

# KINETICS OF DEHYDRATION OF ALCOHOLS OVER DIFFERENT CATALYSTS

S. K. Mondal

Executive Engineer (Operation)  
Bangladesh Chemical Industries Corporation

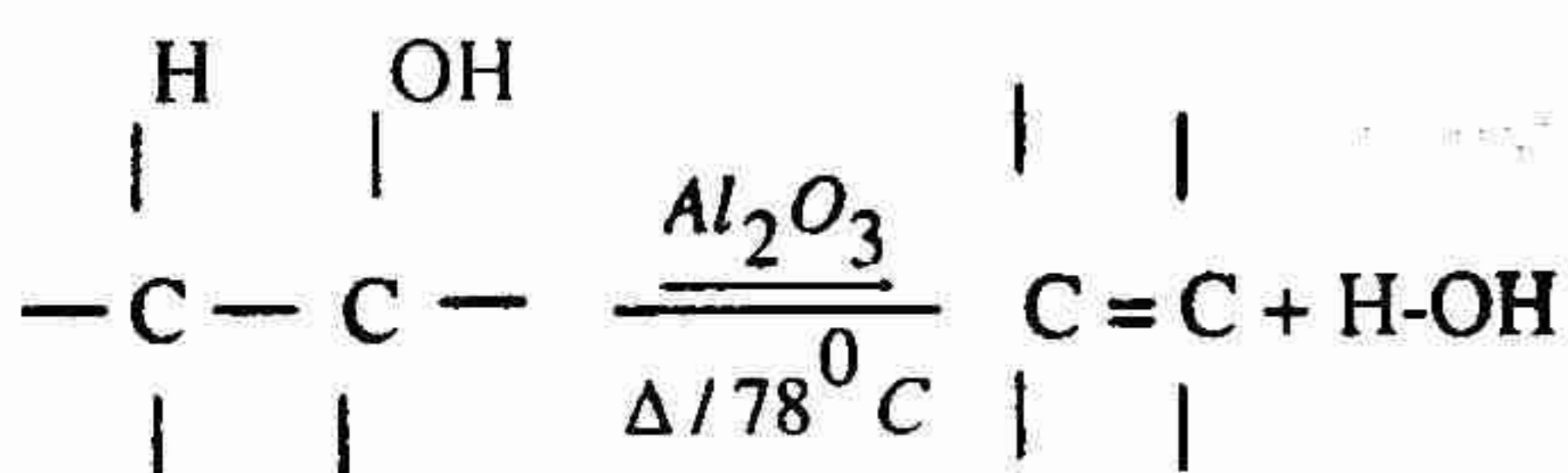
## Abstract

The purpose of the present study is to investigate the Kinetics of Dehydration of Normal and Tertiary Butyl Alcohols and Iso-propyl Alcohol over Alumina, Titania and Cation exchange Resin. The dehydration rate expression is developed theoretically and experiments are conducted to test the model. Concentrations of reactants are measured at different times at constant temperature for determining the rate of reaction. The results show reasonable agreement of the data with the proposed model.

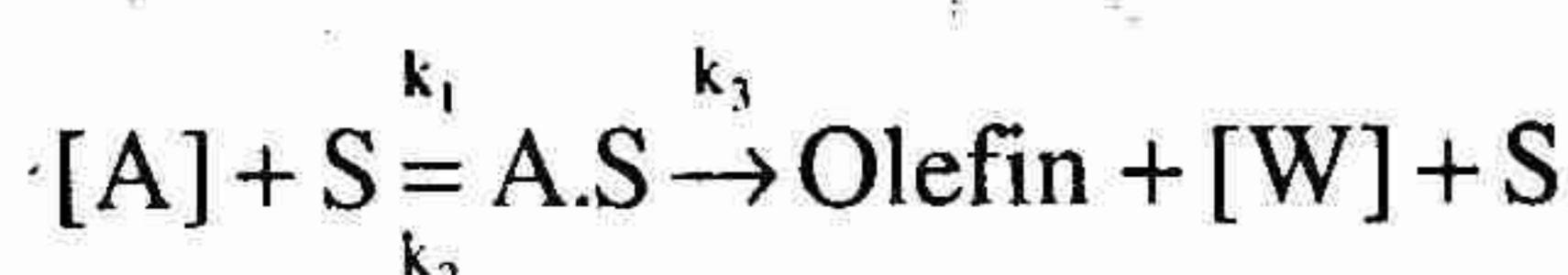
## Introduction

The catalytic properties of ion exchange resin, alumina, and titania have received considerable attention. These materials are of practical interest since they are readily available and easily separated from the reactant mixture. The physical characteristics of these materials have evoked academic interest<sup>1,2,3</sup>. This has ranged from studies of the effect of the polymeric moiety on the activity of simple catalytic centers to the simulation of enzyme behavior by the introduction of complex prosthetic group. Tertiary and Normal Butyl alcohol and Isopropyl are well suited to the present study. Although thermally stable at high temperature, they decompose at their boiling points in the presence of the catalyst. The studies were performed with simple equipments at atmospheric pressure. The gaseous reaction products were measured through a bubble flow meter and kinetics analysis was carried out based on this measurement.

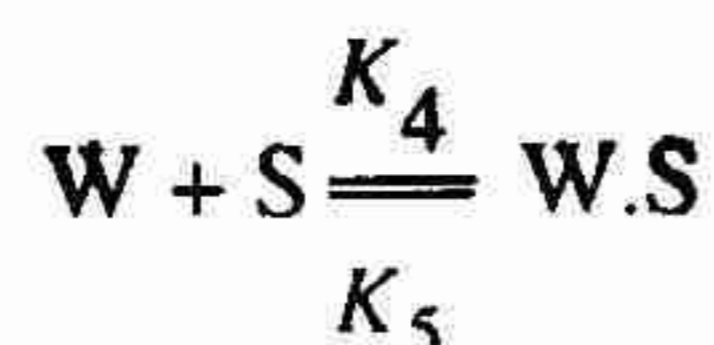
Alcohol possess hydrogen atom on the carbon adjacent to one holding the OH group, undergo dehydration when heated with catalyst



The productive reaction sequence representing the chemisorption of alcohol on the catalytic sites followed by desorption of product which is given by



where [A], S and [W] are the concentration of alcohol, free sites of catalyst at any time and the water concentration respectively. The desorption of water may be written as



where  $K_1$ ,  $K_2$ ,  $K_3$ ,  $K_4$  and  $K_5$  are stepwise rate constant respectively. The standard state being chosen as pure vapor at 1 atm and 80°C. A, S and W, S are the number of sites occupied by chemisorbed alcohol or inactivated by chemisorbed water at any time. At any instant, the rate of alkenes formation  $\frac{dn}{dt}$  is given by

$$\frac{dn}{dt} = K_3 \text{A.S}$$

At steady state approximation, we may write

$$\frac{d}{dt} [\text{A.S}] = K_1[\text{A}]\text{S} - K_2\text{A.S} - K_3\text{A.S} = 0$$

$$\text{i.e. } \text{A.S} = K_A[\text{A}].\text{S}$$

$$\text{where } K_A = \frac{K_1}{K_2 + K_3}$$

Again

$$\frac{d}{dt}[W.S] = K_4[W].S - K_5W.S = 0$$

and

$$W.S = K_w[W].S$$

$$\text{where } K_w = \frac{K_4}{K_5}$$

Now total number of sites N is given by  
 $N = S + A.S + W.S$

and rate of reaction R is given by  $\frac{1}{N} \frac{dn}{dt}$

$$\text{i.e. } R = \frac{K_3AS}{S + AS + W.W}$$

After rearranging

$$\frac{R}{[A]} = \frac{K_3}{[A] + \frac{1}{K_A} + \frac{K_w}{K_A}[W]}$$

This equation is known as isotherm of alcohol because adsorption occurred on the catalytic sites at constant temperature. In the experiment as performed, the partial pressure of alkenes is always quite small. So we may write

$$[A] + [W] = 1 \text{ i.e., } [A] = 1 - [W].$$

If we substitute [A] on our isotherm and rearranging the rate expression is obtained

$$\frac{R}{[A]} = \frac{K_3}{1 + \frac{1}{K_A} + \frac{K_w/K_A - 1}{K}} \cdot \frac{R}{[A]} \cdot [W].$$

This straight-line equation with respect to  $\frac{R}{[A]}$

versus  $\frac{R}{[A]} [W]$  is known as specific rate equation

of kinetics of alcohols over catalyst.

### Experimental

In 100 ml alcohol and 1 gm catalyst and are taken in a 250 ml boiling flask and a magnetic stirrer use. A condenser and a thermometer with a rubber cork is used to the mouth of the boiling flask. It is also

connected a tube of a burette and a rubber bulb with soap solution to the bottom of the burette. The whole apparatus are carefully corked so that the product gas cannot be leaked. The procedure for experimental work is elsewhere<sup>1</sup>. The experimental setup is shown in Figure 1.

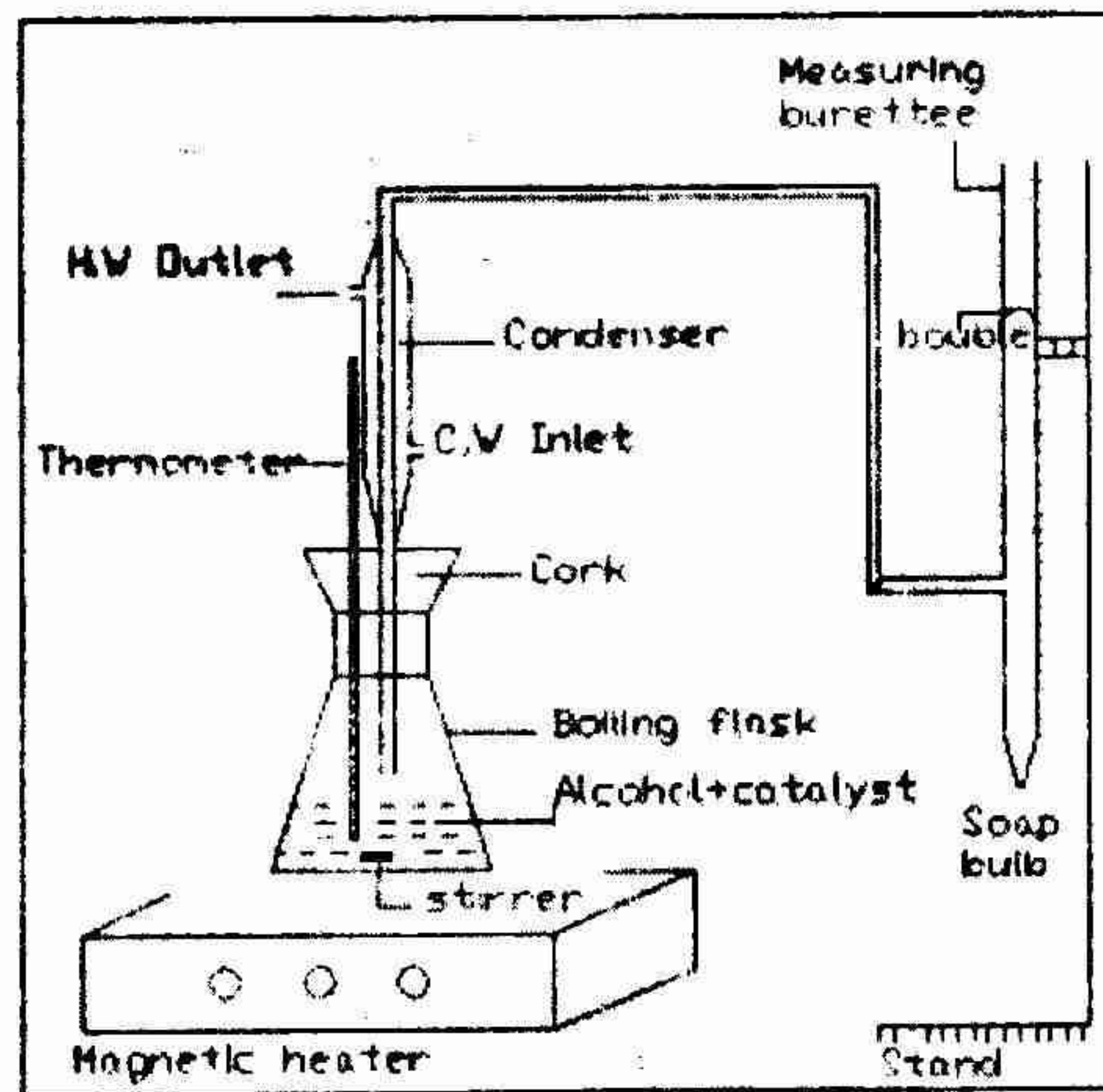


Fig.1- Experimental Setup

The boiling flask is heated through magnetic heater and is stirred continuous, so that the catalyst is well mixed with alcohol. Soap bubble indicates the starting of the reaction and the starting time is recorded by stopwatch. A constant volume of gaseous product (alkaline) is allowed to flow through the soap bubble flow meter. 10 to 12 readings are recorded at constant temperature.

### Results and Discussions

It is easily to get the specific rate of reaction and concentration of alcohol and water activity from the series of experimental and is observed that the specific rate expression agrees with experimental data. The results of the experimental findings is given on table-1.

For heterogeneous catalysts, it is well known that the observed kinetics may be very different from the relations in the immediate vicinity of the catalytic site. These differences originate from concentration gradients of various types. Although the complete elimination of such gradients is not possible, it is very desirable to reduce them to extent that they are no longer of consequence. A reactor system in which this is achieved is called a differential reactor and the system used in the present study includes a solid catalyst. Furthermore during the course of a series of measurements there is a gradual change in the composition of the reactants as water produced by the

dehydration accumulates and the intrinsic behavior of the catalyst<sup>2,3,4</sup>.

Table - 1

	Resin catalyst		Alumina catalyst		Titania catalyst	
	Slope Mole	Intercept $\times 10^{-5}$ sec	Slope Mole	Intercept $\times 10^{-5}$ sec	Slope Mole	Intercept $\times 10^{-5}$ sec
Tert butyl alcohol	667	1.32	375	1.79	480	2.8
N-butyl alcohol	1400	1.45	400	1.02	733	0.8
Iso-butyl alcohol	2000	2.26	437	1.16	1467	1.14

The value of the slope ( $\text{Slope} = \frac{k_w/k_A - 1}{1 + 1/k_A}$ ) and the intercept ( $\text{Intercept} = \frac{k_1}{1 + 1/k_A}$ ) are calculated

If we neglect for the moment, the problem of gradients within the catalyst particle itself, we may consider the catalyst as an emitter of alkenes and water. These are distributed uniformly through the liquid phase by agitation and the course of refluxing the alkenes is expelled from the system to form a gas phase while the water tends to equilibrate with the vapor phase. High local concentrations of the alkenes even in the immediate vicinity of the catalyst particle are not likely to persist since they would be removed by the bubble formation due to lowering of the boiling point. A qualitative examination of  $(R/[A])$  vs.  $[W]$  plot shows that the initial rate of evolution of alkenes is high but falls rapidly as water accumulates. From the plot of  $(R/[A])$  vs.  $[W]$  a drastic reduction in the amount of catalyst produces little change in data and we may assume that the measured rates and concentration adequately reflect the instantaneous situation at the catalyst foundry<sup>4,5</sup>.

Figure 2 shows the specific rate of dehydration with water activity vs. specific rate of dehydration of tertiary butyl alcohol over resin catalyst. This linear graph means the rate of dehydration increase with the increase in water activity because the carbon chain with -OH group is situated in butyl position.

Figure 3 indicates the specific rate of dehydration with water activity versus specific rate of dehydration of normal butyl alcohol over resin catalyst and this curve means the rate of dehydration becomes constant at the value of specific rate with water activity of normal butyl alcohol of  $5 \times 10^{-4}$  moles/sec because the normal carbon chain with -OH group.

Figure 4 indicates the specific rate of dehydration with water activity against specific rate of dehydration of isopropyl over resin catalyst. It shows

the similar behavior as like as tertiary butyl alcohol because the carbon chain with -OH group is situated in iso position.

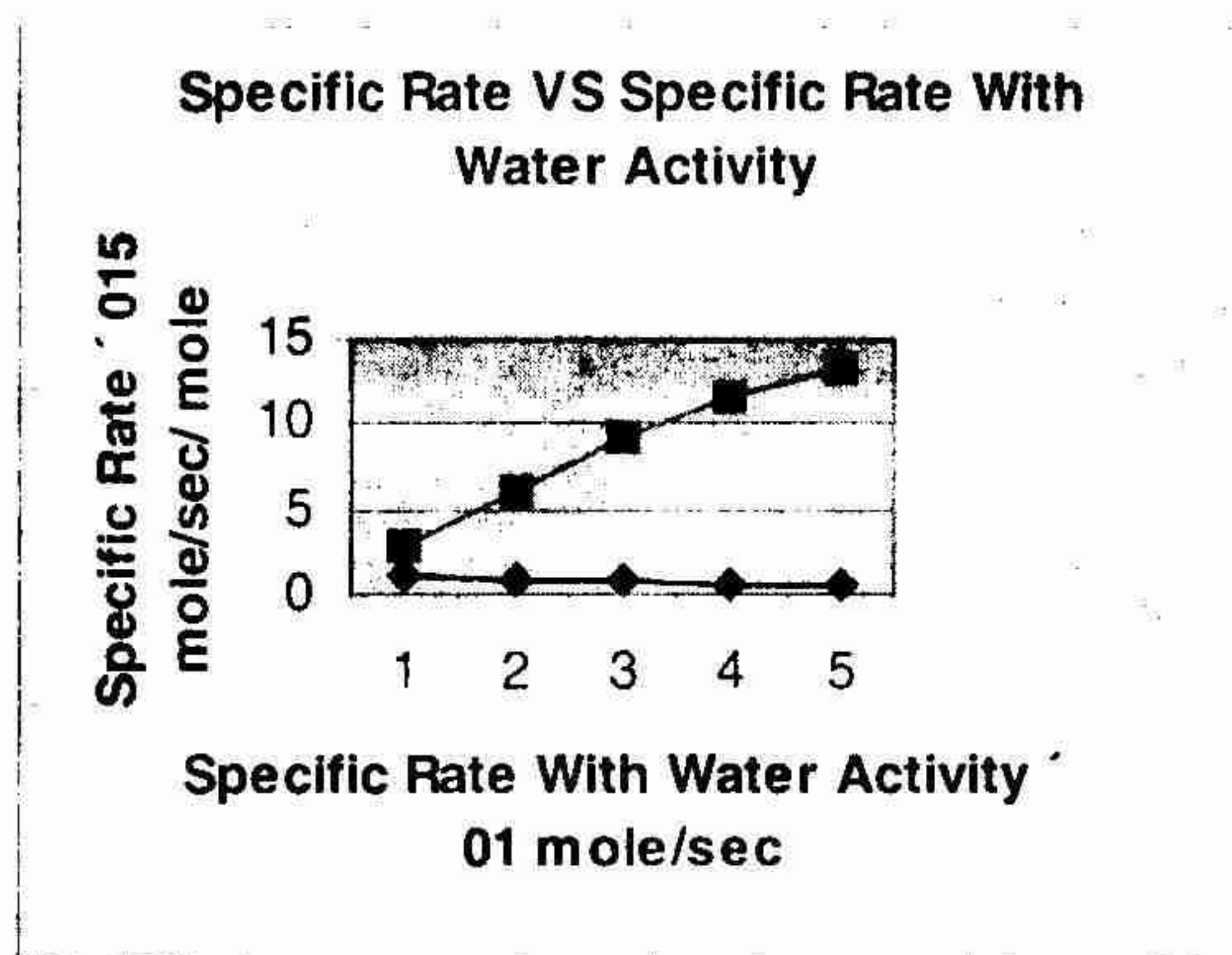


Fig. 2 Specific rate versus specific rate with water activity of dehydration tertiary butyl alcohol over resin catalyst.

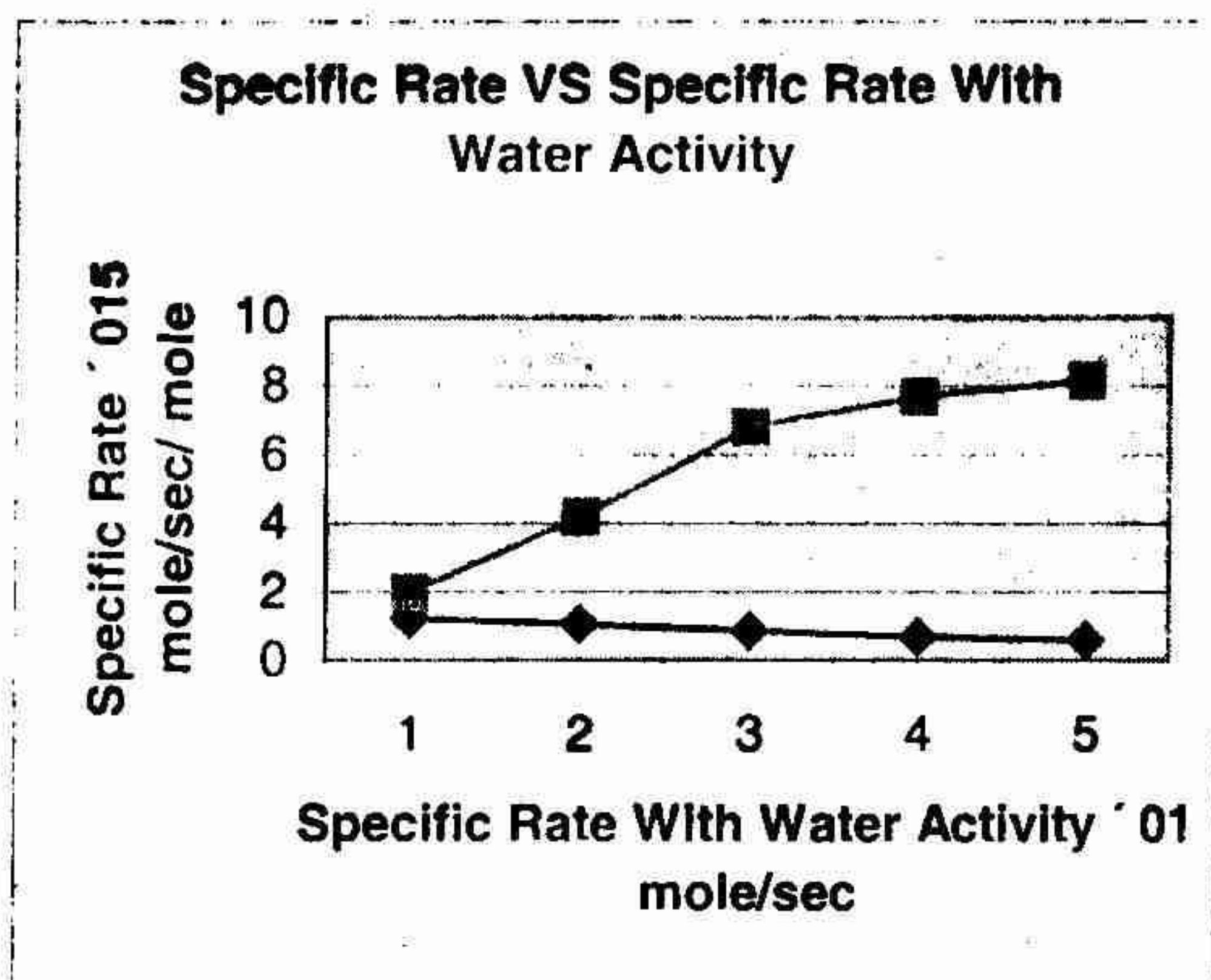


Fig. 3 Specific rate versus specific rate with water activity of dehydration normal butyl alcohol over resin catalyst.

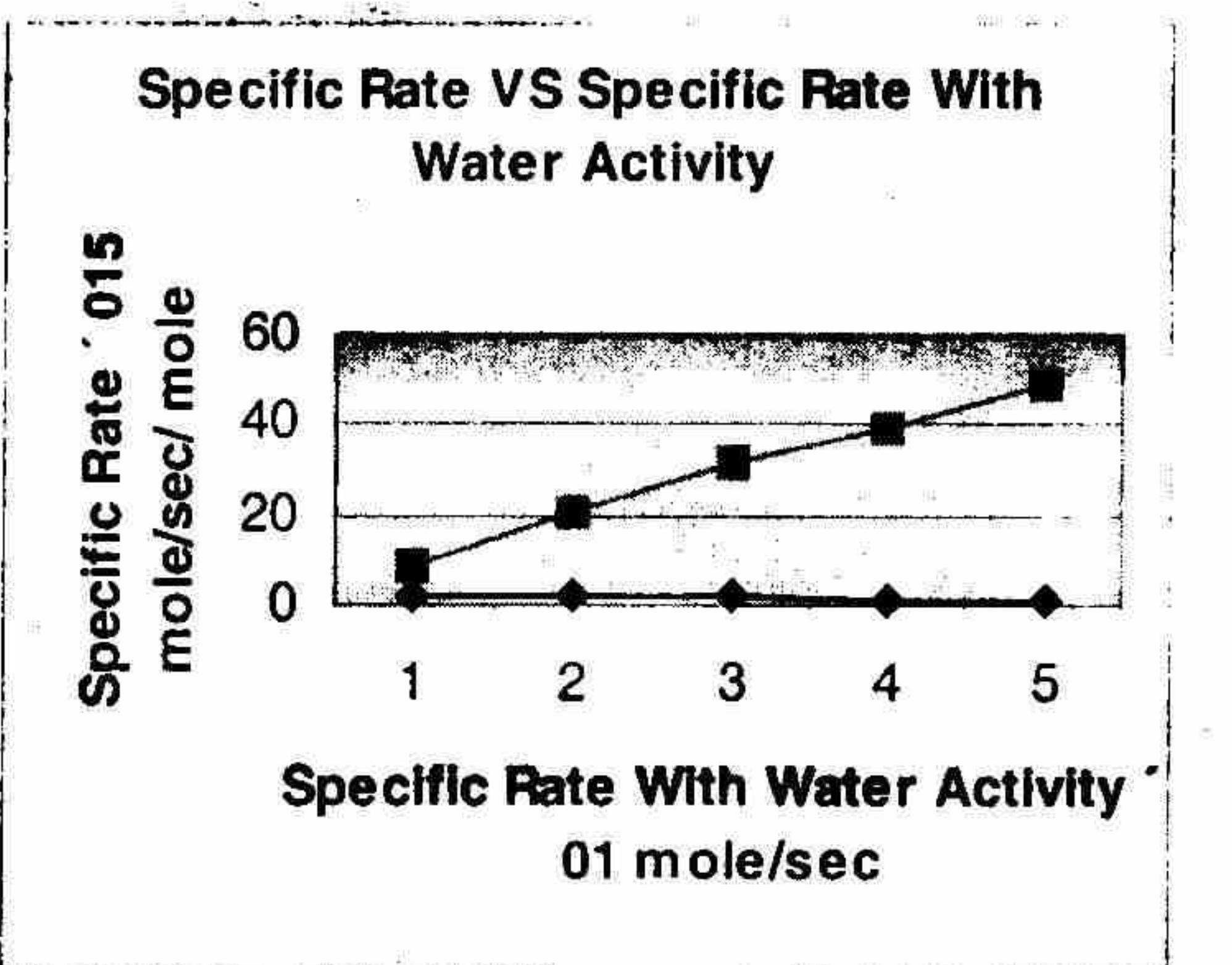


Fig. 4 Specific rate versus specific rate with water activity of dehydration iso propyl alcohol over resin catalyst.

## Conclusions

The purpose of the present study is to investigate the kinetics of dehydration of three different alcohols over these different catalysts. From experiments we get nine sets of data for three alcohols over three catalysts the data fitted to a model suggested in the literature. The values of the parameters of the model for different catalysts and alcohols have been calculated

## References

1. Sunil Kumar Mondal, "Kinetics of Dehydrations of Alcohols over different Catalyst", B. Sc. Engineering thesis, Chemical Engineering Department, BUET, (1991).
2. Frilette, V.J., Mower and M.K. Rubin: "Kinetics of Dehydration of Ter-Butyl Alcohol Catalyzed by Low Exchange Resins", J. Catal., 25031 (1964).
3. Hill, C.G.: "An Introduction to Chemical Engineering Kinetics and Reactor Design", John Wiley and Sons, New York, (1977).
4. Pines, Heman and Joost Manassen: "Mechanism of Alcohol Dehydration over Alumina Catalyst.
5. Bahl, B.S. and A.: "Advanced Organic Chemistry", S. Chand and Company, Ltd., New Delhi, (1985).
6. Warren L. Mc Cabe, Julian C Smith and Peter Harriott "Unit Operation of Chemical Engineering" Mc Craw Hill Book Company, 4<sup>th</sup> edition New York.
7. Richard M. Felder, Ronald W. Roasseau "Elementary Principles of Chemical Processes" John Wiley & Sons 2<sup>nd</sup> edition, New York.
8. R. Byron Bird, Warren E. Stewort, Edwin N. Light Fort "Transport Phenomena" John Wiley & Sons, New York, (1994).