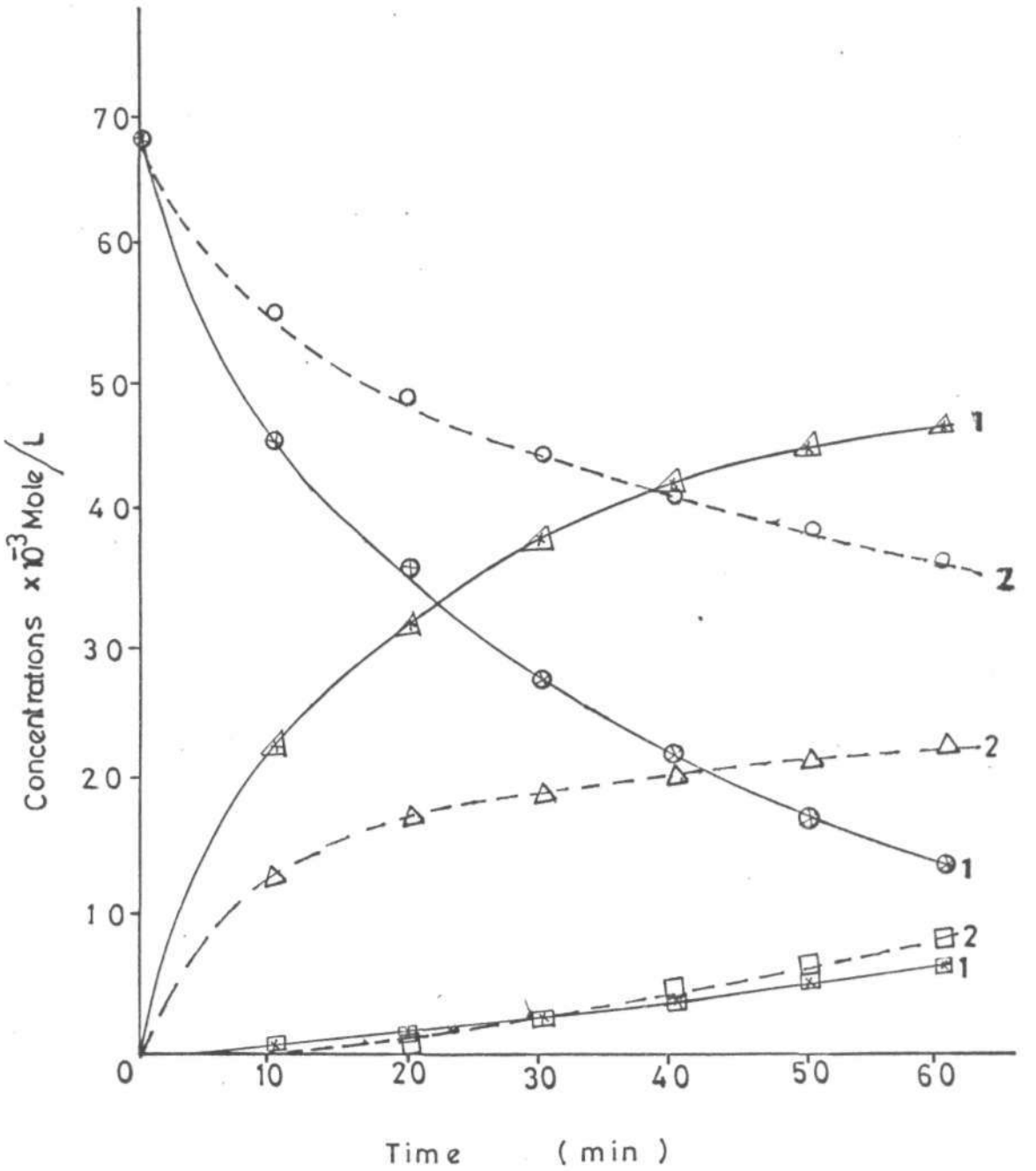


Fig (5 -3b) Products distribution in the course of Maleic acid epoxidation using:(1) immobilized (2)homogeneous catalysts

$$[H_2O_2]_o = 6.8 \times 10^{-2} M$$

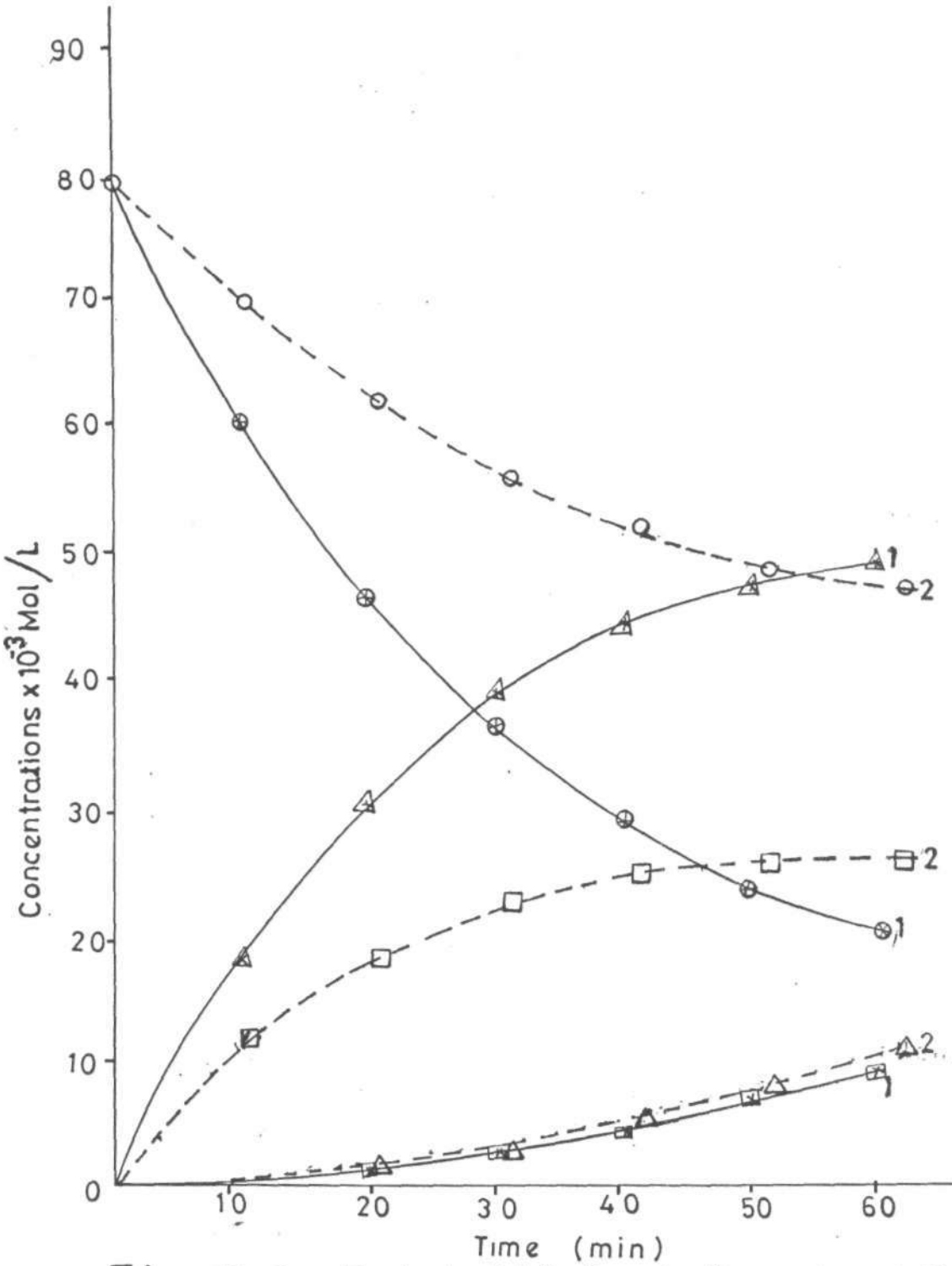


Fig. (5–3c) Product distribution in the course of Maleic acid epoxidation using (1) immobilized, (2) homogeneous

$[H_2O_2]_o = 7.86 \times 10^{-2}$ M

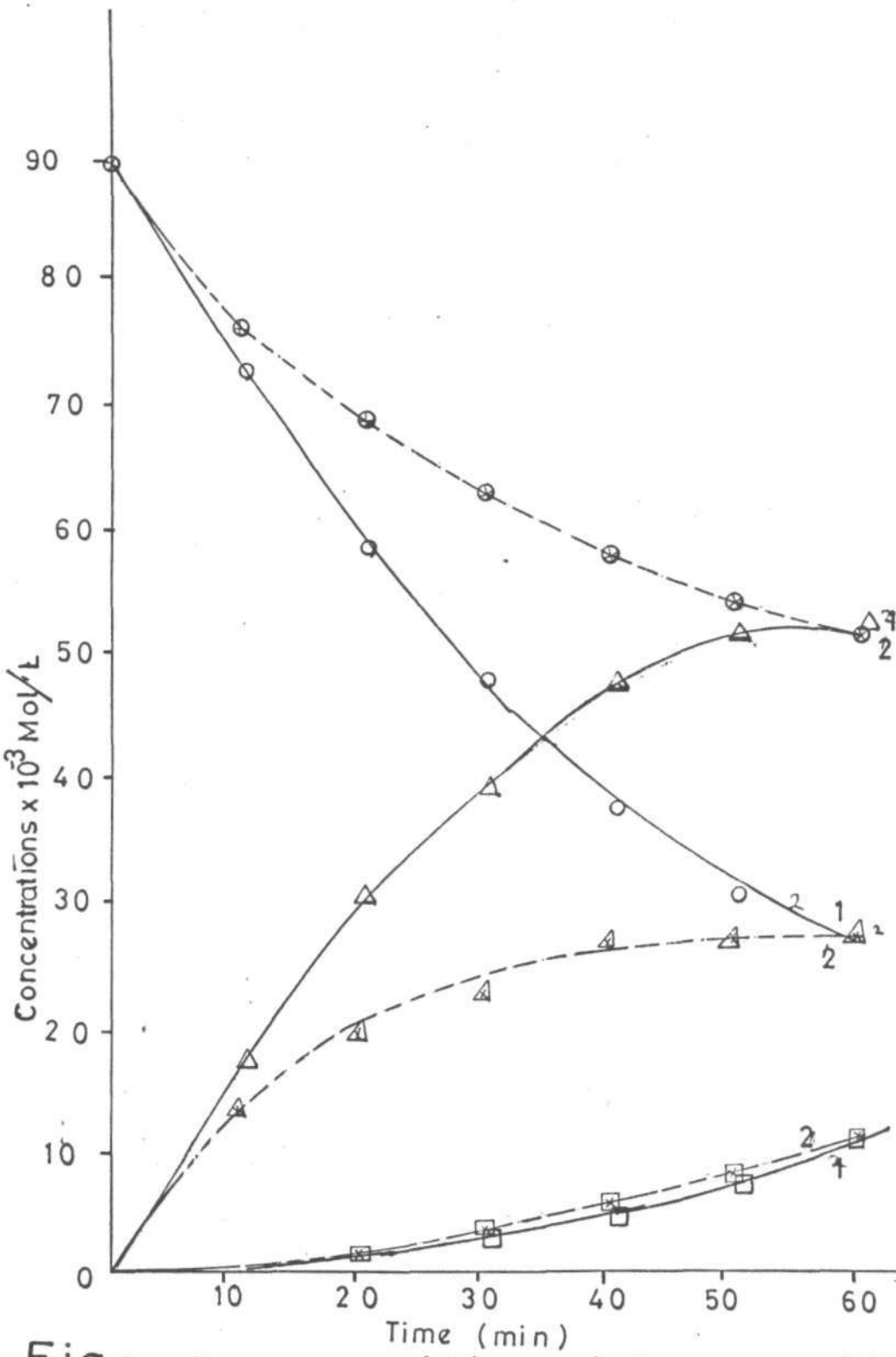


Fig (5-3d) Product distribution in the course of Maleic acid epoxidation using (1) immobilized (2) homogeneous catalysts $\left[H_2O_2\right]_o = 8.97 \times 10^{-2}$ M

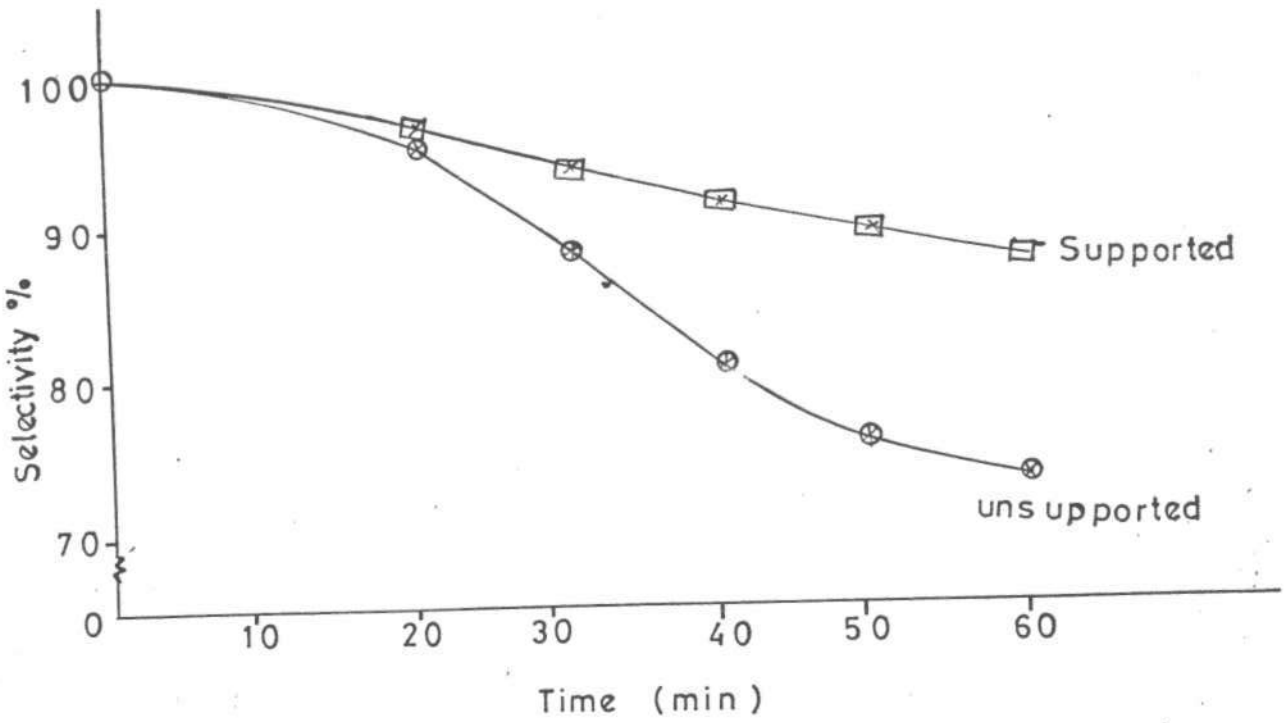


Fig (5-4) A Typical time dependence of catalyst selectivities in epoxidation of Maleic acid as initial concentration of H_2O_2 is varied.

5.4 EFFECT OF MALEIC ACID CONCENTRATION

Similarly, in order to determine the effect of changes in maleic acid concentration on the rate of the epoxidation reaction, a series of experiments were carried out in which the initial maleic acid concentrations were varied within the range of 4.8×10^{-2} to 6.0×10^{-2} mole/litre under the following conditions: T = 65°C, $[H_2O_2] = 6.8 \times 10^{-2}$ mole/litre, [cat.] $= 2.97 \times 10^{-5}$ mole/litre (immobilized on supported resin and also in homogeneous system).

Plots showing typical kinetic curves for maleic acid epoxidation with hydrogen peroxide are presented in fig. (5-5), (with immobilized and homogeneous catalysts). Figs. (5-6.a) to fig. (5-6.c) show typical products distribution during the course of the reaction under various initial maleic acid concentrations (within the range stated above). Fig. (5-7) shows the product distribution for epoxidation reaction of maleic acid concentration, 6.0×10^{-2} mole/l and hydrogen peroxide concentration, 6.8×10^{-2} mole/l. for 6.5 hours (immobilized catalysis) and 8 hours (unsupported catalysis). Furthermore, fig.(5-8) shows typical selectivity-time curves for both immobilized and homogeneous catalysts. It can be seen that the selectivity of the immobilized catalyst is higher than that of homogeneous catalyst.

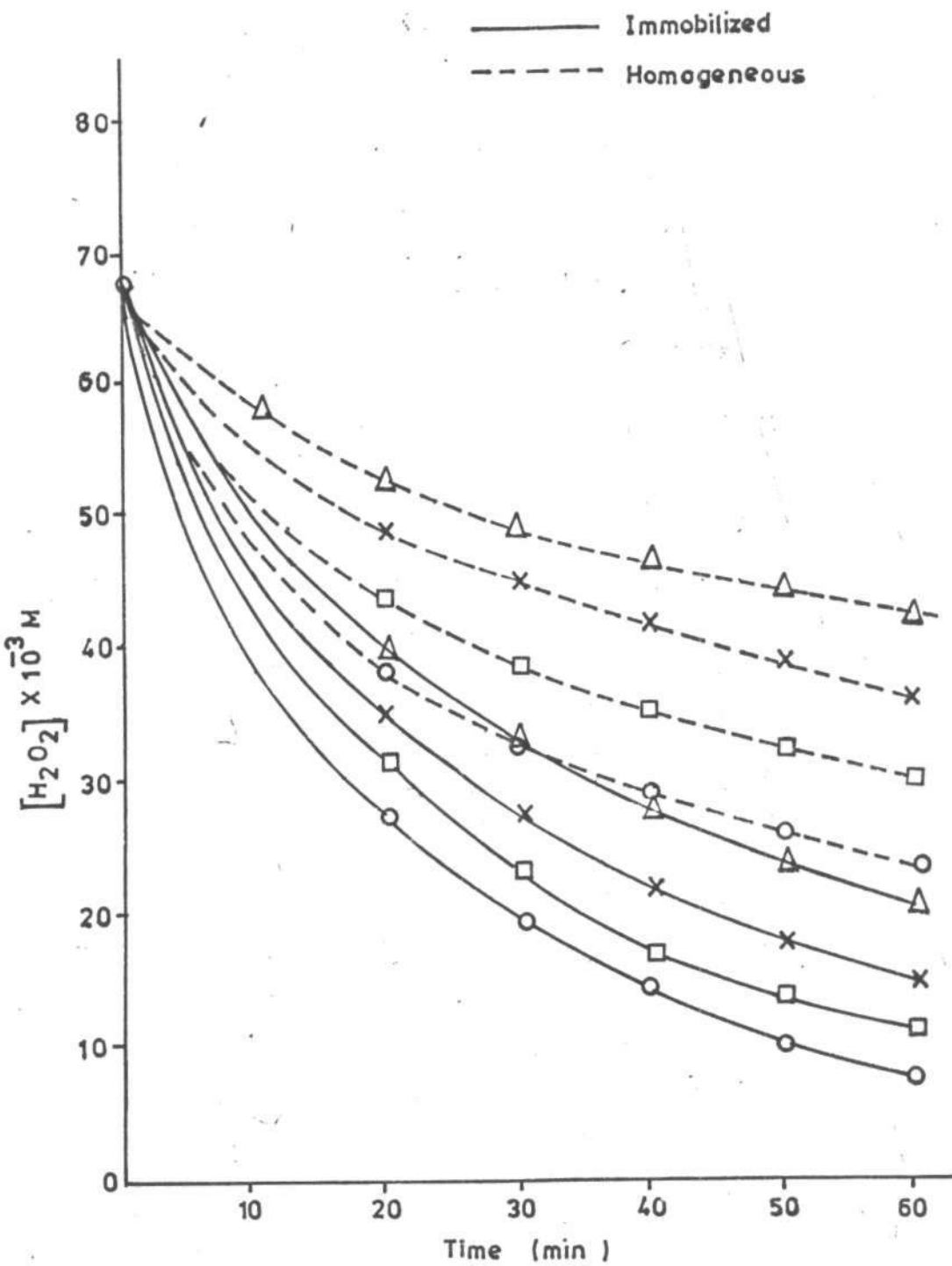


Fig. (5-5) Plot of typical kinetic curves of Maleic acid epoxidation at fixed $[H_2O_2]$ while initial concentration of Maleic acid is varied

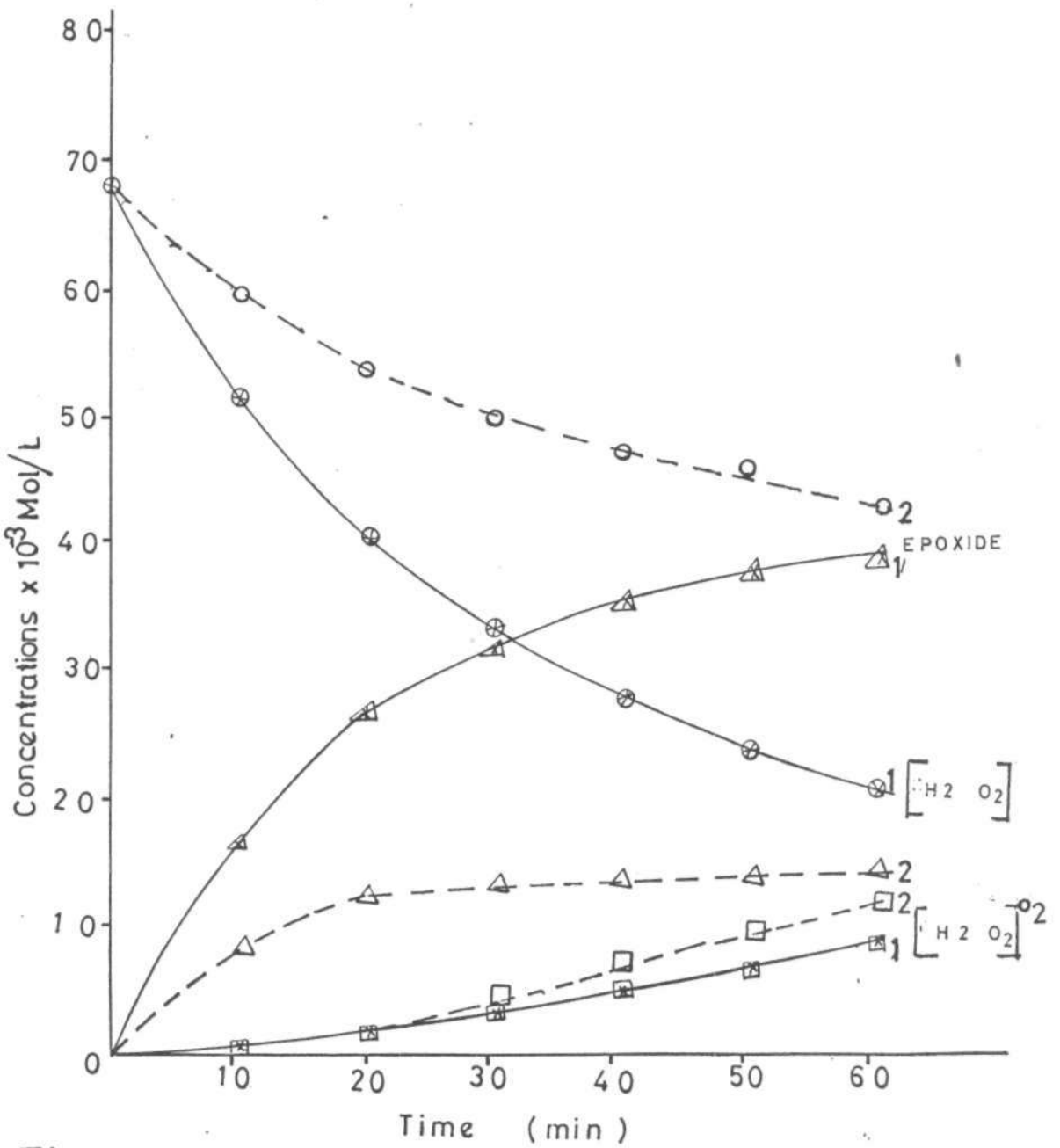


Fig (5-6a) Product distribution in the course of Maleic acid epoxidation using (1) immobilized (2) homogeneous catalysts with H_2O_2

$[MA]_o = 4.80 \times 10^{-2} M$

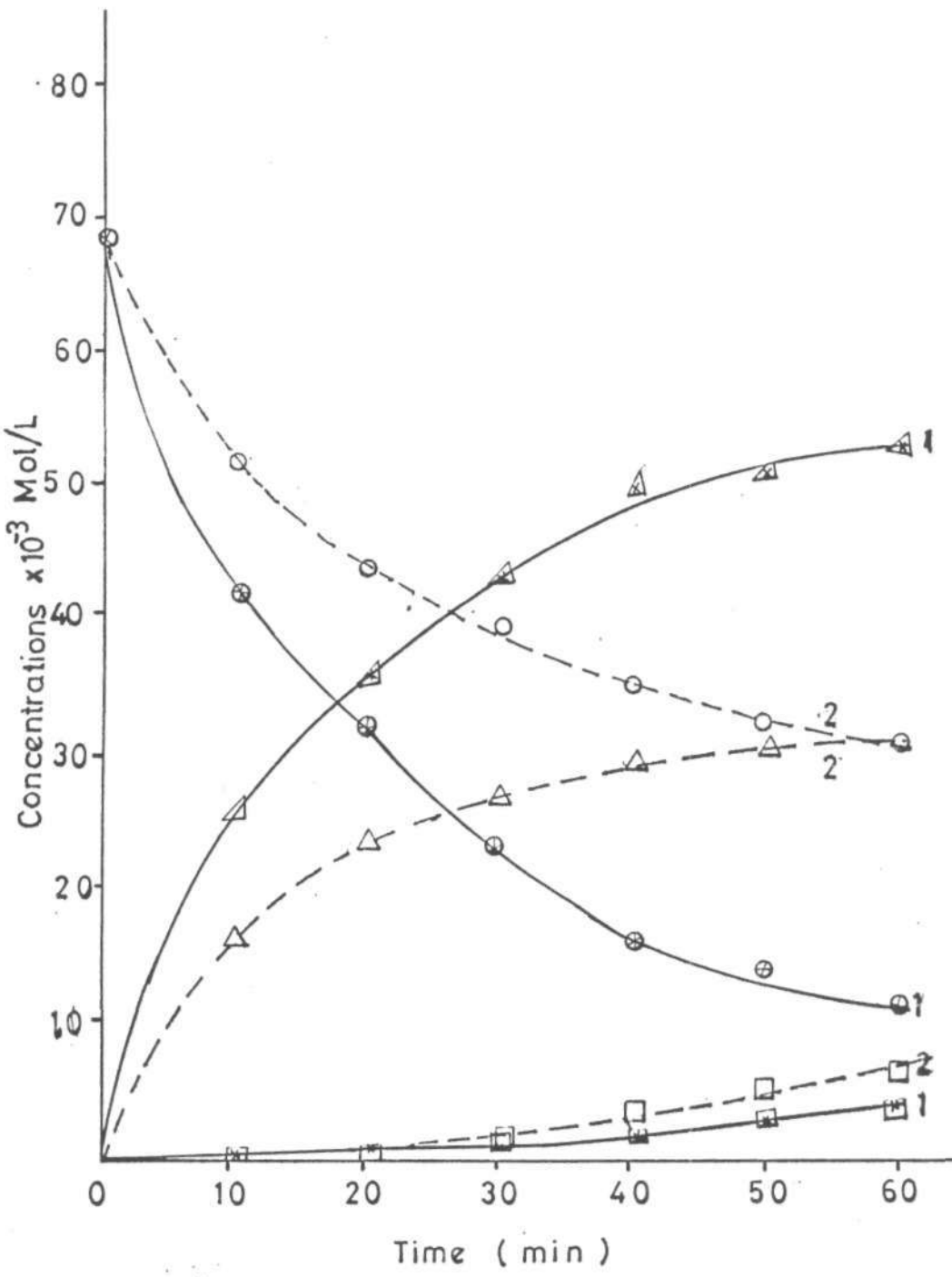


Fig (5-6b): Product distribution in the course of Maleic acid epoxidation using (1) immobilized (2) homogeneous catalysts with H_2O_2 $[M\ A]_o = 5{\cdot}60 \times 10^{-2}$ M

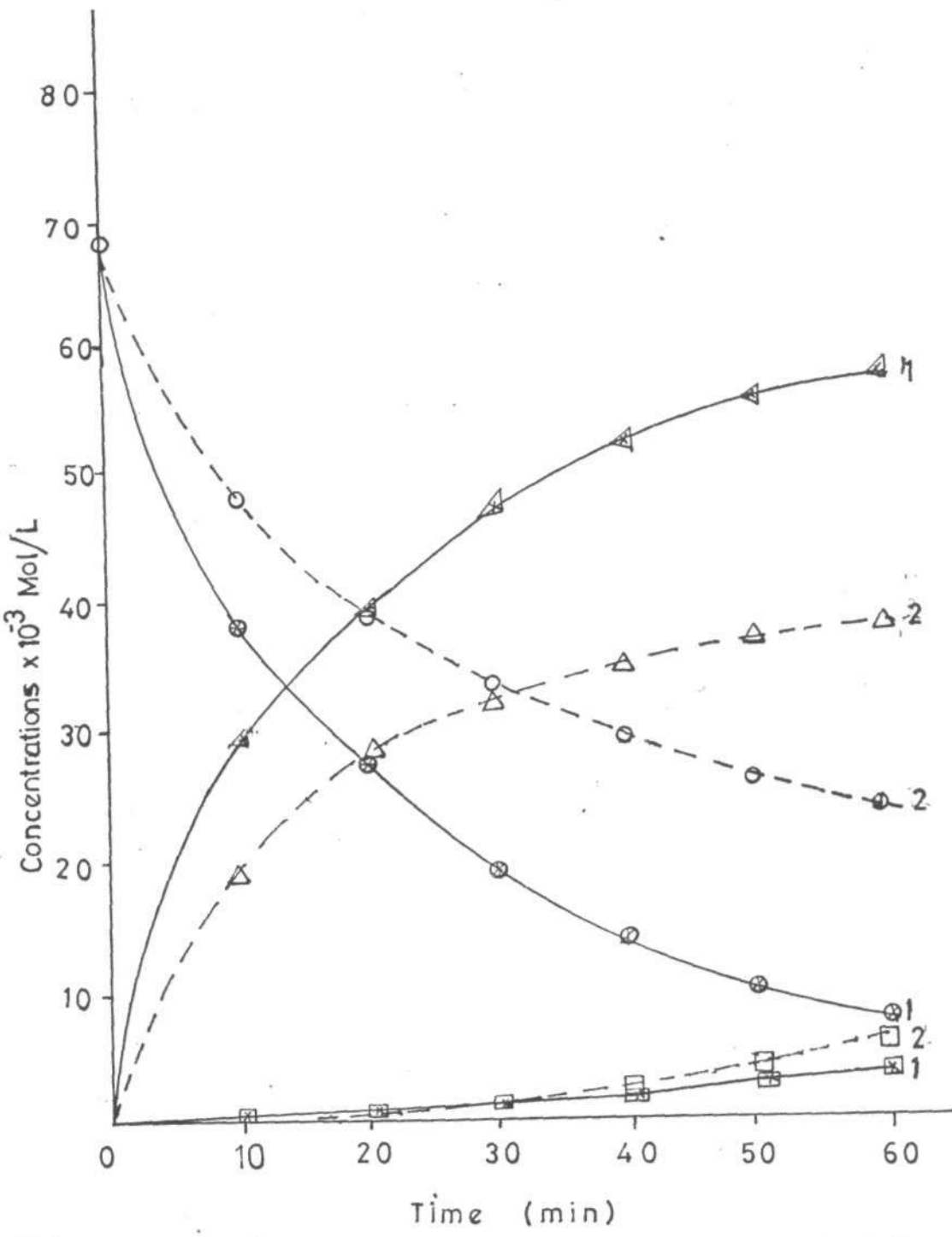
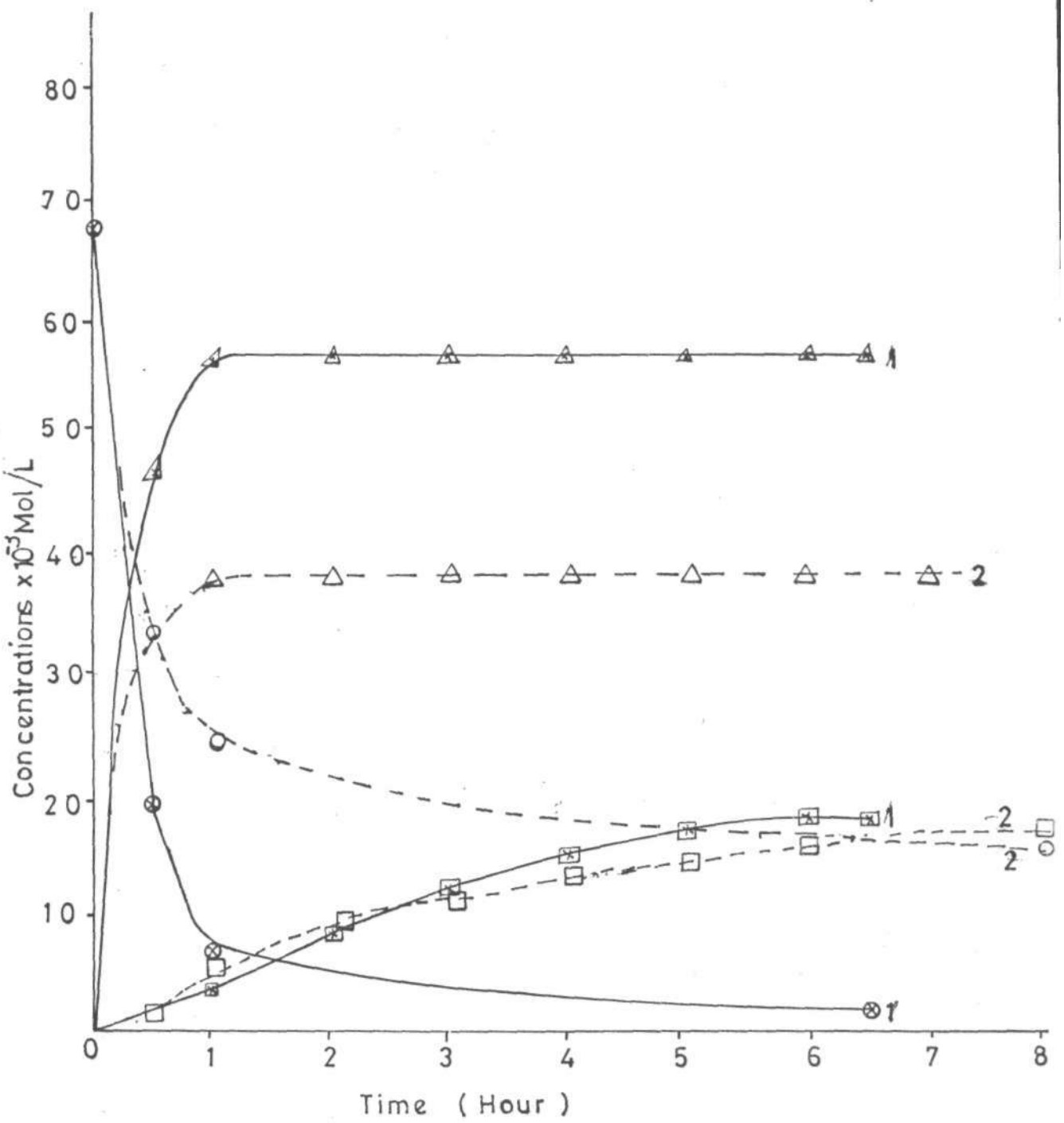


Fig (5 –6c): Product distribution in the course of Maleic acid epoxidation using (1) immobilized (2) homogeneous catalyst .. with H_2O_2

$$[M.A]_o = 6{\cdot}00 \times 10^{-2}\ M$$



Fig(5 -7) Product distribution in the course of Maleic acid epoxidation using (1) immobilized (2) homogeneous catalysts

$[H_2O_2]_o = 6.80 \times 10^{-2}$ M

$[MA]_o = 6.00 \times 10^{-2}$ M

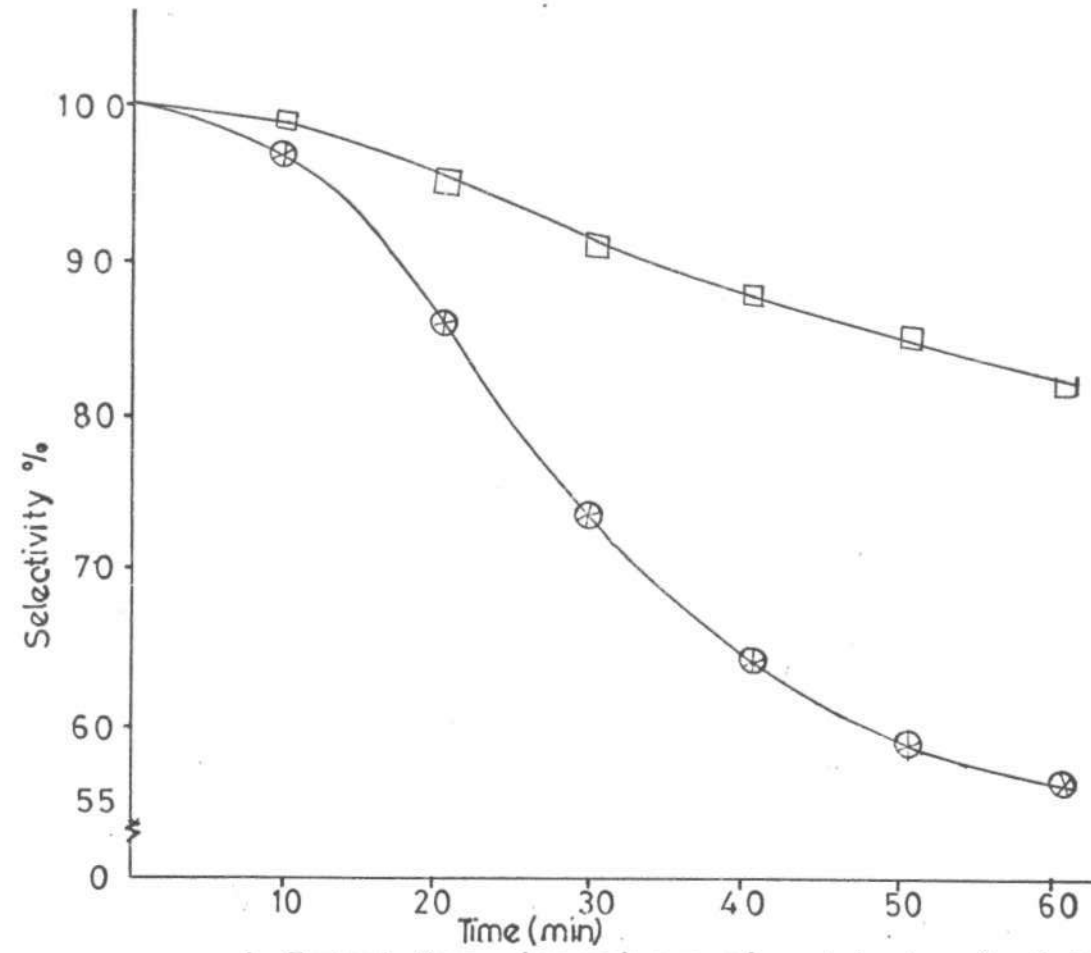


Fig (5-8) A Typical time dependence of catalyst selectivity in epoxidation reaction as initial concentration of Maleic acid is varied

5.5 STABILITY AND REUSABILITY OF THE RESIN-ANCHORED CATALYST

In section (2.0), it has been stated that immobilized catalysts possess the advantages of heterogeneous catalysis, in the area of easy separation and reusability. To establish this fact, the prepared immobilized catalyst as described in chapter three, was employed for repeated use (as discussed in section 5.1) and the results are presented in fig. (5-9). The results of stability (in terms of activity), yield and conversion with corresponding number of repeated uses are shown in table (5-2) below. Morealso, the physical structure of the immobilized catalyst started deteriorating after five repeated uses; due to the drying temperature and abrasion.

TABLE (5-1): STABILITY OF RESIN IMMOBILIZED CATALYST.

No. of Repeated use	Epoxide yield %	Activity %	Conversion $X_{H_2O_2}$(%)
1st	84	100	89
2nd	68	81	72
3rd	55	66	59
4th	43	51	46
5th	35	42	38
6th	32	38	35
7th	32	38	35

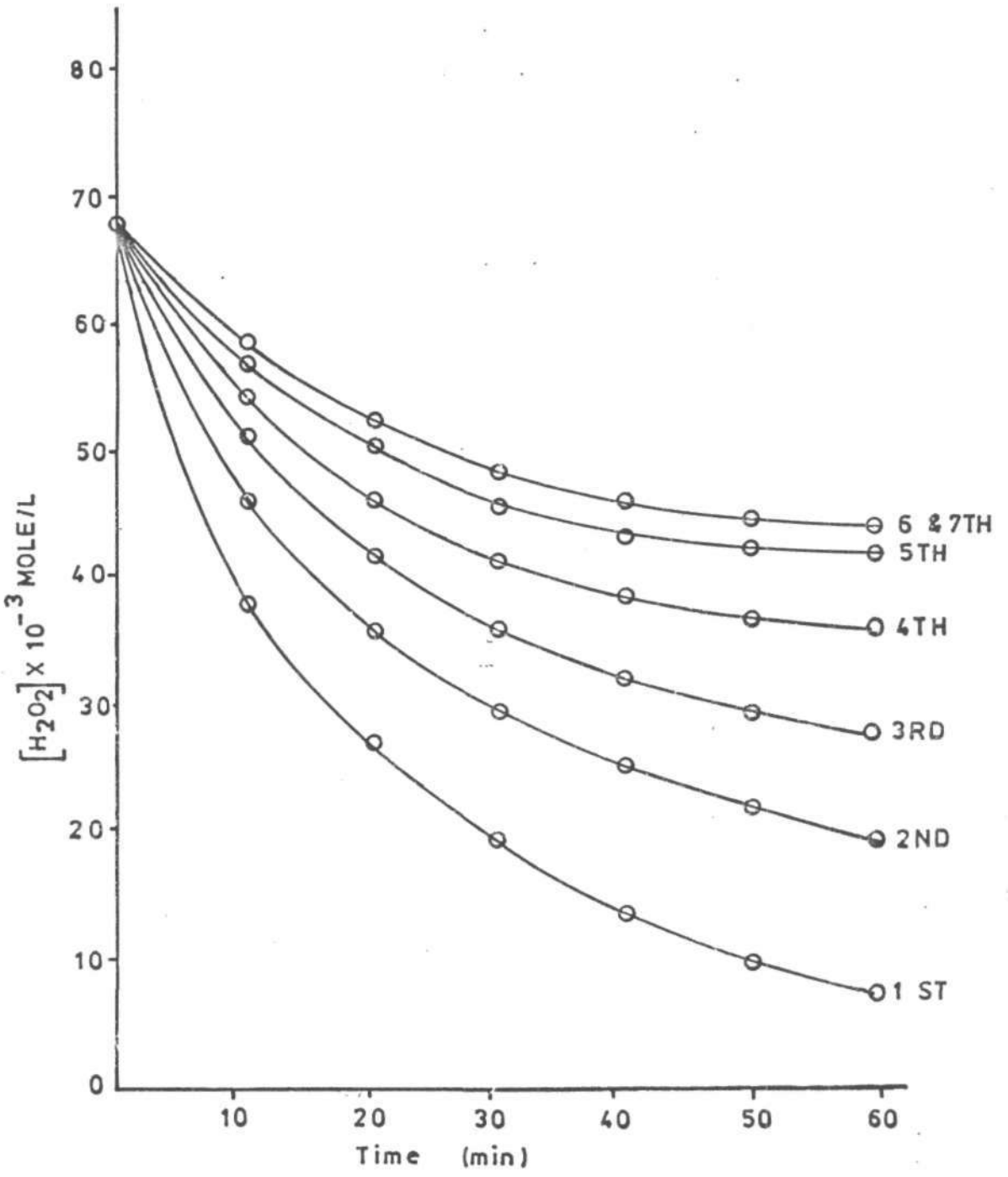


Fig. (5-9) Concentration vs Time during repeated use of anchored catalyst

This result shows that the immobilized catalyst can be used repeatedly for four batch operations with a drop from 100 to 51% in activity, which then proves its superiority over the pure homogeneous catalyst that can only be used once. The progressive drop in activity of the immobilized catalyst can be attributed to its contraction and expansion due to the drying temperature, and abrasion effect, which subsequently cause desorption of Molybdenum from the resin.

5.6 DEVELOPMENT OF MATHEMATICAL MODEL

(1) Rate of Hydrogen peroxide Consumption:

The treatment of kinetic curves (Fig. 5-2) by the-differential method of analysis, and the plots of initial rate $(\Gamma H_2O_2)_0$ versus initial concentration of hydrogen peroxide $[H_2O_2]_0$ (Fig. 5-10) shows the typical values for epoxidation reaction, pseudo-zero order dependency which is often described by the equation;

$$-r_{H_2O_{2,0}} = \frac{\alpha * [H_2O_2]_0}{\beta + \gamma [H_2O_2]_0} \qquad \ldots(5\text{-}1)$$

where α, β, γ - are kinetic parameters.

Equation (5-1) at the initial condition is valid for both immobilized and homogeneous catalysis. At small values of $[H_2O_2]_0$, the influence of the term $\gamma * [H_2O_2]_0$ in the

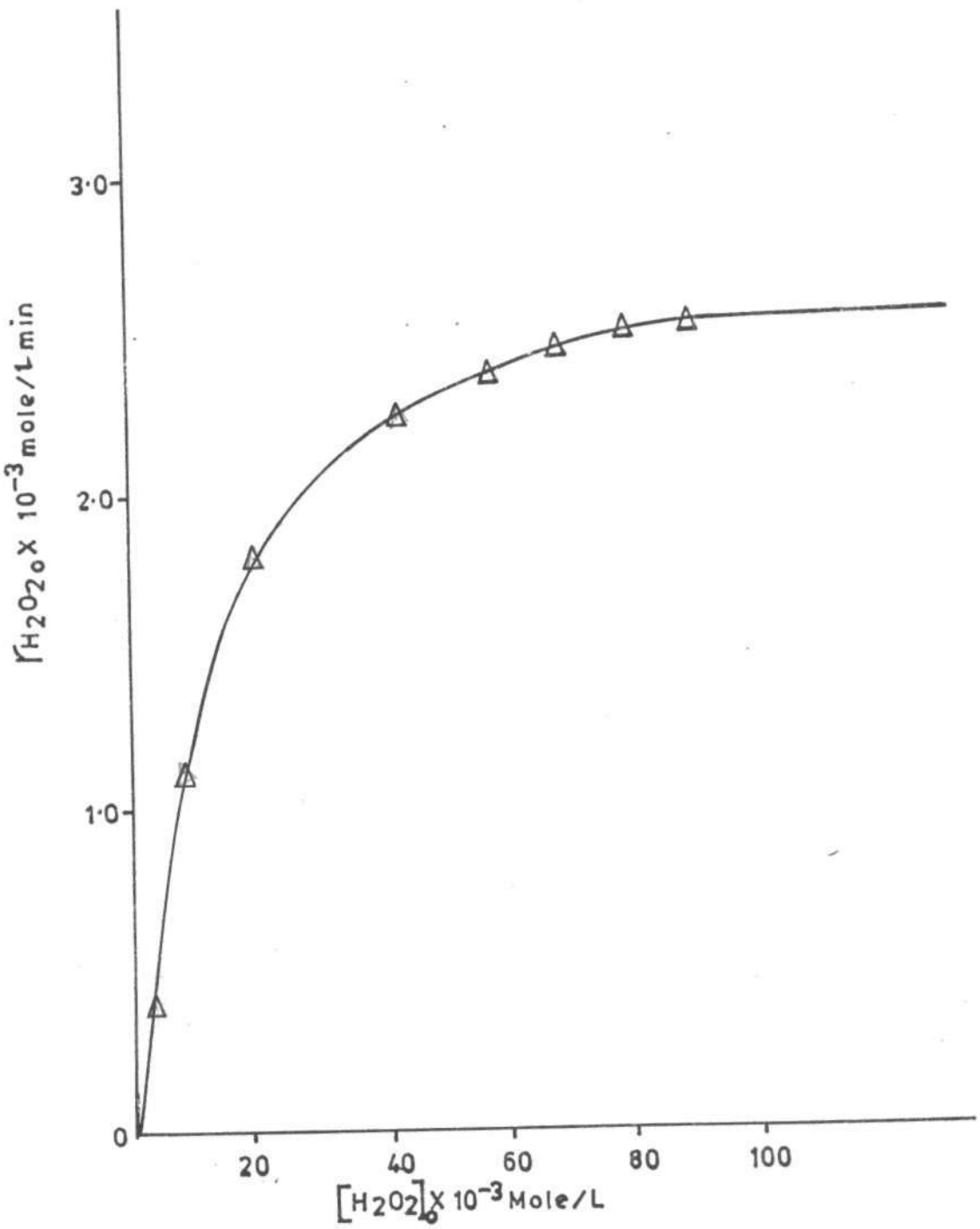


Fig. (5-10) Plot of initial rate vs initial concentration of Hydrogen peroxide

denominator can be neglected and equation (5-1) reduces to a first order equation of the type

$$-r_{H_2O_2,0} = k_{eff} * [H_2O_2]_0 \qquad ...(5\text{-}2)$$

where K_{eff} = $a/ß$, is the effective rate constant which include the influence of the concentrations of the catalyst and maleic acid.

ß = 1

The lineweaver-Burk plot ($1/r_{H_2O_2,0}$ vs $1/[H_2O_2]_0$) gave straight line for both immobilized and homogeneous catalyst (Fig. 5-11).

(2) Order of Reaction with respect to Maleic acid:

The plot of initial rate of disappearance of hydrogen peroxide (in the series when $[M.A]_0$ was varied) against initial concentration of maleic acid, resulted in a straight line from the origin as seen in Fig (5-12). This shows that the reaction rate is first order with respect to [M.A] for both homogeneous and immobilized catalysis.

Then Equation (5-1) becomes:

$$-r_{H_2O_2} = \frac{a'[H_2O_2][M.A]}{1 + \gamma[H_2O_2} \qquad ...(5.3)$$

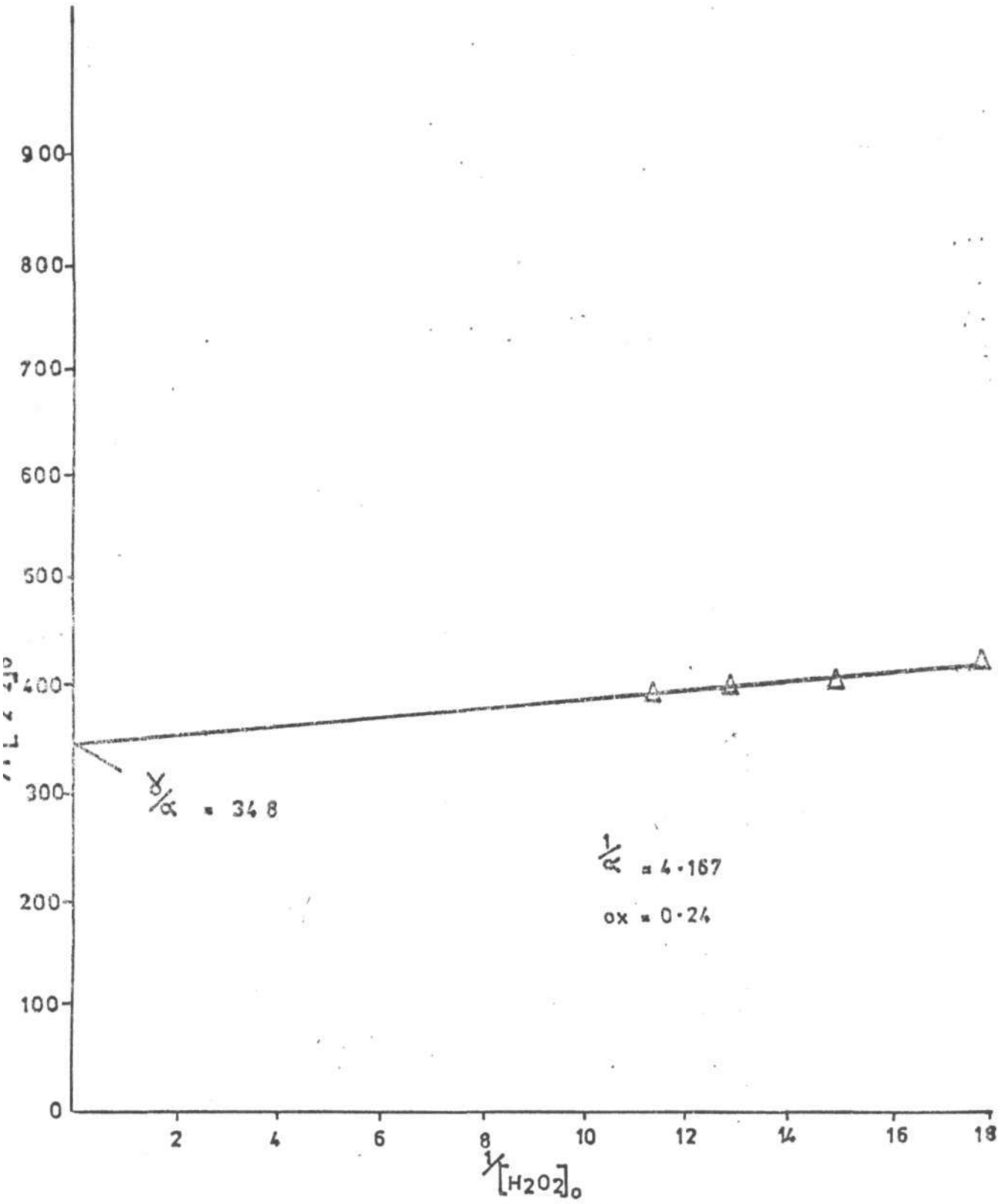


Fig. (5–11) Lineweaver–Burk plot for Homogeneous and Immobilized catalyst

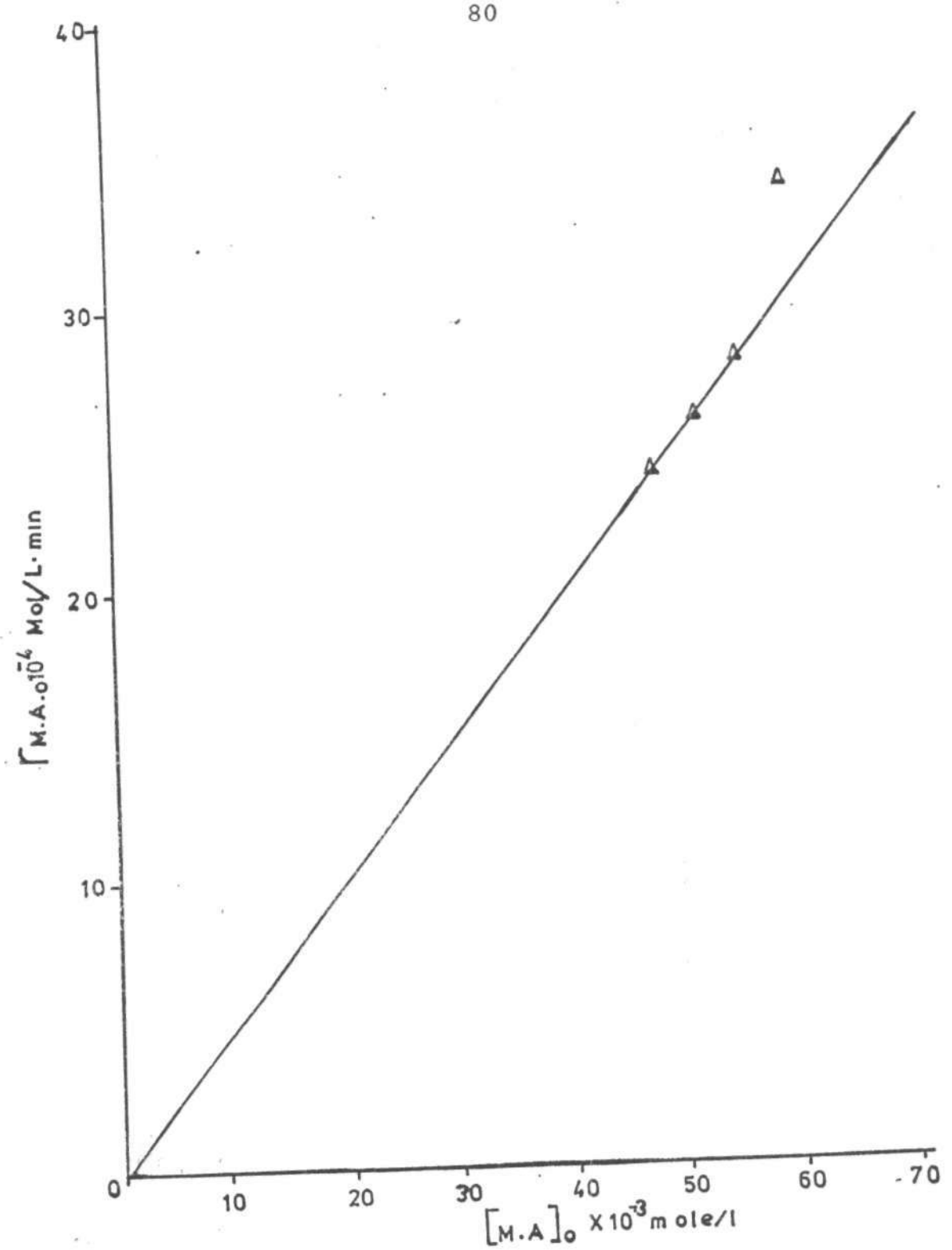


Fig. (5–12) Plot of Initial rate vs initial concentrations of Maleic acid

Since the reaction rate is also a function of the catalyst, in proportional dependency, the equation (5-3) becomes:

$$-r_{H_2O_2} = \frac{\alpha''[H_2O_2][M.A][cat.]}{1 + \gamma[H_2O_2]} \qquad \ldots(5.4)$$

where α'' = rate constant.

(3) Rate model equation for epoxidation reaction:

The slope for points (Δ) of fig (5-11) is;

$$\frac{1}{\alpha} = 4.167$$

Therefore, $\alpha = 0.24$.

The intercept on the vertical axis (Δ) of fig. (5.11) is

$$\frac{\gamma}{\alpha} = 348$$

Therefore, $\gamma = 348 * \alpha$

$$\gamma = 348 * 0.24 = 83.52$$

Hence $\alpha' = 0.24/5.2 \times 10^{-2}$

$$\alpha' = 4.62$$

By substituting these values into equation (5-3) we have;

$$-r_{H_2O_2} = \frac{4.62[H_2O_2][M.A]}{1 + 83.527[H_2O_2]} \qquad \ldots(5.5)$$

as the rate model equation for catalytic epoxidation reaction.

By testing the plots of points evaluated by the rate model equation (5-5) (Δ) with the experimental points (0) as seen in Fig (5-13), it was observed that there was great deviation of the model evaluated points from the experimental points, but there was agreement between these points (0 and Δ) at the initial rates (that is rate of reaction at time, zero). A critical view of these phenomenon, shows that, as epoxidation reaction progresses, the epoxide being formed hydrolyses to form tartaric acid which then forms complexes with the homogeneous catalyst since its surface area is available for complex formation with the acid (as discussed in section 2.8), whereby deactivating the catalyst. A detailed study on this phenomenon have been carried out by Oludipe, et al (1992).

On the other hand, comparing the plots of points evaluated by the rate model equation (5-5) (Δ) with the experimental points (0) as seen in Fig. (5-14), it was observed that good agreement was obtained between the points evaluated by the model and those determined experimentally as seen in fig (5-14). This makes our assumption, model equation (5-5) valid for the immobilized catalyst.

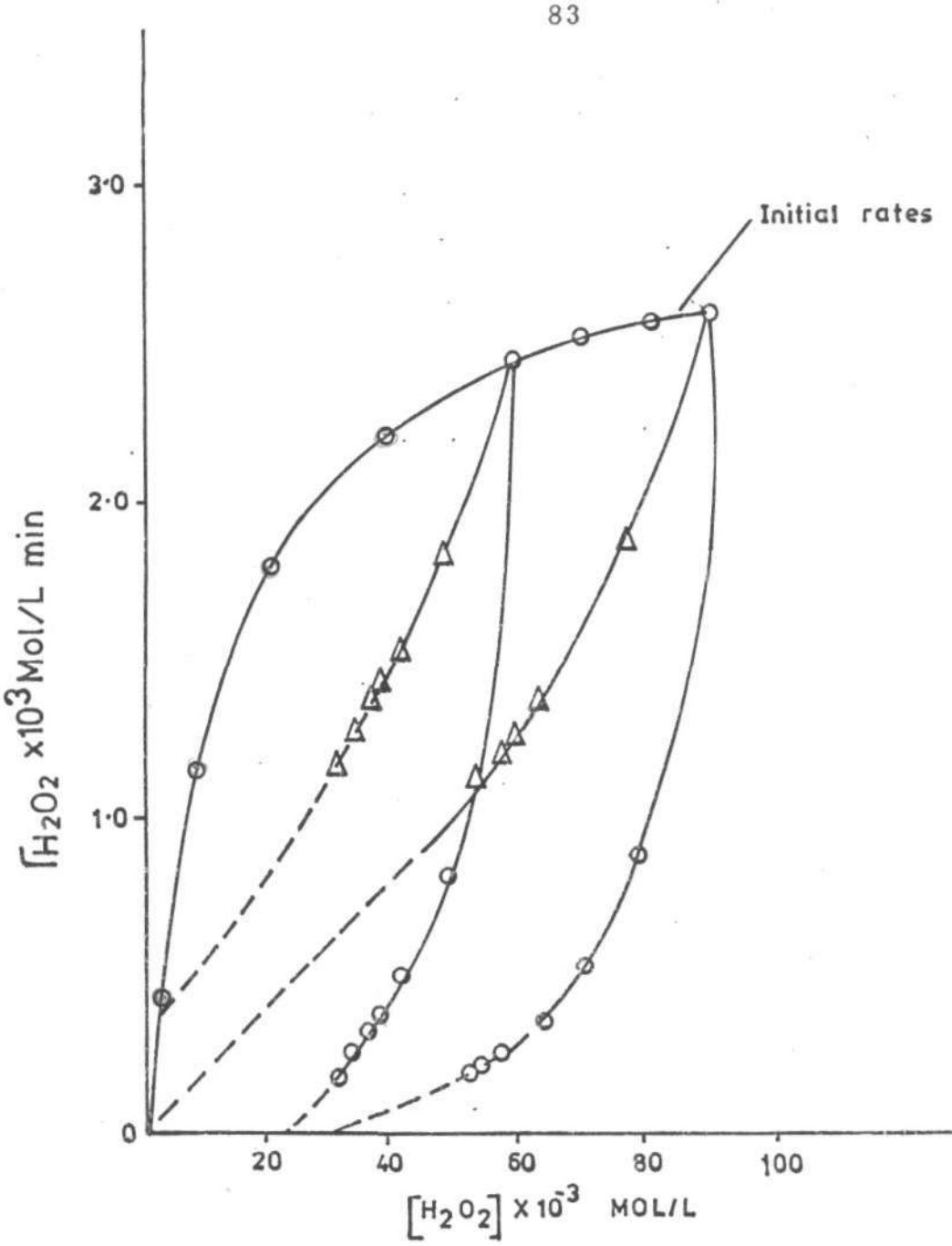


Fig. (5-13) Plot of rate vs $[H_2O_2]$ showing disagreement between experiment and model equation for homogeneous catalyst

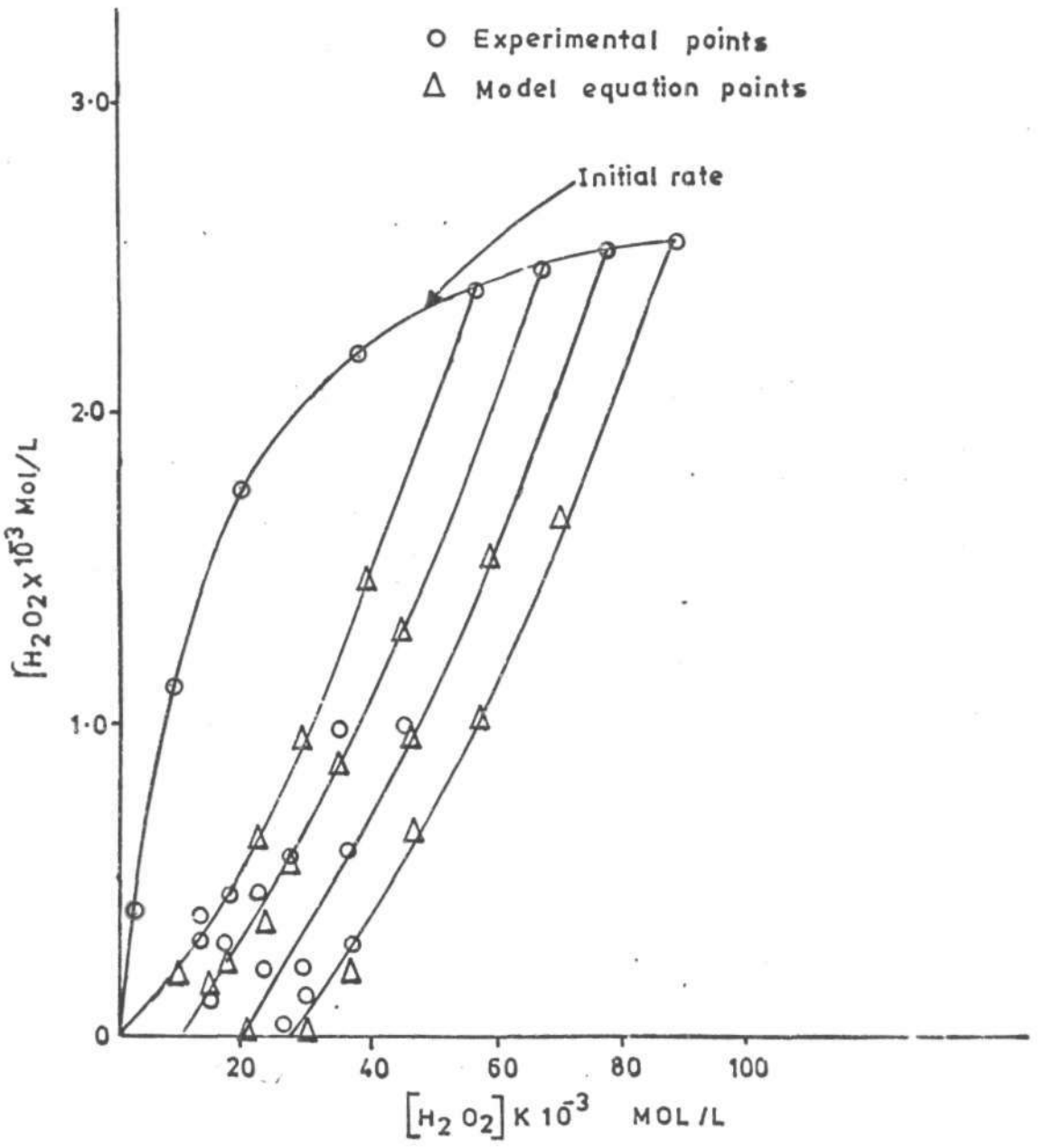


Fig. (5-14) Plot of rate vs $[H_2O_2]$ showing agreement between experiment and model equation for immobilized catalyst

CHAPTER SIX

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

Polymer resin immobilized molybdenum catalyst has been synthesised under the conditions which include, 40°C temperature, 0.4gm resin, and molybdenum concentration of 3.47 x 10^{-5}M. Under these conditions, the amount of ammonium molybdate sorbed into the resin after one hour of sorption process was 2.97 x 10^{-5} M. This ammonium molybdate concentration contains 1.6% molybdenum which is the active catalytic component in the resin-molybdenum system. The sorption process was found to be first-order both with respect to the amount of resin and molybdenum concentration. It was established that the resin possess two active sites, hence the following model equation was proposed for the sorption process:

$$[Mo] = 3.47 \times 10^{-5}[0.45e^{-0.081t} + (1 - 0.45)e^{-0.026t}]$$

Thermodynamic analysis showed that the sorption process is spontaneous and favoured adsorption (forward reaction) more than desorption (backward reaction) at equilibrium. Under equilibrium conditions, an adsorption isotherm model was established as:

$$[Mo\text{-}Re] = \frac{2.53\ Re[Mo]}{1 + 612[Mo]}$$

These two equations (model equation and adsorption isotherm) above, adequately represent the process of sorption of molybdenum into the resin.

The catalyst has been exploited in liquid-phase oxidation reaction of epoxidation of maleic acid by hydrogen peroxide (in a pseudo-homogeneous system) and the results obtained are compared with those for pure homogeneous reaction, conversion, selectivity and yield obtained in 6 hours are 76, 74 and 56% respectively. While under the same conditions with the immobilized catalytic (Pseudo-homogeneous) reaction, conversion, selectivity and yield obtained in 6 hours are 97, 87 and 84% respectively. The resin immobilized catalyst was successfully subjected to repeated use 7 times, with 61% drop in conversion, 3% drop in selectivity and 62% drop in yield. But the homogeneous catalyst was only used once, because it could not be separated from the reaction mixture by mere filtration as with the immobilized catalyst. A rate model equation for the immobilized catalytic epoxidation reaction was established thus,

$$-r_{H_2O_2} = \frac{4.62[H_2O_2][M.A]}{1 + 83.52[H_2O_2]}$$

which was tested and found to adequately represents experimental data.

On the basis of comparison therefore, industrial and economic viability, and superiority of the immobilized

catalyst over the homogenous one was observed in terms of such parameters as stability, activity, selectivity, yield, and the ease of separation from the reaction mixture.

6.2 RECOMMENDATIONS

(1) The governments and private financial bodies should give financial support to research institute and allied institutions for further researches into this concept of immobilized catalysis.

(2) Fur is a locally available natural material from animals, which, as protein is known to be made up of amino acids, which possess both anionic and cationic polar ends. So Molybdenum ion can as well form complex with the anionic polar end of the amino acid structure when they are soaked under appropriate conditions, such that Fur could replace polymer resin.

(3) Studies should be carried out to examine diffusional effect of reactants and products moving into and from the polymer immobilized catalyst, such that the overall rate and the rate determining step of the catalytic epoxidation reaction can be evaluated.

(4) The physical structure of the polymer immobilized catalyst started deteriorating after five repeated uses. The phenomenon may be attributed to the effect of drying temperature and abrasion due to stirring of the reaction mixture. Hence, a further research into this catalysis

using the immobilized molybdenum catalyst could reveal results to improve the stability of the catalyst structure.

(5) If the deterioration problem of the physical structure of the immobilized catalyst is resolved, the catalyst can be conveniently used in fixed bed reactor where separation processes (such as filtration and decantation) will not be required.

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APPENDIX A
Experimental data for sorption processes

Table (A-1) Different Amounts of Resin Operating at fixed temperature of 40°C

Amount	0.3g	0.4g	0.5g	0.8g
Time (min)	Conc. of Mo. (mol/L)	Conc. of Mo. (mol/L)	Conc. of Mo. (mol/L)	Conc. of Mo. (mol/L)
0	3.47×10^{-5}	3.47×10^{-5}	3.47×10^{-5}	3.47×10^{-5}
10	2.44×10^{-5}	2.16×10^{-5}	1.20×10^{-5}	0.80×10^{-5}
20	1.60×10^{-5}	1.20×10^{-5}	0.36×10^{-5}	0.00
30	0.86×10^{-5}	0.50×10^{-5}	0.25×10^{-5}	0.00
40	0.78×10^{-5}	0.40×10^{-5}	0.22×10^{-5}	0.00
50	0.80×10^{-5}	0.53×10^{-5}	0.25×10^{-5}	0.00
60	0.78×10^{-5}	0.50×10^{-5}	0.24×10^{-5}	0.00

Table A.2 Choice of Optimum Amount of Resin at Fixed time, 30 minutes, and 1 hour.

S/N	No. Conc. in 30 (min) (mole/L.)	Amount of Resin (g)	Change in Amount. (g)	Change in Concent.Dc mole/L.
1	$0.86x10^{-5}$	0.3	0	0
2	$0.50x10^{-5}$	0.4	0.1	$0.28x10^{-5}$
3	$0.25x10^{-5}$	0.5	0.1	$0.26x10^{-5}$
4	0.00	0.8	0.3	$0.24x10^{-5}$

Table A-3: Different Operational Temperature at Fixed Weight of Resin, 0.4g

Temperature : Time (min)	30^0C Conc. of Mo (mole/L.)	40^0C Conc. of Mo (mole/L.)	50^0C Conc. of Mo (mole/L.)	70^0C conc. of Mo (mole/l.)
0	$3.47x10^{-5}$	$3.47.x10^{-5}$	$3.47x10^{-5}$	$3.47x10^{-5}$
5	-	-	-	$1.00x10^{-5}$
10	$2.50x10^{-5}$	$2.16x10^{-5}$	$1.00x10^{-5}$	0.00
20	$1.80x10^{-5}$	$1.20x10^{-5}$	0.00	0.00
30	$1.10x10^{-5}$	$0.50x10^{-5}$	0.00	0.00
40	$1.16x10^{-5}$	$0.40x10^{-5}$	0.00	0.00
50	$1.03x10^{-5}$	$0.53x10^{-5}$	0.00	0.00
60	$1.10x10^{-5}$	$0.50x10^{-5}$	0.00	0.00

Table A-4 Choice initial Mo concentrations at 40^0C using 0.4g Resin.

S/N	No.Conc. in 30(Min) (Mole/l.)	Tempera-ture (^{0}C)	Change in temp. ^{0}C	Change in conc. Mole/L.
1	$1.10x10^{-5}$	30	0	0.0
2	$0.50x10^{-5}$	40	10	$0.60x10^{-5}$
3	0.00	50	10	$0.50x10^{-5}$
4	0.00	70	20	0.00

Table A-8 Data of Sorption Order of Molybdenum with respect to Amount of Resin.

Amount of Resin (gram)	Log [Resin]	Initial Rate of Sorption r_{sorpo} mol./L. min	Log r_{sorp}
0.3	-0.5229	$1.584x10^{-6}$	-5.80
0.4	-0.3979	$2.398x10^{-6}$	-5.62
0.5	-0.3010	$3.388x10^{-6}$	-5.47
0.8	-0.0969	$6.309x10^{-6}$	-5.20

Table (A-9) Rates of Sorption at different molybdeum concentraition with respect to two active sites of the resin .

Initial Mo Concentration Mol/L.							
$1.50x10^{-5}$		$3.47x10^{-5}$		$6.10x10^{-5}$		$10.40x10^{-5}$	
[Mo]	Rate	[Mo]	Rate	[Mo]	Rate	[Mo]	Rate
mol/L.	mol/L.	Mol/L.	Mol/L.	Mol.L	Mol/L.	Mol/l.	Mol/.
$1.50x10^{-5}$	$0.91x10^{-5}$	$3.47x10^{-5}$	$1.55x10^{-5}$	$6.10x10^{-5}$	$2.24x10^{-6}$	$10.40x10^{-5}$	$3.0x10^{-6}$
$0.70x10^{-5}$	$0.20x10^{-6}$	$2.16x10^{-5}$	$0.44x10^{-6}$	$4.40x10^{-5}$	$0.80x10^{-6}$	$8.2x10^{-5}$	$1.36x^{-6}$
0	0	$1.20x10^{-5}$	$0.16x10^{-6}$	$3.00x10^{-6}$	$0.32x10^{-6}$	$4.6x10^{-5}$	$0.32x10^{-6}$
0	0	$0.50x10^{-5}$	0	$2.00x10^{-5}$	0	$3.5x10^{-5}$	0

Table A-5 Different initial Mo Concentrations at 40°c using 0.4g Resin.

Time (min)	Conc. of Mo (mole/L.)	Conc. of Mo (mole/L.)	Conc. of Mo (mole/L.)	Conc. of Mo (mole/l.)
0	1.50×10^{-5}	3.47×10^{-5}	6.10×10^{-5}	10.40×10^{-5}
10	0.60×10^{-5}	2.16×10^{-5}	4.50×10^{-5}	6.80×10^{-5}
20	0.00	1.20×10^{-5}	3.00×10^{-5}	4.60×10^{-5}
30	0.00	0.50×10^{-5}	2.00×10^{-5}	3.50×10^{-5}
40	0.00	0.40×10^{-5}	2.10×10^{-5}	3.50×10^{-5}
50	0.00	0.53×10^{-5}	2.00×10^{-5}	3.80×10^{-5}
60	0.00	0.50×10^{-5}	2.00×10^{-5}	3.50×10^{-5}

Table A-6 Data of Sorption order of Molybdenum at Varying Mo Concentrations

S/N	Initial Conc of Mo. [Mo] (mole/L.)	Log [Mo]	Intial Rates $-r_{Mo}$ (mole/L.min)	Log $(-r_{Mo})$
1	10.40×10^{-5}	-3.98	3.31×10^{-6}	-5.48
2	6.10×10^{-5}	-4.22	2.24×10^{-6}	-5.65
3	3.47×10^{-5}	-4.46	1.55×10^{-6}	-5.81
4	1.50×10^{-5}	-4.82	0.91×10^{-6}	-6.04

Table A-7 Sorption rates of Molybodenum into Resin at Various temperatures.

S/N	[Mo] mole/L	$-r_{30}$ at 30.°C	$-r_{40}$ at 40.°C	$-r_{50}$ at 50.°C	$-r_{70}$ 70.°C
1	3.47×10^{-5}	1.20×10^{-6}	1.58×10^{-6}	4.20×10^{-6}	9.72×10^{-6}
2	2.00×10^{-5}	0.75×10^{-6}	1.07×10^{-6}	2.40×10^{-6}	5.60×10^{-6}
3	1.40×10^{-5}	0.60×10^{-6}	0.80×10^{-6}	1.67×10^{-6}	3.90×10^{-6}

APPENDIX B

Experimental records for the catalytic epation/hydroxylation of Maleic acid with hydrogen peroxide, using homogeneous and immobilized catalysts.

Table (B-1) Preliminary study showing Activities of Catalyst (Molybdenum) at the concentration of 2.97×10^{-5} mole/litre

Time (min)	Homogeneous Catalysis		Immobilized Catalysis	
	[M.A] mole/litre	Activity %	[M.A] mole/litre	Activity %
0	12.90×10^{-4}	100	12.90×10^{-4}	100
10	11.59×10^{-4}	56	10.17×10^{-4}	76
20	10.48×10^{-4}	45	7.70×10^{-4}	59
30	9.42×10^{-4}	39	6.23×10^{-4}	49
40	8.51×10^{-4}	33	4.91×10^{-4}	40
50	7.65×10^{-4}	28	3.86×10^{-4}	34
60	6.93×10^{-4}	25	3.03×20^{-4}	30

Table (B-2): Expoxidation/Hydroxylation of Maleic Acid (2M) with Hydrogen Peroxide $[H_2O_2]_0 = 57.2 \times 10^{-3}$ mole/litre

Time (min)	$[H_2O_2]^0_2$ mole/l	$[H_2O_2]$ mole/l	Epoxide mole/l	Selectivity %	$X_{H_2O_2}$ %
HOMOGENEOUS					
0	0.0	57.2×10^{-3}	0.00	100	0
10	0.087×10^{-3}	46.6×10^{-3}	10.5×10^{-3}	99	19
20	0.577×10^{-3}	40.2×10^{-3}	16.4×10^{-3}	97	30
30	1.153×10^{-3}	37.8×10^{-3}	18.3×10^{-3}	94	34
40	2.047×10^{-3}	36.0×10^{-3}	19.2×10^{-3}	91	37
50	3.084×10^{-3}	33.0×10^{-3}	21.1×10^{-3}	87	42
60	4.064×10^{-3}	30.2×10^{-3}	22.9×10^{-3}	85	47
Immobilized					
0	0.0	57.2×10^{-3}	0.00	100	0
10	0.115×10^{-3}	39.0×10^{-3}	18.1×10^{-3}	100	32
20	0.576×10^{-3}	29.0×10^{-3}	27.6×10^{-3}	98	49
30	1.009×10^{-3}	22.2×10^{-3}	34.0×10^{-3}	97	61
40	1.874×10^{-3}	17.2×10^{-3}	38.1×10^{-3}	95	70
50	2.709×10^{-3}	13.0×10^{-3}	41.5×10^{-3}	94	77
60	3.517×10^{-3}	9.2×10^{-3}	44.5×10^{-3}	93	84

Table (B-4): Epoxidation/hydroxylation of Maleic Acid (2M) and Hydrogen Peroxide $[H_2O_2]_o$ = 78.6 x 10^{-3} mole/litre

Time (min)	$[H_2O_2]^o_2$ mole/l	$[H_2O_2]$ mole/l	Epoxide mole/l	Selectivity %	$X_{H_2O_2}$ %
HOMOGENEOUS					
0	0.0	$78.6x10^{-3}$	0.00	100	0
10	$0.173x10^{-3}$	$67.3x10^{-3}$	$11.1x10^{-3}$	99	14
20	$1.153x10^{-3}$	$60.0x10^{-3}$	$17.5x10^{-3}$	94	24
30	$2.882x10^{-3}$	$53.8x10^{-3}$	$21.9x10^{-3}$	88	32
40	$4.612x10^{-3}$	$50.2x10^{-3}$	$23.8x10^{-3}$	84	36
50	$7.379x10^{-3}$	$47.0x10^{-3}$	$24.2x10^{-3}$	77	40
60	$9.224x10^{-3}$	$45.2x10^{-3}$	$24.2x10^{-3}$	72	43
IMMOBILIZED					
0	0.0	$78.6x10^{-3}$	0.00	100	0
10	$0.187x10^{-3}$	$60.0x10^{-3}$	$18.4x10^{-3}$	99	24
20	$1.182x10^{-3}$	$46.8x10^{-3}$	$30.6x10^{-3}$	96	41
30	$2.796x10^{-3}$	$36.7x10^{-3}$	$39.1x10^{-3}$	93	53
40	$4.497x10^{-3}$	$29.2x10^{-3}$	44.9 x 10^{3}	91	63
50	$7.004x10^{-3}$	$23.8x10^{-3}$	$47.8x10^{3}$	87	70
60	$8.993x10^{-3}$	$20.4x10^{-3}$	$49.2x10^{3}$	85	74

Table (B-5): Epoxidation/hydroxylation of Maleic Acid (2M) and Hydrogen Peroxide $[H_2O_2]_o$ = 89.7 x 10^{-3} mole/litre

Time (min)	$[H_2O_2]^o_2$ mole/l	$[H_2O_2]$ mole/l	Epoxide mole/l	Selectivity %	$X_{H_2O_2}$ %
HOMOGENEOUS					
0	0.0	$89.7x10^{-3}$	0.00	100	0
10	$0.202x10^{-3}$	$76.0x10^{-3}$	$13.5x10^{-3}$	98	15
20	$1.902x10^{-3}$	$68.3x10^{-3}$	$19.5x10^{-3}$	91	24
30	$3.891x10^{-3}$	$63.0x10^{-3}$	$22.8x10^{-3}$	85	30
40	$5.995x10^{-3}$	$57.2x10^{-3}$	26.5×10^{3}	82	36
50	$8.215x10^{-3}$	$54.5x10^{-3}$	$27.0x10^{3}$	77	39
60	$10.982x10^{-3}$	$51.4x10^{-3}$	$27.3x10^{3}$	71	43
IMMOBILIZED					
0	0.0	$89.7x10^{-3}$	0.00	100	0
10	$0.202x10^{-3}$	$72.2x10^{-3}$	$17.3x10^{-3}$	99	20
20	$1.211x10^{-3}$	$58.2x10^{-3}$	$30.3x10^{-3}$	96	35
30	$3.603x10^{-3}$	$47.8x10^{-3}$	$38.3x10^{-3}$	91	47
40	$4.987x10^{-3}$	$37.2x10^{-3}$	47.5×10^{3}	91	59
50	$7.811x10^{-3}$	$30.2x10^{-3}$	$51.7x10^{3}$	87	66
60	$10.953x10^{-3}$	$26.8x10^{-3}$	$52.0x10^{3}$	83	70

Table (B-6): Epoxidation/hydroxylation of 48.0×10^{-3} mole/litre Maleic Acid and Hydrogen Peroxide $[H_2O_2]_0$ = 68.0 x 10^{-3} mole/litre

Time (min)	$[H_2O_2]^0_2$ mole/l	$[H_2O_2]$ mole/l	Epoxide mole/l	Selectivity %	$X_{H_2O_2}$ %
HOMOGENEOUS					
0	0.0	68.0×10^{-3}	0.00	100	0
10	0.288×10^{-3}	59.2×10^{-3}	8.5×10^{-3}	97	13
20	1.989×10^{-3}	53.5×10^{-3}	12.5×10^{-3}	86	21
30	4.612×10^{-3}	50.2×10^{-3}	13.2×10^{-3}	74	26
40	7.490×10^{-3}	47.2×10^{-3}	13.3×10^{3}	64	31
50	9.454×10^{-3}	45.2×10^{-3}	13.3×10^{3}	59	34
60	11.212×10^{-3}	42.7×10^{-3}	14.1×10^{3}	56	37
IMMOBILIZED					
0	0.0	68.0×10^{-3}	0.00	100	0
10	0.173×10^{-3}	51.2×10^{-3}	16.6×10^{-3}	99	25
20	1.499×10^{-3}	40.0×10^{-3}	26.5×10^{-3}	95	41
30	2.998×10^{-3}	33.2×10^{-3}	31.8×10^{-3}	91	51
40	5.015×10^{-3}	27.8×10^{-3}	35.2×10^{3}	88	59
50	6.514×10^{-3}	23.7×10^{-3}	37.8×10^{3}	85	65
60	8.589×10^{-3}	20.7×10^{-3}	38.7×10^{3}	82	70

Table (B-7): Epoxidation/hydroxylation of 56.0 x 10^{-3} mole/litre Maleic Acid and $[H_2O_2]_0$ = 68.0 x 10^{-3} mole/litre

Time (min)	$[H_2O_2]^0_2$ mole/l	$[H_2O_2]$ mole/l	Epoxide mole/l	Selectivity %	$X_{H_2O_2}$ %
HOMOGENEOUS					
0	0.0	$68.0x10^{-3}$	0.00	100	0
10	$0.202x10^{-3}$	$51.7x10^{-3}$	$16.1x10^{-3}$	99	24
20	$0.749x10^{-3}$	$43.7x10^{-3}$	$23.6x10^{-3}$	97	36
30	$1.989x10^{-3}$	$39.2x10^{-3}$	$26.8x10^{-3}$	93	42
40	$3.488x10^{-3}$	$35.1x10^{-3}$	29.4 x 10^3	89	48
50	$5.188x10^{-3}$	$32.2x10^{-3}$	$30.6x10^3$	86	53
60	6.60 $x10^{-3}$	$30.5x10^{-3}$	$30.9x10^3$	82	55
IMMOBILIZED					
0	0.0	$68.0x10^{-3}$	0.00	100	0
10	$0.187x10^{-3}$	$41.9x10^{-3}$	$25.9x10^{-3}$	99	38
20	$0.577x10^{-3}$	$32.0x10^{-3}$	$35.4x10^{-3}$	98	53
30	$1.297x10^{-3}$	$23.7x10^{-3}$	$43.0x10^{-3}$	97	65
40	$1.845x10^{-3}$	$15.5x10^{-3}$	50.7 x 10^3	97	77
50	$3.084x10^{-3}$	$14.2x10^{-3}$	$50.7x10^3$	94	79
60	$3.805x10^{-3}$	$11.2x10^{-3}$	$53.0x10^3$	93	84

Table (B-8): Epoxidation/hydroxylation of 60.0 x 10^{-3} mole/litre Maleic Acid and $[H_2O_2]_o$ = 68.0 x 10^{-3} mole/litre

Time (min)	$[H_2O_2]^o_2$ mole/l	$[H_2O_2]$ mole/l	Epoxide mole/l	Selectivity %	$X_{H_2O_2}$ %
HOMOGENEOUS					
0	0.0	$68.0x10^{-3}$	0.00	100	0
10	$0.187x10^{-3}$	$48.0x10^{-3}$	$19.8x10^{-3}$	99	29
20	$0.721x10^{-3}$	$39.2x10^{-3}$	$28.1x10^{-3}$	98	43
30	$1.729X10^{-3}$	$33.8x10^{-3}$	$32.5x10^{-3}$	95	50
40	$2.940x10^{-3}$	$30.0x10^{-3}$	35.1 x 10^3	92	56
50	$4.410x10^{-3}$	$26.4x10^{-3}$	$37.2x10^3$	89	61
60	$5.477x10^{-3}$	$24.2x10^{-3}$	$38.3x10^3$	88	64
IMMOBILIZED					
0	0.0	$68.0x10^{-3}$	0.00	100	0
10	$0.185x10^{-3}$	$38.0x10^{-3}$	$29.8x10^{-3}$	99	44
20	$0.577x10^{-3}$	$27.5x10^{-3}$	$39.9x10^{-3}$	99	60
30	$1.211x10^{-3}$	$19.5x10^{-3}$	$47.3x10^{-3}$	98	71
40	$1.787x10^{-3}$	$14.0x10^{-3}$	52.2 x 10^3	97	79
50	$2.594x10^{-3}$	$10.0x10^{-3}$	$55.4x10^3$	96	85
60	$3.517x10^{-3}$	$7.2x10^{-3}$	$57.3x10^3$	94	89

Table (B-9): Maximum Expoxidation of 60.0 x 10^{-3}mole/litre Maleic Acid and Hydrogen Peroxide $[H_2O_2]_o$ = 68.0 x 10^{-3} mole/litre

Time (hour)	$[H_2O_2]^o_2$ mole/l	$[H_2O_2]$ mole/l	Epoxide mole/l	Selectivity %	$X_{H_2O_2}$ %
HOMOGENEOUS					
0	0.0	$68.0x10^{-3}$	0.00	100	0
0.5	$1.729x10^{-3}$	$33.8x10^{-3}$	$32.5x10^{-3}$	95	50
1	$5.477x10^{-3}$	$24.2x10^{-3}$	$38.3x10^{-3}$	88	64
2	$8.935x10^{-3}$	$21.1x10^{-3}$	$38.3x10^{-3}$	82	69
3	$10.953x10^{-3}$	$19.0x10^{-3}$	$38.3x10^{-3}$	78	72
4	$12.971x10^{-3}$	$17.6x10^{-3}$	38.3×10^{3}	76	74
5	$14.412x10^{-3}$	$16.9x10^{-3}$	$38.3x10^{3}$	75	75
6	$15.421x10^{-3}$	$16.1x10^{-3}$	$38.3x10^{3}$	74	76
7	$10.516x10^{-3}$	$15.9x10^{-3}$	$38.3x10^{-3}$	74	77
7.5	$16.718x13^{-3}$	$15.8x10^{-3}$	$38.3x10^{-3}$	73	77
8	$16.718x10^{-3}$	$15.8x10^{-3}$	$38.3x10^{-3}$	73	77
HETEROGENEIZED					
0	0.0	$68.0x10^{-3}$	0.00	100	0
0.5	$1.211x10^{-3}$	$19.5x10^{-3}$	$47.3x10^{-3}$	98	71
1	$3.545x10^{-3}$	$7.2x10^{-3}$	$57.3x10^{-3}$	94	89
2	$8.301x10^{-3}$	$5.3x10^{-3}$	$57.3x10^{-3}$	91	92
3	$12.192x10^{-3}$	$3.9x10^{-3}$	$57.3x10^{-3}$	89	94
4	$14.988x10^{-3}$	$3.0x10^{-3}$	57.3×10^{3}	88	96
5	$17.006x10^{-3}$	$2.4x10^{-3}$	$57.3x10^{3}$	87	97
6	$18.101x10^{-3}$	$2.1x10^{-3}$	$57.3x10^{3}$	87	97
6.5	$18.447x10^{-3}$	$2.0x10^{-3}$	$57.3x10^{-3}$	87	97

Table (B-10): Repeated Uses of Resin - Anchored Catalyst with [malic Acid = 60.0×10^{-3} mole/litre $[H_2O_2] = 68.0 \times 10^{-3}$

Time (min)	$[H_2O_2]^0_2$ mole/l	$[H_2O_2]$ mole/l	Epoxide mole/l	Selectivity %	$X_{H_2O_2}$ %
FIRST USE (Table (B-9) IMMOBILIZED					
SECOND USE					
0	0.0	68.0×10^{-3}	0.00	100	0
10	0.130×10^{-3}	46.2×10^{-3}	21.7×10^{-3}	99	32
20	0.519×10^{-3}	36.0×10^{-3}	31.5×10^{-3}	98	47
30	1.009×10^{-3}	30.1×10^{-3}	36.9×10^{-3}	97	58
40	1.729×10^{-3}	24.9×10^{-3}	41.4×10^{3}	96	63
50	2.162×10^{-3}	22.0×10^{-3}	43.8×10^{3}	95	68
60	3.027×10^{-3}	19.0×10^{-3}	46.0×10^{3}	94	72
THIRD USE					
0	0.0	68.0×10^{-3}	0.00	100	0
10	0.115×10^{-3}	51.0×10^{-3}	16.9×10^{-3}	99	25
20	0.288×10^{-3}	41.8×10^{-3}	25.9×10^{-3}	99	39
30	0.865×10^{-3}	36.5×10^{-3}	30.6×10^{-3}	97	46
40	1.441×10^{-3}	32.6×10^{-3}	34.0×10^{3}	96	52
50	1.787×10^{-3}	30.0×10^{-3}	36.2×10^{3}	95	56
60	2.825×10^{-3}	28.0×10^{-3}	37.2×10^{3}	93	59
FOURTH USE					
0	0.0	68.0×10^{-3}	0.00	100	0
10	0.058×10^{-3}	54.6×10^{-3}	13.3×10^{-3}	100	20
20	0.231×10^{-3}	46.2×10^{-3}	21.6×10^{-3}	99	32
30	0.807×10^{-3}	41.8×10^{-3}	25.4×10^{-3}	97	39
40	1.153×10^{-3}	38.0×10^{-3}	28.9×10^{3}	96	44
50	1.672×10^{-3}	37.0×10^{-3}	29.3×10^{3}	95	46
60	2.364×10^{-3}	36.5×10^{-3}	29.3×10^{3}	93	46

FIFTH USE

0	0.0	68.0×10^{-3}	0.00	100	0
10	0.058×10^{-3}	57.2×10^{-3}	10.7×10^{-3}	100	16
20	0.216×10^{-3}	50.2×10^{-3}	17.6×10^{-3}	99	26
30	0.577×10^{-3}	46.0×10^{-3}	21.4×10^{-3}	97	32
40	1.095×10^{-3}	44.0×10^{-3}	22.9×10^{3}	95	35
50	1.499×10^{-3}	42.8×10^{-3}	23.7×10^{3}	94	37
60	2.306×10^{-3}	42.0×10^{-3}	23.7×10^{3}	91	38

SIXTH USE

0	0.0	68.0×10^{-3}	0.00	100	0
10	0.058×10^{-3}	58.9×10^{-3}	9.0×10^{-3}	99	13
20	0.202×10^{-3}	52.8×10^{-3}	15.0×10^{-3}	99	22
30	$0.577X10^{-3}$	48.8×10^{-3}	18.6×10^{-3}	97	28
40	0.865×10^{-3}	46.2×10^{-3}	20.9×10^{3}	96	32
50	1.441×10^{-3}	45.0×10^{-3}	21.6×10^{3}	94	34
60	2.191×10^{-3}	44.2×10^{-3}	21.6×10^{3}	91	35

SEVENTH USE

0	0.0	68.0×10^{-3}	0.00	100	0
10	$0.058\times10_{-3}$	58.7×10^{-3}	9.2×10^{-3}	99	14
20	0.202×10^{-3}	52.8×10^{-3}	15.0×10^{-3}	99	22
30	0.577×10^{-3}	48.6×10^{-3}	18.8×10^{-3}	97	29
40	0.865×10^{-3}	46.2×10^{-3}	20.9×10^{3}	96	32
50	1.441×10^{-3}	45.2×10^{-3}	21.4×10^{3}	94	34
60	2.191×10^{-3}	44.1×10^{-3}	21.7×10^{3}	91	35

Table (B-11): Lineweaver-Burk data for order of Epoxidation with respect to Hydrogen peroxide.

$[H_2O_2]_0$	Homogeneous	Immobilized/Homogeneous	
mol/l	$1/[H_2O_2]_0$	$\Gamma_{H_2O_2,0}$ mol/l.min	$1/\Gamma_{H_2O_2,0}$
57.2×10^{-3}	17.5	2.38×10^{-3}	420
68.0×10^{-3}	14.7	2.45×10^{-3}	408
78.6×10^{-3}	12.7	2.51×10^{-3}	398
89.7×10^{-3}	11.2	2.54×10^{-3}	394

Table (B-12): Search for order of Epoxidation with respect to Maleic Acid.

$[M.A.]_0$ mole/l	$\Gamma_{M.A.0}$ immobilized/homogeneous, mole/l.min
48.0×10^{-3}	24.0×10^{-4}
52.0×10^{-3}	26.0×10^{-4}
56.0×10^{-3}	28.0×10^{-4}
60.0×10^{-3}	32.2×10^{-4}

Table (B-13): Testing and Comparing the epoxidation models with Experimental Readings at Initial conditions.

$[H_2O_2]_0$	Homogeneous		Immobilized	
mole/1	ΓH_2O_2,0 Exp. mole/1.min	Γ_2O_2,0 mod. mole/1.min	ΓH_2O_2,0 Exp. mole/1.min	ΓH_2O_2,0 Mod. mole/1.min
$89.7x10^{-3}$	$1.60x10^{-3}$	$1.63x10^{-3}$	$2.54x10^{-3}$	$2.54x10^{-3}$
$78.6x10^{-3}$	$1.57x10^{-3}$	$1.57x10^{-3}$	$2.51x10^{-3}$	$2.5x10^{-3}$
$68.0x10^{-3}$	$1.53x10^{-3}$	$1.49x10^{-3}$	$2.45x10^{-3}$	$2.45x10^{-3}$
$57.2x10^{-3}$	$1.40x10^{-3}$	$1.39x10^{-3}$	$2.38x10^{-3}$	$2.38x10^{-3}$
$40.0x10^{-3}$	$1.18x10^{-3}$	$1.18x10^{-3}$	$2.21x10^{-3}$	$2.21x10^{-3}$
$20.0x10^{-3}$	$0.79x10^{-3}$	$0.79x10^{-3}$	$1.80x10^{-3}$	$1.80x10^{-3}$
$8.0\ x10^{-3}$	$0.39x10^{-3}$	$0.39x10^{-3}$	$1.15x10^{-3}$	$1.15x10^{-3}$

Table (B-14) Testing the Epoxidation Models.

Time	Homogeneous			Immobilized		
min	$[H_2O_2]$ mol/l.	$\Gamma_{Hom,Exp}$ mol/l.min	$\Gamma_{Hom,Mod}$ mol/l.min	$[H_2O_2]$ mol/l	$\Gamma_{im,Exp}$ mol/l.min	$\Gamma_{im,mod}$ mol/l.min
For CH_2O_2 = 57.2 x 10^{-3} mol/l.						
0	$57.2x10^{-3}$	$1.40x10^{-3}$	$1.39x10^{-3}$	$57.2x10^{-3}$	$2.38x10^{-3}$	2.38×10^{-3}
10	$46.6x10^{-3}$	$0.79x10^{-3}$	$1.02x10^{-3}$	$39.0x10^{-3}$	$1.44x10^{-3}$	$1.44x10^{-3}$
20	$40.2x10^{-3}$	$0.48x10^{-3}$	$0.81x10^{-3}$	$29.0x10^{-3}$	$0.90x10^{-3}$	0.95×10^{-3}
30	$37.8x10^{-3}$	$0.36x10^{-3}$	$0.74x10^{-3}$	$22.2x10^{-3}$	$0.62x10^{-3}$	$0.65x10^{-3}$
40	$36.0x10^{-3}$	$0.31x10^{-3}$	$0.71x10^{-3}$	$17.2x10^{-3}$	$0.45x10^{-3}$	0.45×10^{-3}
50	$33.0x10^{-3}$	$0.25x10^{-3}$	$0.64x10^{-3}$	$13.0x10^{-3}$	$0.38x10^{-3}$	$0.30x10^{-3}$
60	$30.2x10^{-3}$	$0.20x10^{-3}$	$0.57x10^{-3}$	$9.2x10^{-3}$	$0.20x10^{-3}$	0.18×10^{-3}
For $[H_2O_2]$ = 68.0 x 10^{-3}mol.l						
0	$68.0x10^{-3}$	$1.53x10^{-3}$	$1.49x10^{-3}$	$68.0x10^{-3}$	$2.45x10^{-3}$	2.45×10^{-3}
10	$54.7x10^{-3}$	$0.72x10^{-3}$	$1.02x10^{-3}$	$45.2x10^{-3}$	$1.30x10^{-3}$	$1.29x10^{-3}$
20	$49.7x10^{-3}$	$0.48x10^{-3}$	$0.87x10^{-3}$	$35.5x10^{-3}$	$1.00x10^{-3}$	0.85×10^{-3}
30	$45.7x10^{-3}$	$0.37x10^{-3}$	$0.79x10^{-3}$	$27.5x10^{-3}$	$0.59x10^{-3}$	$0.54x10^{-3}$
40	$42.2x10^{-3}$	$0.31x10^{-3}$	$0.73x10^{-3}$	$22.0x10^{-3}$	$0.46x10^{-3}$	0.35×10^{-3}
50	$39.2x10^{-3}$	$0.27x10^{-3}$	$0.68x10^{-3}$	$17.6x10^{-3}$	$0.30x10^{-3}$	$0.22x10^{-3}$
60	$36.7x10^{-3}$	$0.23x10^{-3}$	$0.63x10^{-3}$	$14.8x10^{-3}$	$0.11x10^{-3}$	0.16×10^{-3}

Table (B-14) Testing the Epoxpdation Models.(cont'd)

Time	Homogeneous			Immobilized		
min	$[H_2O_2]$ mol/l.	$\Gamma_{Hom.Exp}$ mol/l.min	$\Gamma_{Hom.Mod}$ mol/l.min	$[H_2O_2]$ mol/l	$\Gamma_{im.Exp}$ mol/l.min	$\Gamma_{im.mod}$ mol/l.min
For CH_2O_2 = 78.6 x 10^{-3} mol/l.						
0	$78.6x10^{-3}$	$1.57x10^{-3}$	$1.57x10^{-3}$	$78.6x10^{-3}$	$2.51x10^{-3}$	2.50×10^{-3}
10	$67.3x10^{-3}$	$0.92x10^{-3}$	$1.17x10^{-3}$	$60.0x10^{-3}$	$1.53x10^{-3}$	$1.55x10^{-3}$
20	$60.0x10^{-3}$	$0.54x10^{-3}$	$0.94x10^{-3}$	$46.8x10^{-3}$	$1.00x10^{-3}$	0.94×10^{-3}
30	$53.8x10^{-3}$	$0.36x10^{-3}$	$0.79x10^{-3}$	$36.7x10^{-3}$	$0.60x10^{-3}$	$0.54x10^{-3}$
40	$50.2x10^{-3}$	$0.28x10^{-3}$	$0.71x10^{-3}$	$29.2x10^{-3}$	$0.22x10^{-3}$	0.28×10^{-3}
50	$47.0x10^{-3}$	$0.26x10^{-3}$	$0.68x10^{-3}$	$23.8x10^{-3}$	$0.21x10^{-3}$	$0.16x10^{-3}$
60	$45.2x10^{-3}$	$0.25x10^{-3}$	$0.67x10^{-3}$	$20.4x10^{-3}$	$0.06x10^{-3}$	0.10×10^{-3}
For $[H_2O_2]$ = 89.7 x 10^{-3}mol.l						
0	$89.7x10^{-3}$	$1.60x10^{-3}$	$1.63x10^{-3}$	$89.7x10^{-3}$	$2.54x10^{-3}$	2.54×10^{-3}
10	$76.0x10^{-3}$	$0.83x10^{-3}$	$1.15x10^{-3}$	$72.2x10^{-3}$	$1.65x10^{-3}$	$1.65x10^{-3}$
20	$68.3x10^{-3}$	$0.51x10^{-3}$	$0.93x10^{-3}$	$38.2x10^{-3}$	$1.01x10^{-3}$	1.00×10^{-3}
30	$63.0x10^{-3}$	$0.37x10^{-3}$	$0.81x10^{-3}$	$47.8x10^{-3}$	$0.63x10^{-3}$	$0.61x10^{-3}$
40	$57.2x10^{-3}$	$0.25x10^{-3}$	$0.68x10^{-3}$	$37.2x10^{-3}$	$0.29x10^{-3}$	0.19×10^{-3}
50	$54.5x10^{-3}$	$0.23x10^{-3}$	$0.66x10^{-3}$	$30.2x10^{-3}$	$0.14x10^{-3}$	$0.01x10^{-3}$
60	$51.4x10^{-3}$	$0.21x10^{-3}$	$0.63x10^{-3}$	$26.8x10^{-3}$	$0.04x10^{-3}$	0.0×10^{-3}