# Kinetic And Viscometric Studies Of Oxidation Of Sucrose And Fructose By Vanadium(V) In Sulphuric Acid Medium

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*Abstract:* **Investigations were carried out on the oxidation of fructose and sucrose by Vanadium (V) in aqueous sulphuric acid at temperature 298 K. The $k_{obs}$ increases linearly with concentration of both the sugars. The effect of viscosity of the aqueous sulphuric acid on rate constant has also been investigated to make a study of viscosity of the medium on the rate of oxidation. In case of both the substrates the rate of oxidation follow the linear relationship with the viscosity of the reaction medium with linearity coefficient greater than 0.98.The reaction was first order with respect to substrates and accelerated with the increase in the sulphuric acid concentration. The proposed mechanism of the oxidation based on the formation of the vanadium (V) complex ion leads to the formation of free radical of the substrates.**

**Keywords : Redox reactions, Sugars, Vanadium (V), Complex ion, Viscosity, Sulphuric acid**

## INTRODUCTION

The study of saccharides has special importance due to their multidimensional physical, biological and industrial relevance [1, 2, 3, 4]. The behaviour of electrolytes in aqueous carbohydrates and carbohydrates containing small quantity of ions which are present in body fluids has became subject of interest [5, 6, 7]. Simple saccharides have received attention due to their ability to protect biological macro molecules in addition to their importance to pharmaceutical and food [8].

The molecular interaction of sugars in solutions plays an important role in governing the mechanism of any system. The aqueous solutions of sugar have been used by many workers in studying the solute – solvent interaction in aqueous and mixed solvent system including studies related to viscosity of the medium [9, 10, 11, 12, 13, 14, 15]. The solvent – solvent interaction produced in solvent mixture can effect solute – solvent interaction and preferential solvation [16].

Solvent plays an important role in many chemical processes. Organic liquids are characterized by several properties that make them suitable for dissolving and providing reaction media for various type of solutes or reactant [17]. During recent past workers have shown considerable interest in explaining the role of solvent properties like preferential solvation on reaction rates [18, 19, 20, 21].

The study of the oxidation of organic compounds by vanadium (V) has an importance due to role of vanadium in relation to the insuline – mimetic act and catalytic activities [22, 23, 24]. The study of oxidation mechanism of compounds by vanadium (V) has also an importance in the studies concerning possible role of transient ions of chromium and manganese on certain oxidation reactions by both chromic acid and potassium permanganate [25]. The coordination chemistry of various aqua complexes has been reported in different oxidation states [26]. In pure sulphuric acid the formation of polymeric species of ammonium metavanadate or vanadium pentoxide has been reported in the spectroscopic study[27].The solution of pure sulphuric acid in water may influence the vanadium species and secondly the sulphuric acid is highly viscous in pure state .Dilution of acid with water also influence the viscosity.

The present study is therefore undertaken to study the effect of medium mainly viscosity on rate of oxidation of sugars by vanadium (V) in sulphuric acid.

Oxidation of carbohydrates by transition metal ions vanadium (V), chromium (VI), thallium (III), manganese (VII), cerium (IV) and colloidal $MnO_2$ are of especial interest due to there application in biological sciences [28]. The oxidation of sugars by vanadium (V) has special importance due to there biological relevance and application in oxidation reaction by chromium / potassium permanganate [25] In the higher acid concentration range ($> 4.5$ mol dm$^{-3}$) the following active species and equilibrium have been reported.

$$VO_2^+ \quad + \quad 2H^+ \quad + \quad 2HSO_4^- \quad \rightleftharpoons \quad [V(OH)_2(HSO_4)_2]^+ \qquad (1)$$

The vanadium (V) is amphoteric [29] and at lower acid concentration (pH $\geq 1.0$) exist in a form of pervanadyl ion $VO_2^+$. The ion $VO_2^+$ may be in hydrated form in lower concentration range.

$$VO_3^- \quad + \quad 2H^+ \quad \overset{\text{fast}}{\rightleftharpoons} \quad VO_2^+ \quad H_2O \qquad (2)$$
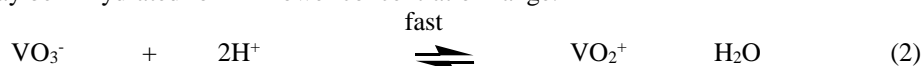
The results of these studies have revealed that in some cases the mechanism was proposed on the basis of the formation of intermediate complex between substrate and the oxidant while in some cases the mechanism were proposed on the basis of formation of free radical in the oxidation process. All these studies have reported that the oxidation of sugars shows first order dependence on vanadium (V), H$^+$ ion and HSO$_4^-$ ion.

The effect of sulphuric acid concentration on rate of oxidation has both acid independent and dependant path, depending upon the concentration range. The plot between $k_{obs}$ and [H$_2$SO$_4$] has non linear nature but the rate increases with the increase of sulphuric acid concentration. The various explanations have been proposed for the justification of the effect of acid concentration on rate of reaction.

## EXPERIMENTAL

All the reagents used were of A.R. Grade chemicals and used without further purification. Double distilled water was used throughout this work. The strength of the acid of the each solutions checked by titration against a standard solution of sodium hydroxide using phenolphthalein as an indicator.

The viscosity measurements were taken in a calibrated suspended-level Viscometer placed in a thermostatic water bath for constant temperature. The solutions of sulfuric acid of knowing concentration was taken at Viscometer and flow time of the solution was measured. Each measurement was repeated thrice and average time of flow was used to calculate the viscosity. The Viscometer used in the study was purchased from Infusil India Pvt. Ltd. Having number BG43500 size 2 and BG43499 size 1. The densities of the solutions were measured with calibrated Pyknometer and single pan electronic balance citizen make..

## RESULTS

### Dependence of Rate on Initial [Oxidant]

The effect of [Vanadium (V)] on the reaction rate was studied at constant concentration of sulphuric acid, sugars and temperature. The values of rate constant $k_{obs}$ are summarized in Table 1 in the concentration range of vanadium (V) used in the study, the rate constant $k_{obs}$ was independent of the [vanadium (V)]. These observation are in agreement with a first order dependence on [vanadium (V)]$_T$ and the reaction follows a first order rate law given by equation .

**Dependence**   $-d[\text{vanadium (V)}]/dt$     $=$     $k_{obs}[\text{vanadium (V)}]_T$                 (3)

**of Rate on Initial [Substrate]**

The pseudo first order rate constant $k_{obs}$ were calculated at constant [V (V)] and sulphuric acid but at different substrate concentrations in the range 0.04 to 0.09 mol dm$^{-3}$. The plots of $k_{obs}$ against [Sugars] are linear in all the cases. These plots give a straight line with a negative slope and positive slope depending upon the nature of sugar. The values of rate constant are given in Table 1. The detailed study related to variations of the reactant has not been carried out in the study, but we have tried to correlate the viscosity and reaction rate in these oxidations of sugars by V (V) in sulfuric acid. The plot between [sugars] and $k_{obs}$ are linear with linearity coefficient 0.9956 for fructose and 0.9923 for sucrose.

**Table 1: Effect of [Reactants] on the Reaction rate $k_{obs}$ At 298 K**

| S. No | [Substrate] mol dm$^{-3}$ | [H$_2$SO$_4$] mol dm$^{-3}$ | [V(V)] mol dm$^{-3}$ | Value of $10^5$ $k_{obs}$ (sec$^{-1}$) | |
|-------|----------|---------|---------|----------|---------|
|       |          |         |         | Fructose | Sucrose |
| 1  | 0.04 | 2.0 | 0.002 | 17.1 | 9.0 |
| 2  | 0.04 | 2.0 | 0.003 | 17.2 | 9.1 |
| 3  | 0.04 | 2.0 | 0.004 | 17.0 | 9.2 |
| 4  | 0.04 | 2.0 | 0.005 | 17.3 | 9.1 |
| 5  | 0.04 | 2.0 | 0.006 | 17.2 | 9.2 |
| 6  | 0.04 | 2.0 | 0.004 | 1.6  | 0.8 |
| 7  | 0.05 | 2.0 | 0.004 | 2.1  | 1.1 |
| 8  | 0.06 | 2.0 | 0.004 | 2.5  | 1.3 |
| 9  | 0.07 | 2.0 | 0.004 | 2.9  | 1.6 |
| 10 | 0.08 | 2.0 | 0.004 | 3.2  | 1.7 |
| 11 | 0.09 | 2.0 | 0.004 | 3.7  | 1.9 |
| 12 | 0.04 | 1.0 | 0.004 | 9.1  | 2.2 |
| 13 | 0.04 | 1.5 | 0.004 | 17.1 | 3.7 |
| 14 | 0.04 | 2.0 | 0.004 | 25.4 | 5.5 |
| 15 | 0.04 | 2.5 | 0.004 | 33.5 | 7.3 |
| 16 | 0.04 | 3.0 | 0.004 | 42.2 | 9.2 |

### Dependence of Rate on Initial [H$_2$SO$_4$]

The concentration range 1.0 to 3.0 mol dm$^{-3}$ was used for the variations in [H$_2$SO$_4$] in the study. The concentrations of oxidant and substrate were taken constant. The observed dependence of the rate on the concentration of sulphuric acid in case of all the substrates shows that the rate increases with increase in concentration of sulphuric acid. The reaction rates are represented in Table 1.

## MECHANISM AND DISCUSSION

The results shown in Table 1 were used to analyse the effect of various reactant on rate of oxidation of sugars. The pseudo first order rate at constant [oxidant] and [H$_2$SO$_4$], increased with increasing [sugars]. The plot between [sugars] and $k_{obs}$ is shown in Fig 1, for both the substrates. The plots are linear and the linearity coefficient is > 0.98. The rate constant is increased with increasing [H$_2$SO$_4$]. The plot between [H$_2$SO$_4$] and the rate constant were also linear for both the sugars. The representative plots are given in Fig 2.
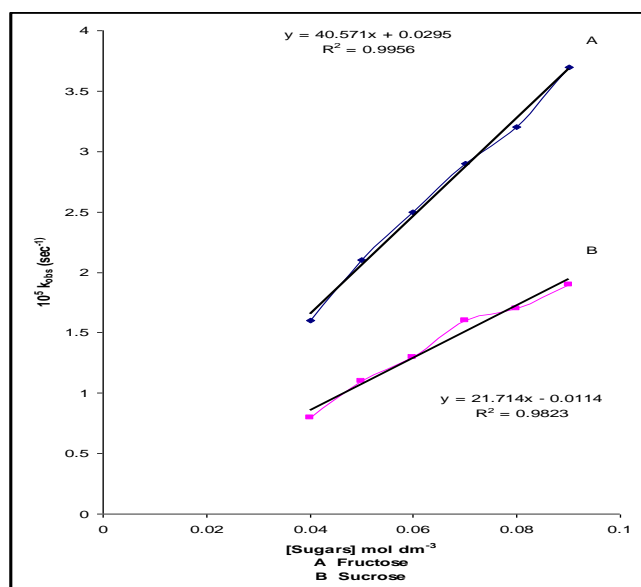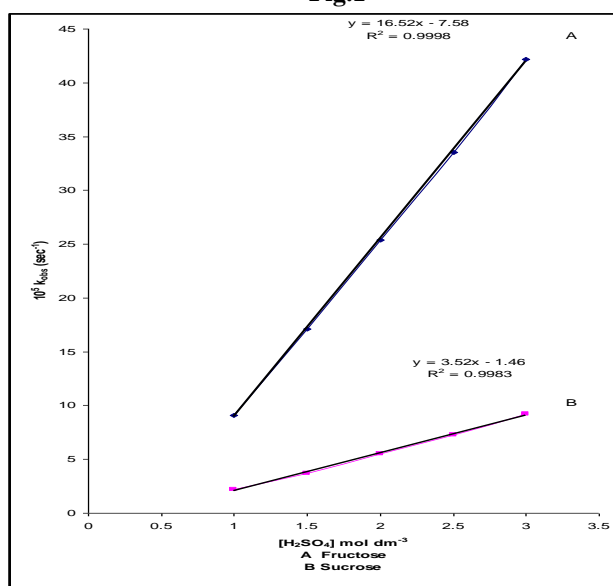
**Fig.1**



**Fig.2**

These results confirm that the order of reaction with respect to substrate is one in the sulphuric acid medium. The reaction rate was accelerated with the increase in the sulphuric acid concentrations. The very high concentrations of sulphuric acid were not used to avoid the undesirable solvent effect such as viscosity, dielectric constant etc in the kinetic measurement because we have proposed to study the effect of solvent related to the viscosity of the medium on rate of oxidation. The solvent effect related to the viscosity can be studied only at constant acid concentration to eliminate the catalytic effect of the acid. It results that the oxidation of glucose would not be carried out by changing the concentration of reactant according to experimental conditions.
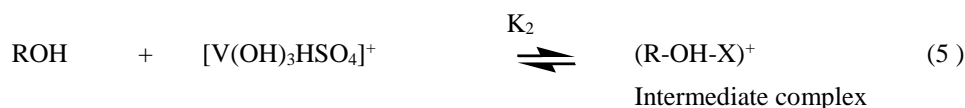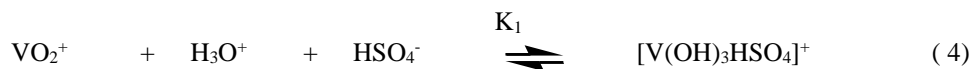
The results of the study of the kinetics of the oxidation of two sugars reported above namely fructose and sucrose could be summarized as below-

(i) The reactions have a first order dependence on vanadium (V), confirmed by the experimental data which was independent of the initial vanadium (V) concentration.

(ii) The reactions are acid catalyzed and the catalytic effect increases with increasing concentration of sulphuric acid.

(iii) The reaction rates have linear dependence on concentration of sulphuric acid. The plot between concentration of sulphuric acid and rate constant indicates the order of the reaction nearly unity with respect to sulphuric acid concentration.

(iv) The order with respect to the substrate concentration is also one for both the sugars. The linear plot of rate constant against substrate concentration passing through the origin is an indication of second order kinetics, first order with respect to sugar and first order with respect to vanadium.

(v) The addition of substrate to the solution of vanadium results in a shift in the absorbance wave length measured in the spectrophotometric study, which is an indication of the intermediate complex formation between vanadium (V) and substrate. Similar shift was also noted on increasing the acid concentration which is indication of protonation equilibria between various vanadium (V) species in sulphuric acid.

(vi) The reaction mixture on partial oxidation polymerizes the acrylonitrile with in few minutes, indicating the presence of free radical in the progress of the reaction.

(vii) It is well established by earlier worker that the $[V(OH)_3HSO_4]^+$ is kinetically active species of vanadium in aqueous sulphuric
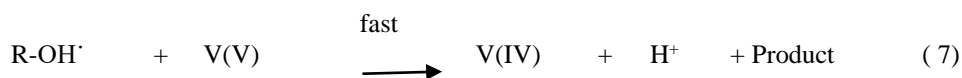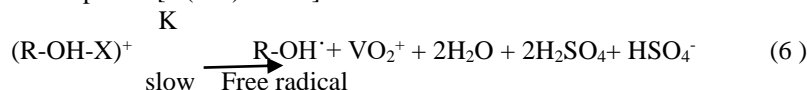
acid [30].

## MECHANISM

On the basis of the above facts and experimental results the mechanism for the oxidation of sugars by vanadium(V) in aqueous sulphuric acid medium has been proposed by considering the complex ion and free radical formation as given in scheme I

$$VO_2^+ \quad + \quad H_3O^+ \quad + \quad HSO_4^- \quad \overset{K_1}{\rightleftharpoons} \quad [V(OH)_3HSO_4]^+ \qquad (4)$$

$$ROH \quad + \quad [V(OH)_3HSO_4]^+ \quad \overset{K_2}{\rightleftharpoons} \quad (R\text{-}OH\text{-}X)^+ \qquad (5)$$
$$\text{Intermediate complex}$$

Where X represent the species $[V(OH)_3HSO_4]^+$

$$(R\text{-}OH\text{-}X)^+ \quad \overset{K}{\underset{slow}{\longrightarrow}} \quad R\text{-}OH^{\cdot} + VO_2^+ + 2H_2O + 2H_2SO_4 + HSO_4^- \qquad (6)$$
$$\text{Free radical}$$

$$R\text{-}OH^{\cdot} \quad + \quad V(V) \quad \overset{fast}{\longrightarrow} \quad V(IV) \quad + \quad H^+ \quad + Product \qquad (7)$$

Scheme I

According to scheme I the overall reaction rate is given by equation (8).

$$\text{Rate} \quad = \quad k\,K_1K_2\,[R\text{-}OH]_T\,[H^+]\,[V(V)]\,[HSO_4^-] \qquad (8)$$

$$\text{Rate} \quad = \quad \frac{k\,K_1K_2\,[R\text{-}OH]_T\,[H^+]\,[V(V)]_T\,[HSO_4^-]}{[1+K_1H^+]\,[HSO_4^-]} \qquad (9)$$

When the values of $K_1\,[H^+]\,[HSO_4^-]$ is less than one rate equals to

$$\text{Rate} \quad = \quad k\,K_1K_2\,[R\text{-}OH]_T\,[H^+]\,[V(V)]_T\,[HSO_4^-] \qquad (10)$$

The above mechanism is in agreement with the experimental results and mechanism proposed for oxidation of glucose [31].

## DEEPENDENCE OF REACTION RATE ON VISCOSITY OF THE MEDIUM

The reaction rate obtained on the basis of viscosity approach can be compared with the increase in the rate with increase in concentration of the substrate. The comparison shows that the graph between viscosity of the medium and concentration of the substrate has a considerable importance. The graph between concentration and viscosity of the substrate in aqueous solutions at 298 K are given in Fig 3 and Fig. 4 .
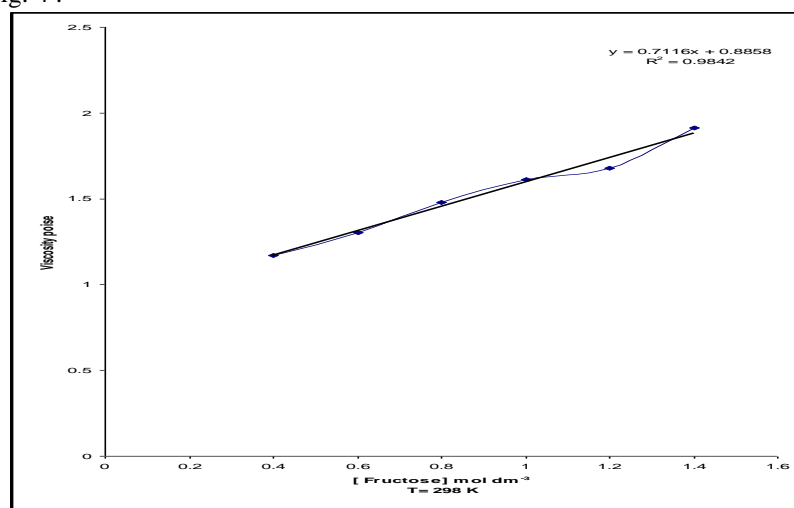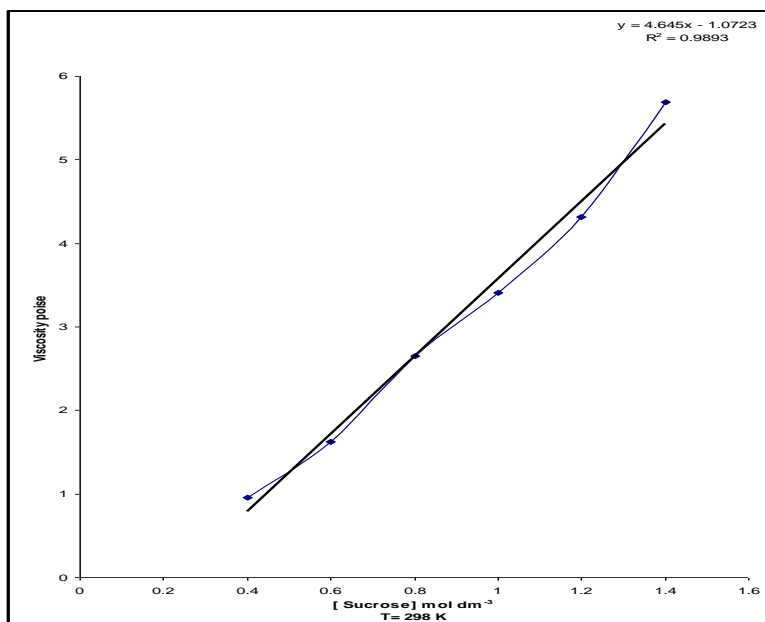


**Fig.3**

**Fig. 4**

In the measurement of the viscosity the effect of other reactant, oxidant and acid has not considered because the concentration of these reactants have constant magnitude. Thus the viscosity of the substrate in aqueous medium can be taken as the viscosity of the reaction media as an experimental purpose. This assumption has been used in order to assess the effect of viscosity on the rate of reaction of the medium.

A simple way of obtaining the relationship between viscosity of the medium and rate of reaction is careful study of rate of reaction with change of concentration of the substrate used in the determination of the viscosity of the medium.

The plots between viscosity and rate of reaction are shown in Fig. 5 and Fig. 6 . It is seen that for both the substrates the curves are linear in nature Fig .7 and Fig. 8. For both the substrate it has been found that the values of rate constant obtained experimentally are in reasonable agreement with the relation obtained between concentration and viscosity of the substrate.
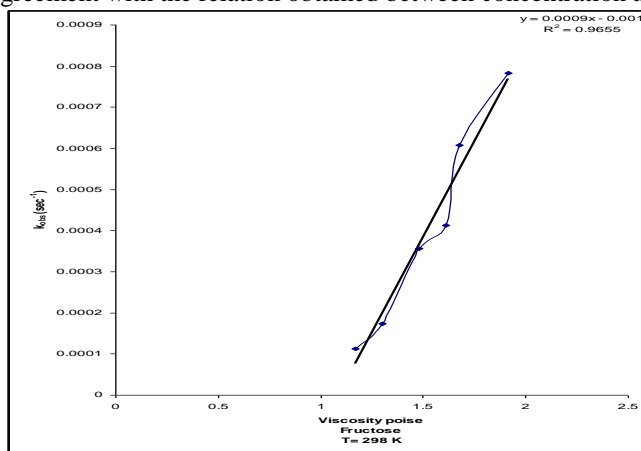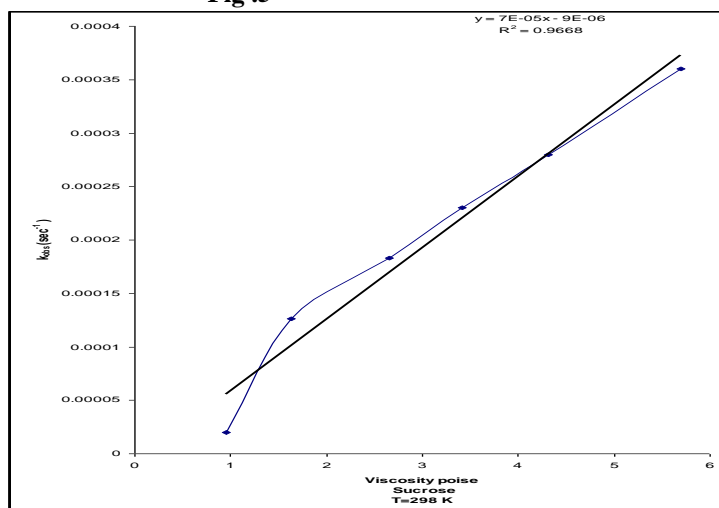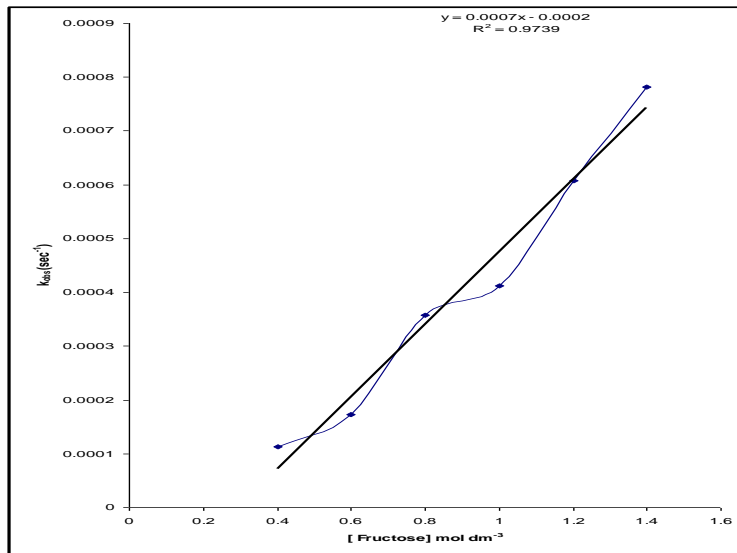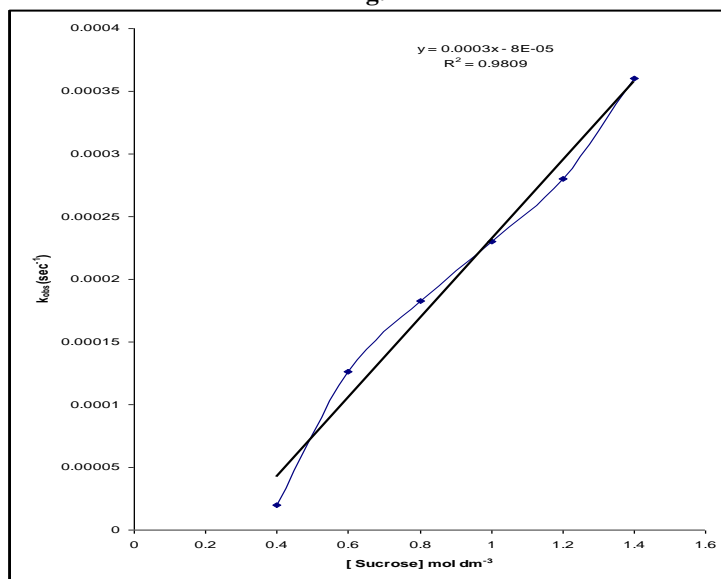


**Fig .5**



**Fig .6**

**Fig.7**



**Fig .8**

In acidic solutions the moment $H_3O^+$ ion loses its proton to a neighbouring water molecule it itself transforms into water molecule. However the time taken in the transfer process is about $10^{-14}$ sec. While the time of $H_3O^+$ ion wait for its adjacent water molecules to reorient is about $2.4 \times 10^{-13}$ sec. [32]. The contribution towards viscosity by the $H^+$ ions can be considered negligible and the contribution of sugars mainly at higher concentration is responsible for the increase in viscosity in aqueous solutions.

Spectroscopic studies have shown that the hydration of saccharides depends upon the hydroxyl group, the hydrogen bonding sites and the relative position of the hydroxyl groups in the carbohydrate molecules [33]. In purely aqueous solutions mono and disaccharides have structure – maker character as observed from viscometric measurement [34].

In our study the following linear relations are applicable for fructose (Fig. 3 and Fig. 7)

$$\eta = 0.7116 \, [S] + 0.8858 \qquad (11)$$

$$k_{obs} = 0.0007 \, [S] - 0.0002 \qquad (12)$$

These equations can be rearranged and equation (11) can be divided by equation (12).

$$\frac{0.7116 \, [S]}{0.0007 \, [S]} = \frac{\eta - 0.8858}{k_{obs} + 0.0002} \qquad (13)$$

Where [S] = fructose

$$k_{obs} = 0.0009 \, \eta - 0.0009$$

or

$$k_{obs} = 0.0009 \, (\eta - 1) \qquad (14)$$

The eq (14) is in agreement with the linear relation obtained in the graph $\eta$ versus $k_{obs}$ given by equation (15)

$$k_{obs} = 0.0009 \, \eta - 0.001 \qquad (15)$$

The value of intercept 0.001 is nearly equal 0.0009.

      In the same way the relation for sucrose obtained in the study can be taken as actual relation between viscosity and $k_{obs}$.

$$k_{obs} = 0.00007 (\eta - 0.12) \qquad\qquad (16)$$

## CONCLUSION

      From the above discussion and analysis of the kinetic data it is concluded that the value of rate constant for the solutes having structure maker character in aqueous solutions is directly proportional to the viscosity of the solutions used in the kinetic study. Further investigations in the light of influence of viscosity / medium effect on rate of reaction are expected to be an important example as a model.

## ACKNOWLEDGEMENT

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