

## A Revisit to the Kinetics and Mechanistics of Electron-Transfer Process in Oxidation of Poly (Vinyl Alcohol) Macromolecule by Permanganate Ion in Aqueous Perchlorate Solutions with Novel Synthesis of Coordination Biopolymer Precursors

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**ABSTRACT:** The kinetics of oxidation of poly (vinyl alcohol) as synthetic polymer (PVA) by permanganate ion in aqueous perchlorate solutions at a constant ionic strength of  $2.0 \text{ mol dm}^{-3}$  has been investigated, spectrophotometrically. The reaction kinetic seems to be of considerable complexity. Pseudo first-order plots were found to be of inverted S-shape type throughout the entire course of reaction. The initial rates were relatively slow in the early stages, followed by an increase in the oxidation rates at the longer time periods. The experimental results indicated first-order kinetics in permanganate and fractional second-order dependence in [PVA] for both induction and autoacceleration periods. The influence of the  $[\text{H}^+]$  on the reaction rates showed that the oxidation reaction was acid-catalyzed in both stages. A fractional-second order in  $[\text{H}^+]$  was observed for the induction period, but this order has not maintained throughout the autoacceleration period. Added salts indicated that  $\text{Mn}^{\text{III}}$  and/or  $\text{Mn}^{\text{IV}}$  play an important role in the reaction kinetics. A kinetic evidence for formation of 1:2 intermediate complexes was revealed. The kinetic parameters have been evaluated and a tentative reaction mechanism consistent with the kinetic results is suggested.

[Ishaq A. Zaafarany. A Revisit to the Kinetics and Mechanistics of Electron-Transfer Process in Oxidation of Poly (Vinyl Alcohol) Macromolecule by Permanganate Ion in Aqueous Perchlorate Solutions with Novel Synthesis of Coordination Biopolymer Precursors. *J Am Sci* 2013;9(12):233-247]. (ISSN: 1545-1003). <http://www.jofamericanscience.org>. 29

**Key words:** oxidation; kinetics; synthesis; poly (vinyl alcohol); permanganate.

### INTRODUCTION

The kinetics of permanganate oxidation of pectin<sup>1</sup>, kappa-carrageenan<sup>2</sup>, carboxymethyl cellulose<sup>3</sup> and methyl cellulose<sup>4</sup> as natural polymers in perchlorate solutions has been investigated for the first time by us earlier. The experimental results indicated that the pseudo first-order plots were of inverted S-shape in which the oxidation reactions were proceeding through two distinct stages via intervention of free-radical mechanism. The first stage which corresponding to the induction period was relatively slow at the early stages followed by an increase in the oxidation rates at longer time periods (autoacceleration period). Kinetic evidences for formation of 1:2 intermediate complexes were revealed. Again, the kinetics of permanganate oxidation of alginates<sup>5</sup>, pectates<sup>6</sup>, carboxymethyl cellulose<sup>7</sup>, methyl cellulose<sup>8</sup> and carrageenans<sup>9</sup> as natural polymers, along with that of PVA as a synthetic polymer<sup>10</sup> has been investigated in alkaline solutions elsewhere. The oxidation processes were found to proceed through two measurable distinct stages in absence of free-radical intervention. The first stage was relatively fast which corresponding to the formation of transient coordination biopolymer intermediates involving green manganate (VI) and / or blue hypomanganate (V) short-lived species, followed by a slow decomposition

of these intermediates to give rise to the final oxidation product in the second stage.

Khan and coworkers<sup>11</sup> investigated the oxidation of poly (vinyl alcohol) (PVA) as a synthetic polymer by this oxidant in sulfuric acid media. They reported that the pseudo-first-order plots were linear throughout the entire course of reaction with formation of 1:1 intermediate complex. Unfortunately, the mechanistic aspects on the nature of electron-transfer and transition states in the rate determining steps still remain controversial and incomplete.

Preliminary experiments of permanganate oxidation of PVA in acid perchlorate solutions indicated that the oxidation reaction proceeds through two stages (induction and autoacceleration periods, respectively) with formation of 1:2 intermediate complexes on contrary to the results that observed by Khan and co-workers in sulfuric acid media.<sup>11</sup>

In view of the aforementioned discrepancies and our interest in the kinetics of oxidation of macromolecules by this oxidant, the present study seems to merit an investigation in aqueous perchloric acid solutions with the aims at shedding further highlights on the role of the medium nature on the kinetics and mechanistics of these oxidation reactions in terms electron-transfer process and transition states as well as to compare the results obtained in

perchloric acid with that reported in sodium hydroxide<sup>10</sup> and sulfuric acid solutions.<sup>11</sup> Since, the oxidation product obtained, poly (vinyl ketone) (PVK) has a high tendency to chelate with most of known polyvalent metal ions, it can be used as a chelating agent for removal of undesired poisonous toxic heavy metal cations from the environment, soil and wastewater...etc. The characteristics of the formed coordination biopolymer metal-PVK complexes are in progress in our laboratory.

## EXPERIMENTAL

### Materials

Poly (vinyl alcohol) (PVA) (Merck grade powder- reagents -72000; Merck, Japan, Ltd) was used without further purification. The measured inherent and reduced viscosities were found to be 1.97 and 6.88 dl/g, respectively, for a 4% w/w solution in water at 20 °C.

A stock solution of PVA was prepared as described elsewhere.<sup>10</sup> This process was performed by stepwise addition of the reagent powder to deionized water whilst rapidly stirring the solution to prevent the formation of lumps, which swell with difficulty.

A stock solution of potassium permanganate was prepared and standardized as described elsewhere.<sup>12</sup> Then, this stock solution was stored in a dark bottle away from light to avoid the photoreduction and it was restandardized spectrophotometrically before each run.

The ionic strength was maintained constant at 2.0 mol dm<sup>-3</sup> by adding NaClO<sub>4</sub> as an inert electrolyte. The temperature was controlled within ± 0.05 °C.

All other reagents were of analytical grade and prepared by dissolving the requisite amount of the reagent in doubly distilled water.

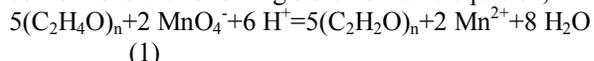
### Kinetic procedure

The kinetic measurements were performed under pseudo-first-order conditions in the presence of a large excess of [PVA] over that of permanganate concentration. If permanganate ion concentration was present in excess, a further side reaction will occur between the produced Mn<sup>2+</sup> as final oxidation product and the excess permanganate ion remained. Therefore the permanganate ion was not kept in a large excess so as to avoid the competitive side reactions which may complicate the reaction kinetics. The procedure of the kinetic measurements was performed as described elsewhere.<sup>1-4, 12</sup> The course of reaction was followed by monitoring the decrease in absorbance of MnO<sub>4</sub><sup>-</sup> ion at its absorption maximum, 525 nm, as a function of time. It was verified that there is no interference from other reagents at this wavelength. The absorption measurements were made in a thermostated cell compartment at the desired temperature within ± 0.05 °C on a Shimadzu UV-2101 automatic scanning

spectrophotometer fitted with a program controller using cells of path length 1 cm. The spectral changes during the redox reaction are shown in Figure 1.

### Stoichiometry and product analysis

Since this redox reaction seems to be of kinetics complexity, it is important to determine the stoichiometric coefficients of the reactants at firstly. Reaction mixtures containing different initial known concentrations of the reactants in 1.0 mol dm<sup>-3</sup> HClO<sub>4</sub> adjusted to a constant ionic strength of 2.0 mol dm<sup>-3</sup> were equilibrated in dark. The unreacted [MnO<sub>4</sub><sup>-</sup>] was estimated periodically until it reached a constant value (~24 h). A stoichiometric ratio of 0.4 ± 0.05 for ([MnO<sub>4</sub><sup>-</sup>]<sub>consumed</sub> / [PVA]<sub>0</sub>) was obtained. This result conforms to the following stoichiometric equation,



where (C<sub>2</sub>H<sub>4</sub>O)<sub>n</sub> and (C<sub>2</sub>H<sub>2</sub>O)<sub>n</sub> are PVA and its keto derivative (PVK), respectively. The monoketo derivative (PVK) was analyzed by elemental analysis and IR spectra as described earlier.<sup>1-4, 11</sup> The product was identified by the reaction with 2,4-dinitrophenylhydrazine and hydroxyl amine to afford the formation of the corresponding 2,4-dinitrophenylhydrazone and dioxime, respectively. Again, the recorded IR spectra of PVA and its oxidation product showed a decay of the band at 3450 cm<sup>-1</sup> and disappearance of the adsorption band of OH of PVA with the appearance of adsorption band at about 1730 cm<sup>-1</sup> indicating the interconversion of the secondary alcoholic (OH) to its keto (C=O) form.

### Synthesis and separation of poly (vinyl ketone) (PVK)

Synthesis and separation of the poly (vinyl ketone) oxidation product as a chelating agent takes place by mixing the stoichiometric molar ratios of the respective carbohydrates or PVA with chromic acid in 1.0 M HClO<sub>4</sub>.<sup>11, 13</sup> The reaction mixture was vigorously stirred for about 48 hours at room temperature to guarantee the complete oxidation of the alcoholic functional groups of the substrate. The solution was then treated overnight with excess freshly prepared saturated 2,4-dinitrophenylhydrazine in 1.0 M HCl. The mixture was kept in the refrigerator overnight, after which the formed precipitate was filtrated. The crude product was crystallized from methanol, dried, weighted and placed into desiccators for analysis. The difference between the two weights was found to be less than 3 %. The FTIR of PVA and PVK are shown in Figure 2. The tendency of such product to form coordination biopolymer cross-linked metal-PVK complexes has been examined.

### Polymerization test

Since this oxidation reaction seems to of complementary type, the possibility of formation of free-radicals was examined by adding 10% (v/v) of

acrylonitrile to the partially oxidized reaction mixtures. A polymeric suspension was noticeable after a lapse of 10 min. Black experiments from which either  $\text{MnO}_4^-$  or PVA were excluded gave no detectable polymerization during this time. This result indicates the intervention of free-radical during the entire course of oxidation.

## RESULT

### Reaction-time curves

The reaction time curves were found to be of inverted S-shape throughout the entire course of reaction. The initial rates were relatively slow in the early stage (induction period), followed by an increase in the reaction rate over longer time periods (autoacceleration period). As the reaction is of auto catalytic nature, the oxidation kinetics obeys the rate-

law expression  $(A_\infty - A_t) = B_0 e^{-k_s t} + P_0 e^{-k_f t}$

where  $k_s$  and  $k_f$  are the pseudo first-order rate constants for the slow and fast reactions.  $A_t$  and  $A_\infty$  are the absorbance at time  $t$  and infinity, while  $B_0$  and  $P_0$  represent the absorbance change for the slow and fast reacting species, respectively. The rate constants,  $k_s$ , listed in Table 1, were obtained by drawing a straight line through the slow-time linear portion of the first-order plot and extrapolating the line back to zero time ( $B_0$ ). Again, the rate constants,  $k_f$ , for the autoacceleration period were obtained from plots of  $-\ln [(A_t - A_\infty) - (A_t - A_\infty)]$  vs. time. The quantity  $(A_t - A_\infty)$  represents the experimental point and  $(A_t - A_\infty)$  represents the extrapolated point at time  $t$ .<sup>1-4,14,15</sup> A typical plot is shown in Figure 3.

### Dependence of reaction rate on $[\text{MnO}_4^-]$ and [PVA]

The order with respect to permanganate ion was determined by studying the reaction at different initial concentrations of permanganate ion and constants of all other reagents. The  $[\text{MnO}_4^-]$  was varied in the range of  $(1-6) \times 10^{-4}$ ,  $[\text{PVA}] = 4 \times 10^{-2}$ ,  $[\text{H}^+] = 1.0$  and  $I = 2.0 \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$ . The independence of the pseudo-first-order rate constants obtained from the linear portions of  $(\ln(\text{absorbance.}) - \text{time})$  plots at various  $[\text{MnO}_4^-]$ , may confirm that the reaction is first-order with respect to the permanganate ion concentration.

The order with respect to PVA was deduced from the kinetic measurements at several  $[\text{PVA}]_0$  and fixed permanganate concentration. The non-constancy obtained for the second-order rate constants, Table 1, derived from dividing the observed first-order rate constant by  $[\text{PVA}]_0$  indicates that the reaction is fractional -order in PVA concentration. The reaction was found to be of fractional-second order in  $[\text{PVA}]$  ( $\log k_s = n \log [\text{PVA}]$  plots). When the values of  $1/k_s$  or  $1/k_f$  were plotted against  $1/[\text{PVA}]^2$ , straight lines with

positive intercept on  $1/k_s$  or  $1/k_f$  axis were obtained as shown in Figure 4. The dependence of the rate constants on the poly (vinyl alcohol) concentration was found to follow Michaelis-Menten kinetics<sup>16</sup> for formation of 1:2 intermediate complexes between the substrate and the oxidant.

At relatively high concentrations of  $\text{PVA} > 7 \times 10^{-2} \text{ mol dm}^{-3}$ , a decrease in the initial rate was observed. This fact may be explained by the formation of more than one complex and at least one of the complexes appear to resist the oxidation process since increasing  $[\text{PVA}]$  decreases the rate. Again, the increase in viscosity of PVA sol with increasing its concentration may also play a role in this behavior where increasing the viscosity tends to slow down the movement of the reactant species and, hence, a decrease in the reaction rate should be occurred as was experimentally observed. Therefore, all of cited experiments were performed under the conditions of  $[\text{PVA}]_0 < 7 \times 10^{-2} \text{ mol dm}^{-3}$ .

### Dependence of reaction rate on $[\text{H}^+]$

To examine the influence of  $[\text{H}^+]$  on the rate of reaction, and to elucidate a suitable reaction mechanism, kinetic measurements were performed in  $\text{HClO}_4 - \text{NaClO}_4$  solutions of different  $[\text{H}^+]$  and constant ionic strength of  $2.0 \text{ mol dm}^{-3}$  and constants of temperature and all other reagents. It found that the rate of oxidation was increased with increasing  $[\text{H}^+]$  (Table 2). When the reciprocal of the observed first-order rate constants were plotted against  $1/[\text{H}^+]^2$ , straight lines with positive intercept on the Y axes were obtained as shown in Figure 5. A fractional second-order of  $1.6 \pm 0.1$  with respect to  $[\text{H}^+]$  was obtained ( $\ln [\text{rate}] - \ln [\text{H}^+]$  plots) for the induction period but such order-dependency was not maintained through out the autoacceleration period.

### Dependence of reaction rate on added salts

Since  $\text{Mn}^{2+}$  is one of the oxidation products, its effect on the rate of reaction was investigated. It is reported<sup>17-19</sup> that acidified permanganate ion is reduced by  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  according to the following equation,



If  $\text{MnO}_4^-$  ions are primarily responsible for oxidation, a reduction in the initial rate should be observed in presence of  $\text{Mn}^{2+}$  ions which reduce the concentration of  $\text{MnO}_4^-$  ions.<sup>18</sup> If on the other hand, the intermediate manganese ions,  $\text{Mn}^{3+}$  and/or  $\text{Mn}^{4+}$ , are the reactive oxidizing species, the addition of  $\text{Mn}^{2+}$  should cause an acceleration of the reaction rates. Similarly, the addition of  $\text{F}^-$  ions should retard the reaction if the intermediate manganese ions are mainly responsible for the oxidation, but should cause no significant change if  $\text{MnO}_4^-$  ions are the principal oxidizing entities.<sup>19-21</sup>

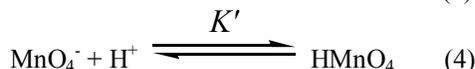
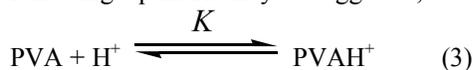
The experimental observations indicated that the reaction rate increased with increasing the  $[Mn^{2+}]$  ions, with complete disappearance of the induction period even at low  $[Mn^{2+}]$ , while a decrease in the reaction rates was observed on addition of  $F^-$  ions. The results are summarized in Table 3.

### Dependence of reaction rate on ionic strength

In order to investigate the effect of ionic strength on the rate of reaction with the aim at shedding some light on the reactive species in the rate determining steps, kinetic runs were performed at constant  $[H^+]$  of  $1.0 \text{ mol dm}^{-3}$  with increasing the ionic strength ( $NaClO_4$ ). It is surprising that the ionic strength has a negligible influence on the reaction rate under the experimental conditions used of ionic strength ranging from  $1.0$  to  $3.0 \text{ mol dm}^{-3}$ .

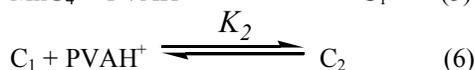
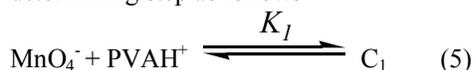
### DISCUSSION

In acidic solutions, both permanganate and PVA have a high tendency for protonation. Therefore, the following equilibria may be suggested,

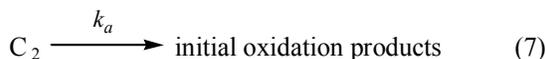


where  $K$  and  $K'$  represent the protonation constants for PVA and  $MnO_4^-$ , respectively.<sup>22, 23</sup> The observed fractional second-order dependence in  $[H^+]$  may indicate that two protonated species of the reactants were involving into the reaction-path in the rate-determining step. Under our experimental conditions of the hydrogen ion concentration used, the protonation of permanganate is negligible small ( $K = 2.99 \times 10^{-3} \text{ dm}^3 \text{ mole}^{-1}$ ).<sup>23</sup> compared to that of the protonation of PVA substrate.<sup>24</sup> Again, the second-order dependence of the rate constant in  $[PVA]$  which obeys the Michaelis-Menten kinetics, may confirm that the protonated species of PVA is the more probable reactive species.

In view of the above aspects and the experimental observations, the most reasonable reaction mechanism which may be suggested involves a complexation between the unprotonated oxidant and the protonated substrate to form the intermediate complex ( $C_1$ ). The formed  $C_1$  complex picks up a further substrate molecule forming the more reactive intermediate complex ( $C_2$ ) prior to the rate-determining step as follows



Then, the complex ( $C_2$ ) decomposes in rate-determining step to give a substrate radical and  $Mn^{3+}$  and/or  $Mn^{4+}$  intermediate species as initial oxidation products in the first induction period.



The change of the rate constant with the change in the hydrogen ion and substrate concentrations may be expressed by the following rate law,

$$\text{Rate} = -\frac{d[MnO_4^-]}{dt} = \frac{k_a K^2 K' K_1 K_2 [H^+]^2 [MnO_4^-] [PVA]_T^2}{1 + K_1 [H^+] + K K' K_1 [H^+] [MnO_4^-] (1 + K K_2 [H^+] [PVA]_T)} \quad (8)$$

where  $[PVA]_T$  is the analytical total concentration of PVA which equals  $[PVA] + [PVAH^+] + [C_1] + [C_2]$ . In the presence of a large excess of the substrate over that of permanganate concentration, the rate-law is as in Eq. (9)

$$\text{Rate} = \frac{d[MnO_4^-]}{dt} = k_s [MnO_4^-] \quad (9)$$

Comparing Eqs. (8) and (9) and rearrangement, ones conclude that

$$1/k_{\text{obs}} = \frac{1}{k_s} \left( \frac{1 + K[H^+]}{k_a K^2 K' K_1 K_2 [H^+]^2} \right) \frac{1}{[PVA]_T^2} + A^* \quad (10)$$

According to Eq. (10), at constant  $[H^+]$  a plot of  $1/k_s$  against  $1/[PVA]_T^2$  should be linear with positive intercept on  $1/k_s$  axis. The experimental results satisfied this requirement as shown by Michaelis-Menten plot (Figure 4). Again, a plot of  $1/k_s$  versus  $1/[H^+]^2$  at constant  $[PVA]$  gave good straight line with positive intercept on  $1/k_s$  axis as shown in Figure 5. The small intercept observed in Figure 4 may lead us to simplify Eq. (10) to (11), which is considered as the appropriate rate-law equation for oxidation of PVA by permanganate ion through the initial induction period.

$$\frac{[H^+] [PVA]_T^2}{k_s'} = \frac{1}{k_s'} \left( \frac{[H^+]^{-1}}{k_a'} + \frac{1}{k_a''} \right) \quad (11)$$

where  $k_s'$  is the third-order rate constant and  $k_a'$  and  $k_a''$  are the apparent rate constants and equal  $k_a K^2 K' K_1 K_2$  and  $k_a K K' K_1 K_2$ , respectively.

Equation (11) requires that plotting of  $1/k_s'$  against  $1/[H^+]$  to be linear with positive intercepts on Y axes as was experimentally observed. Typical plots (Figure 6), from whose slopes and intercepts, the values of  $K$ ,  $k_a'$  and  $k_a''$  can be evaluated.

$$* A = \frac{[MnO_4^-] (1 + K K_2 [H^+] [PVA]_T)}{k_a K K_2 [H^+] [PVA]_T^2}$$

Unfortunately, the rate constant of the elementary reaction ( $k_a$ ) could not be calculated because of the non-availability of the formation constants  $K_1$  and  $K_2$  values. However, some attempts were made to compute the formation constants from the experimental data, but the results were not encouraged. Therefore, the apparent rate constants  $k_a'$  and  $k_a''$  are considered to be composite quantities of the rate constant, the formation constants and the

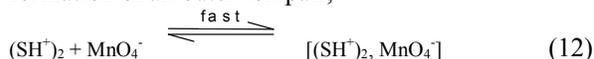
protonation constants. The calculated values of the apparent rate constants ( $k_a'$  and  $k_a''$ ) and the protonation constants ( $K$ ) were calculated by the method of least-squares. The protonation constants ( $K$ ) were found to be 1.01, 0.70 and 0.54  $\text{dm}^3 \text{mol}^{-1}$  at 20, 25 and 30 °C, respectively. The kinetic parameters of the apparent rate constants,  $k_a'$  and  $k_a''$  were calculated from the Arrhenius and Eyring equations using the least-squares method and are summarized in Table 4. Again, the thermodynamic parameters of the protonation constant ( $K$ ) were calculated by the well-known thermodynamic methods and are listed in Table 5. The negative value of  $\Delta H^\circ$  indicates that the protonation process is exothermic process. Again, the calculated values of the protonation constants were found to be in good agreement with that reported for other polysaccharides elsewhere.<sup>1-4</sup>

It was surprising to notice the independence of the rate constants on the ionic strength. This result may be explained by the fact that the ionic strengths used lie far outside the Debye-Huckel region, covering a range over which the activity coefficients of many electrolytes are known to be fairly independent on ionic strength.<sup>25</sup> Similar behavior was observed in some redox reactions involving permanganate ion as an oxidant in aqueous perchlorate solutions.<sup>3, 26, 27</sup> However the ionic strength observed here provides no information about the reactive species; some knowledge may be gained by examining the magnitude of the activation parameters. Again, the rate-law expression here provides no information on the nature of electron transfer, whether it is of inner- or outer-sphere nature, some information may be expected by examining the magnitude of both the rate constants and the activation parameters.<sup>23, 24, 28-30</sup>

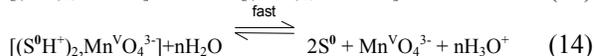
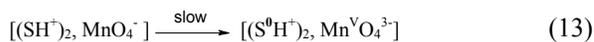
Unfortunately, no data are available on the formation constants ( $K_1$  and  $K_2$ ) at different temperatures in order to evaluate the rate constants of the principal elementary reaction. Therefore, the rate constants observed in the present redox reaction may be interpreted in terms of either inner- or outer-sphere mechanisms. The thermodynamic parameters observed for a series of common reactions may be considered as good evidence to support a certain reaction mechanism.<sup>31-35</sup> It has been suggested that  $\Delta S^\ddagger$  values tend to be more positive for outer-sphere types, whereas the reactions of inner-sphere-nature possess negative values of the activation entropies.<sup>31-35</sup> The magnitude of entropy of activation obtained in the present work may suggest the presence of both inner- and outer-sphere mechanisms.

In view of these arguments and our experimental observations, two reaction mechanisms for electron-transfer may be considered here. The first one corresponds to the transfer of electrons prior to the release of protons. This mechanism corresponds to the

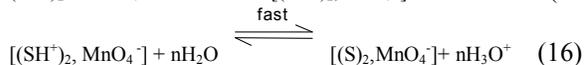
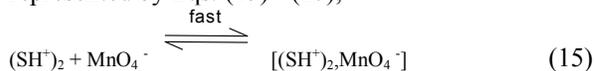
outer-sphere type which initially proceeds by the formation of an outer-ion pair,



followed by electron-transfer from the substrate to the oxidant, and then the release of protons as defined by Eqs. (13) and (14), respectively,



where S,  $\text{SH}^+$ ,  $\text{S}^0\text{H}^+$  and  $\text{S}^0$  denote the PVA substrate, its protonated form and the free-radical forms, respectively. The second mechanism corresponds to an inner sphere type which involves the formation of an outer ion-pair, followed by the release of protons prior to the transfer of electrons as represented by Eqs. (15) - (17),



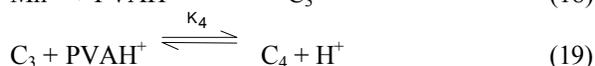
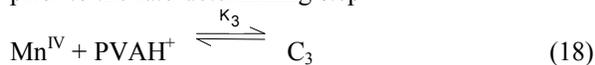
Although, the outer-sphere mechanism is the more probable one based on the thermodynamics grounds with respect to the magnitude of  $\Delta S^\ddagger$  value obtained, the inner-sphere mechanism cannot be excluded based on the Michaelis-Menten kinetics for formation of the intermediate complexes as well as the observed intervention of the free-radical mechanism.

Furthermore, Leffler and Grunwald<sup>36</sup> have pointed out that many reactions show an isokinetic linear relationship  $\Delta H^\ddagger = \alpha + \beta \Delta S^\ddagger$ . Therefore, the activation parameters of the second-order rate constants in the oxidation of PVA by acidic permanganate ion along with that obtained for the oxidation of other alcoholic macromolecules by the this oxidant are summarized in Table 6. As is shown in Figure 7, a plot of  $\Delta H^\ddagger$  against  $\Delta S^\ddagger$  is fairly linear with  $\alpha = 79 \text{ kJ mole}^{-1}$  and  $\beta = 318 \text{ K}$ . This linearity indicates that the kinetics of oxidation of these macromolecules may follow similar reaction mechanism, but may be different in some details with consistence in initials of these regimes. Also, the  $\beta$  value obtained is significant and reflects the high reactivity of these macromolecule. This result may be considered as indirect evidence to support a suggestion of a successive one-electron transfer mechanism in a sequence.

On the other hand, the complete disappearance of the induction period even at low concentrations of  $\text{Mn}^{2+}$  added as well as the decrease of the reaction rate on addition of  $\text{F}^-$  ion may suggest that  $\text{Mn}^{3+}$  and/or

Mn<sup>4+</sup> ions are the reactive species throughout the relatively final fast stage. It is difficult to decide whether Mn<sup>3+</sup> or Mn<sup>4+</sup> species are the sole reactive species throughout this autoacceleration period. This is attributed to the difficulty for examining the oxidation of poly (vinyl alcohol) by Mn<sup>3+</sup> or Mn<sup>4+</sup> ion oxidants since addition of these ions to PVK product leads to the occurrence of a precipitation which makes any spectrophotometric kinetic study very difficult. Such a precipitation results from sol-gel transformation phenomenon as the formation of coordination biopolymer cross-linked metal-PVK complexes. However, in similar redox reactions involving MnO<sub>4</sub><sup>-</sup> as an oxidant, the continuous increase in the reaction rate with increasing [Mn<sup>2+</sup>] added suggested that Mn<sup>4+</sup>, but not Mn<sup>3+</sup> is the more predominant reactive species.<sup>11,32</sup>

In view of the kinetic results obtained of the observed fractional first and second orders in hydrogen ion and PVA concentrations, respectively, throughout the final autoacceleration period, a similar reaction mechanism resembles to that followed in the initial induction period may be suggested. It involves the formation of the intermediate complexes C<sub>3</sub> and C<sub>4</sub> prior to the rate-determining step



followed by electron-transfer from the substrate to the oxidant in the rate-determining step.



Consequently, in a similar manner to that followed previously, the change of the rate constant with the change in the hydrogen ion and the substrate concentrations (suggesting that [Mn<sup>IV</sup>] ≅ [MnO<sub>4</sub><sup>-</sup>]<sub>0</sub>), can be expressed by the following relationship

$$\frac{1}{k_f} = \left( \frac{1 + K[H^+]}{k_b K^2 K_3 K_4 [H^+]} \right) \frac{1}{[PVA]_t^2} + *B' \quad (21)$$

Equation (21) requires a plot of 1/k<sub>f</sub> vs. 1/[PVA]<sub>t</sub><sup>2</sup> at constant [H<sup>+</sup>] to be linear as is observed experimentally (Figure 4). Again, at constant [PVA] plots of 1/k<sub>f</sub> vs. 1/[H<sup>+</sup>] gave good straight lines with positive intercepts on 1/k<sub>f</sub> axis. The small intercept observed in Figure 3 leads us to simplify Eq. (21) to

Eq. (22) which can be considered as a suitable rate-law expression for the autoacceleration period.

$$\frac{[PVA]_t^2}{k_f} = \frac{1}{k_f'} = \left( \frac{[H^+]}{k_b'} + \frac{1}{k_b''} \right) \quad (22)$$

$$*B' = \frac{[MnO_4^-] (1 + KK_4[PVA]_t)}{k_b KK_4 [PVA]_t^2}$$

where k<sub>f</sub>' is the third-order rate constant and k<sub>b</sub>' and k<sub>b</sub>'' are the apparent rate constants which equal k<sub>b</sub>K<sup>2</sup>K<sub>3</sub>K<sub>4</sub> and k<sub>b</sub>KK<sub>3</sub>K<sub>4</sub>, respectively.

According to Eq. (23), plots of 1/k<sub>f</sub>' against 1/[H<sup>+</sup>] gave a good straight lines (Fig. 4) from whose slopes and intercepts, the values of k<sub>b</sub>', k<sub>b</sub>'' and K can be evaluated. These values were calculated by the least-squares method and found to be 6.129 dm<sup>15</sup> mol<sup>-5</sup> s<sup>-1</sup>, 3.474 dm<sup>12</sup> mol<sup>-4</sup> s<sup>-1</sup> and 1.78 dm<sup>3</sup> mol<sup>-1</sup> for k<sub>b</sub>', k<sub>b</sub>'' and K, respectively, at [MnO<sub>4</sub><sup>-</sup>] = 5 × 10<sup>-4</sup>,

[PVA] = 4 × 10<sup>-2</sup>, and I = 2.0 mol dm<sup>-3</sup> at 25 °C. The calculated values of the protonated constants, K, for PVA through the auto-acceleration period were found to be in good agreement with that obtained in the induction period. This result may support the validity of the proposed mechanism.

In view of the cited experimental results and that reported previously for oxidation of PVA by permanganate ion oxidant in sulfuric acid<sup>10</sup> and in alkali<sup>9</sup>, it is evident that the nature of the solvent plays an important role on the reaction kinetics. The rate of oxidation was found to decrease in the order alkali > sulfuric acid > perchloric acid. This result may reflect the influence of the nature of the solvent on the reaction kinetics and mechanistics as well as on the activation parameters.

The tendency of the oxidation product of poly (vinyl alcohol), PVK, for chelation with polyvalent metal ions has been examined. It was found that PVK has a high affinity to chelate with silver (I), divalent-, trivalent-, tetravalent- and hexavalent-metal ions forming coordination biopolymer cross-linked metal-PVK complexes as shown in Scheme (III). The characteristics of the formed coordination biopolymer complexes are in progress in our laboratory.

**Table 1.** Dependence of the rate constants on [PVA] in the oxidation of poly (vinyl alcohol) by permanganate ion in aqueous perchlorate solutions. [MnO<sub>4</sub><sup>-</sup>] = 3.1 × 10<sup>-4</sup>, [H<sup>+</sup>] = 2.0 and I = 2.0 mol dm<sup>-3</sup> at 20 °C.

| 10 <sup>2</sup> [PVA]<br>mol dm <sup>-3</sup> | 10 <sup>4</sup> k <sub>s</sub><br>s <sup>-1</sup> | 10 <sup>2</sup> k <sub>s</sub> '<br>dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> | 10 <sup>3</sup> k <sub>f</sub><br>s <sup>-1</sup> | 10 <sup>2</sup> k <sub>f</sub> '<br>dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> |
|---|---|---|---|---|
| 3.0   | 3.79  | 1.26  | 1.05  | 3.35  |
| 4.0   | 5.67  | 1.42  | 1.65  | 4.13  |

Experimental error ±3%

**Table 2.** Dependence of the rate constants on  $[H^+]$  in the oxidation of poly (vinyl alcohol) by permanganate ion in aqueous perchlorate solutions.  $[MnO_4^-] = 3.1 \times 10^{-4}$ ,  $[PVA] = 4 \times 10^{-2}$  and  $I = 2.0 \text{ mol dm}^{-3}$  at  $20^\circ\text{C}$ .

| $[H^+]$<br>$\text{mol dm}^{-3}$ | $10^4 k_s$<br>$\text{s}^{-1}$ | $10^3 k_s'$<br>$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ | $10^3 k_f$<br>$\text{s}^{-1}$ | $10^2 k_f'$<br>$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ |
|---------------------------------|-------------------------------|--|-------------------------------|--|
| 1.0                             | 2.79                          | 6.98   | 1.21                          | 3.03   |
| 1.5                             | 4.99                          | 12.48  | 1.44                          | 3.60   |

Experimental error  $\pm 3\%$ **Table 3.** Effect of added salts on the autoacceleration rate constants in the oxidation of poly (vinyl alcohol) by permanganate ion in aqueous perchlorate solutions.  $[MnO_4^-] = 3.1 \times 10^{-4}$ ,  $[PVA] = 4 \times 10^{-2}$ ,  $[H^+] = 1.5$  and  $I = 2.0 \text{ dm}^3 \text{mol}^{-1}$  at  $20^\circ\text{C}$ .

| $10^2 [Mn^{2+}]$<br>$\text{mol dm}^{-3}$ | $10^3 k_p \text{ s}^{-1}$ | $10^3 [F^-]$<br>$\text{dm}^3 \text{mol}^{-1}$ | $10^4 k_f \text{ s}^{-1}$ |
|--|---------------------------|---|---------------------------|
| 0.0                                      | 0.49                      | 0.0   | 12.1                      |
| 2.5                                      | 1.51                      | 2.0   | 4.99                      |
| 5.0                                      | 2.47                      | 4.0   | 4.73                      |
| 7.5                                      | 3.13                      | 10.0  | 4.05                      |

Experimental error  $\pm 3\%$ **Table 4.** Activation parameters of  $k_a'$ ,  $k_a''$  and  $k_s'$  in the oxidation of poly (vinyl alcohol) by permanganate ion in aqueous perchlorate solutions.  $[MnO_4^-] = 3.1 \times 10^{-4}$ ,  $[PVA] = 4 \times 10^{-2}$ , and  $I = 2.0 \text{ mol dm}^{-3}$ .

| Constant | Parameter  |   |   |  |  |
|----------|--|---|---|--|--|
|          | $\Delta S^\ddagger$<br>$\text{J mol}^{-1} \text{K}^{-1}$ | $\Delta H^\ddagger$<br>$\text{kJ mol}^{-1}$ | $\Delta G^\ddagger$<br>$\text{kJ mol}^{-1}$ | $E_a^\ddagger$<br>$\text{kJ mol}^{-1}$ | $10^{-13} A \text{ mol}^{-1} \text{ s}^{-1}$ |
| $k_a'$   | + 0.99   | 74.53                                       | 74.24                                       | 76.93                                  | 18.1   |
| $k_a''$  | 147.56   | 117.42                                      | 73.45                                       | 119.82                                 | 0.07   |

**Table 5.** The thermodynamic parameters of the protonation constant ( $K$ ) in the oxidation of poly (vinyl alcohol) by permanganate ion in aqueous perchlorate solutions.  $[MnO_4^-] = 5 \times 10^{-4}$ ,  $[PVA] = 0.02$ , and  $I = 2.0 \text{ mol dm}^{-3}$ .

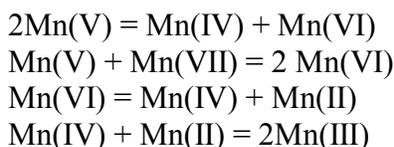
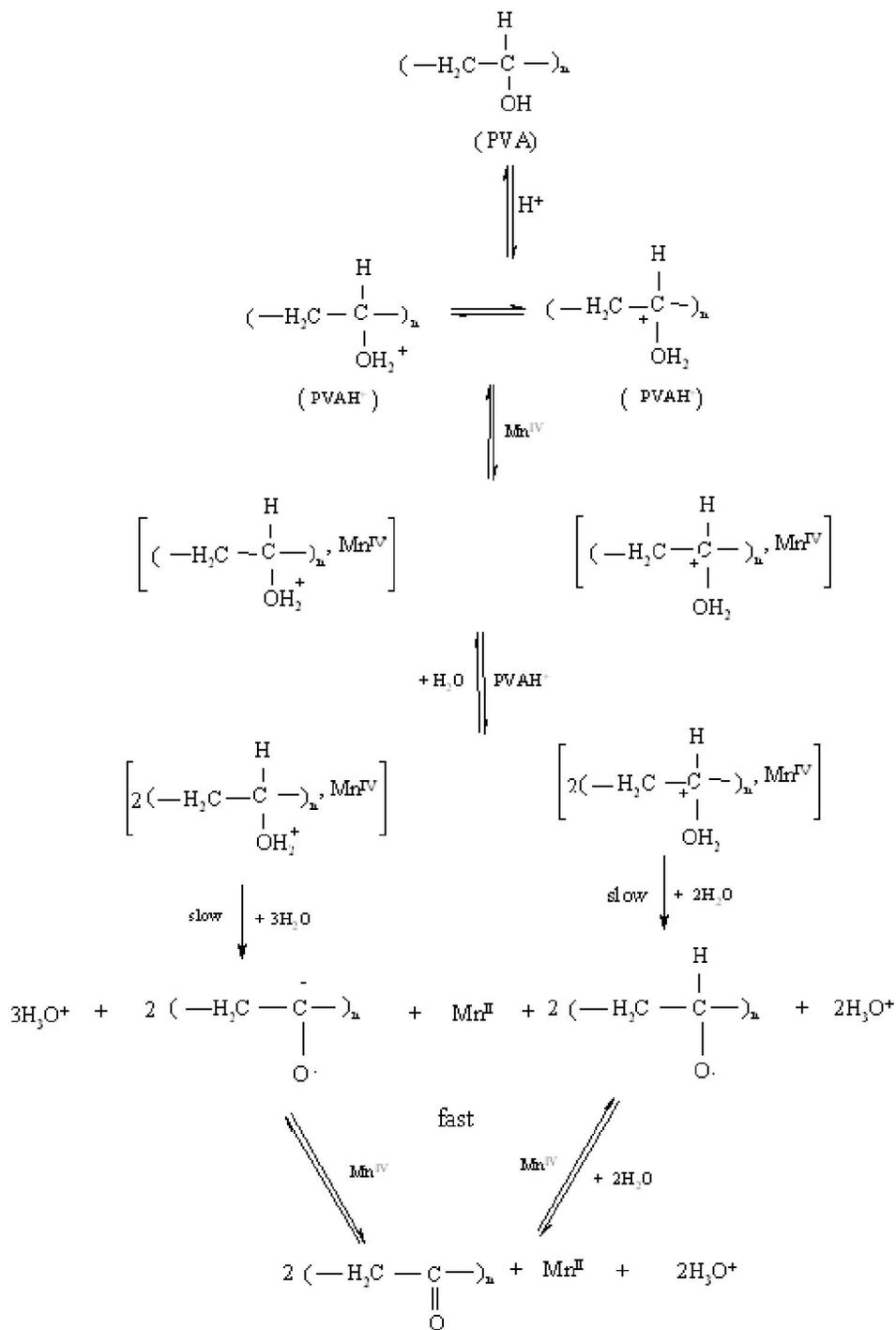
| $\Delta H^\theta$<br>$\text{kJ mol}^{-1}$ | $\Delta G_{298}^\theta$<br>$\text{kJ mol}^{-1}$ | $\Delta S_{298}^\theta$<br>$\text{J mol}^{-1} \text{K}^{-1}$ |
|---|---|--|
| -42.75                                    | +0.91   | -140.39  |

**Table 6.** The activation parameters of the second-order rate constants for the oxidation of various macromolecule substrates by acidic permanganate.

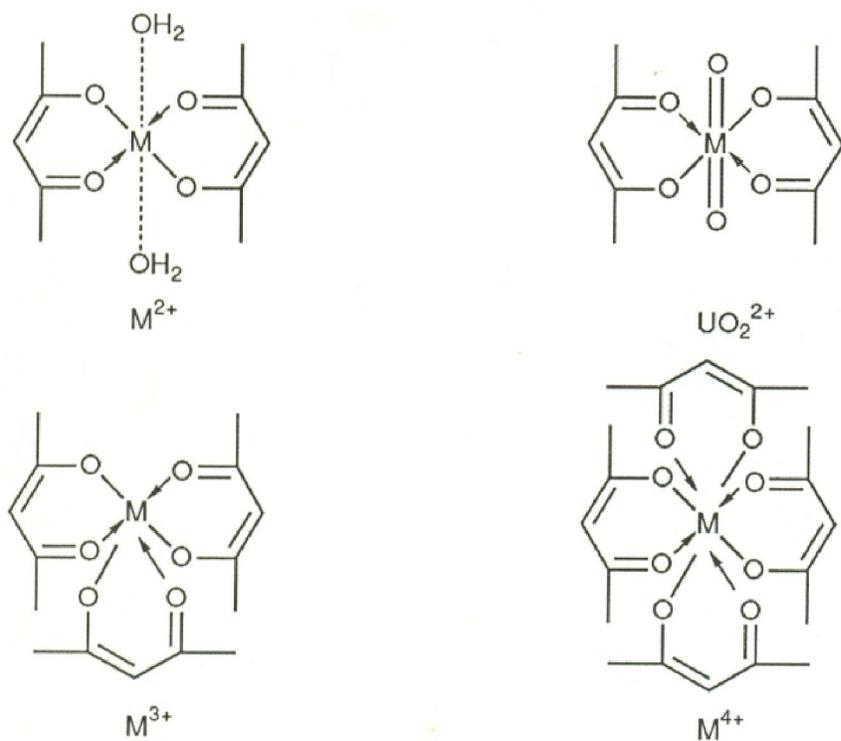
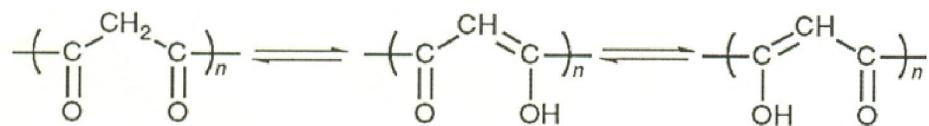
| Substrate | $\Delta H^\ddagger$<br>$\text{kJ mol}^{-1}$ | $\Delta S^\ddagger$<br>$\text{J mol}^{-1} \text{K}^{-1}$ | $\Delta G^\ddagger$<br>$\text{kJ mol}^{-1}$ | $E^\ddagger$<br>$\text{kJ mol}^{-1}$ | $A$<br>$\text{mol}^{-1} \text{s}^{-1}$ | Ref.      |
|-----------|---|--|---|--------------------------------------|--|-----------|
| PVA       | 92.07                                       | +28.44   | 83.58                                       | 94.6                                 | $0.52 \times 10^{12}$                  | This work |
| Pectin    | 92.98                                       | +39.43   | 79.26                                       | 95.88                                | $2.49 \times 10^5$                     | 1         |
| KCAR      | 29.63                                       | -161.30  | 77.70                                       | 32.70                                | $8.67 \times 10^4$                     | 2         |
| ICAR      | 49.57                                       | -79.27   | 78.74                                       | 52.30                                | $1.54 \times 10^8$                     | 2         |
| LCAR      | 57.62                                       | -47.49   | 79.82                                       | 60.13                                | $6.44 \times 10^3$                     | 2         |
| CMC       | 67.92                                       | -17.22   | 73.05                                       | 70.46                                | $2.19 \times 10^{12}$                  | 3         |
| MC        | 72.28                                       | -31.26   | 81.59                                       | 74.13                                | $3.08 \times 10^{11}$                  | 4         |

Calculated at  $[H^+] = 1.0 \text{ mol dm}^{-3}$ Experimental error  $\pm 4\%$

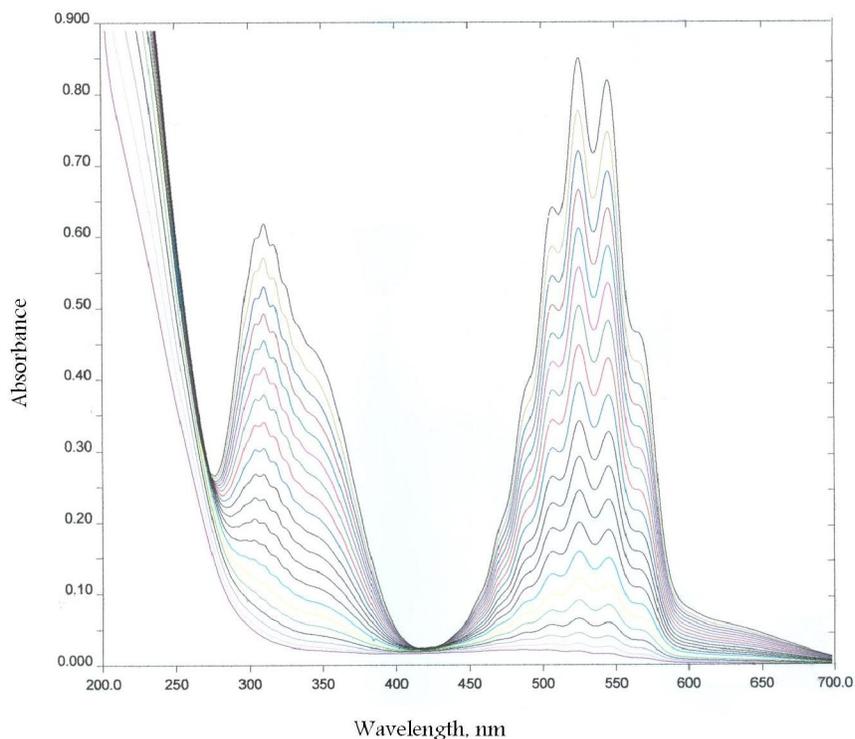




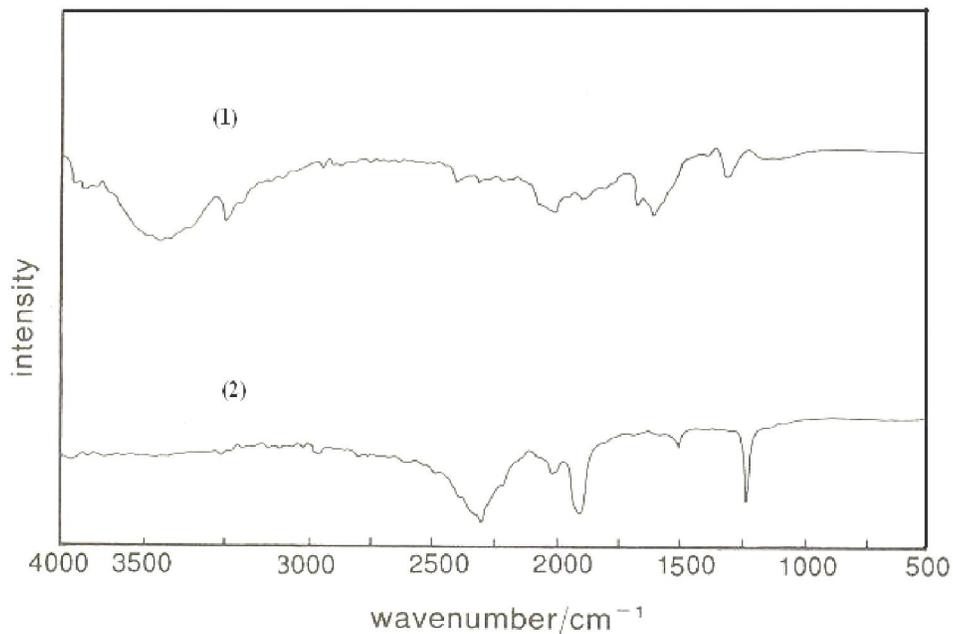
**Scheme (II).** Oxidation of PVA by permanganate ion (final autoacceleration period).



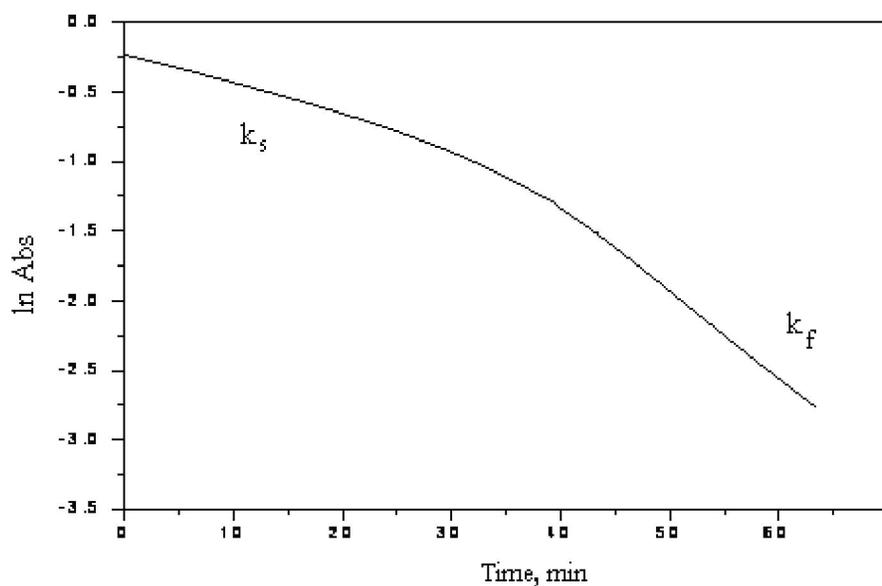
**Scheme (III).** Chelation of PVK oxidation product with polyvalent metal ions.



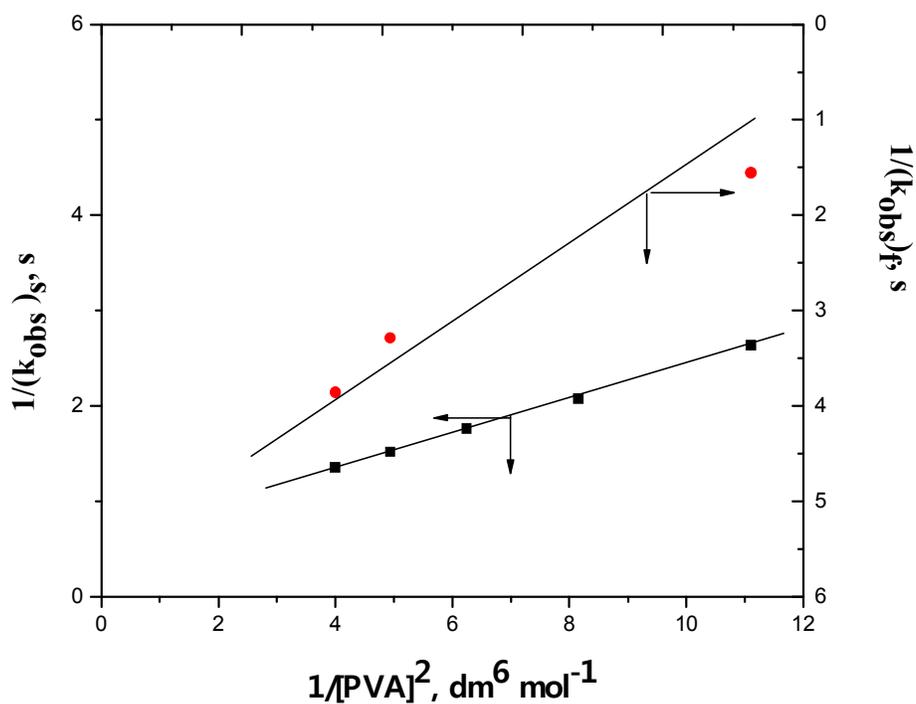
**Figure 1.** Spectral changes (200-700 nm) in the oxidation of poly (vinyl alcohol) by permanganate ion in aqueous perchlorate solutions.  $[\text{MnO}_4^-] = 4 \times 10^{-4}$ ,  $[\text{PVA}] = 4 \times 10^{-2}$ ,  $[\text{H}^+] = 2.0$  and  $I = 2.0 \text{ mol dm}^{-3}$  at  $25^\circ \text{C}$  (scanning time intervals = 2 min).



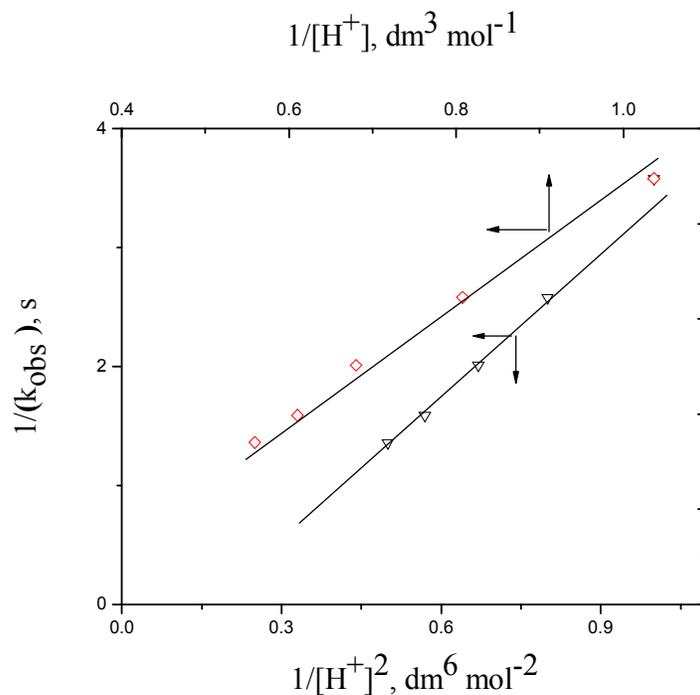
**Figure 2.** FTIR of poly(vinyl alcohol) and its oxidation product. (1): PVA; (2) PVAK.



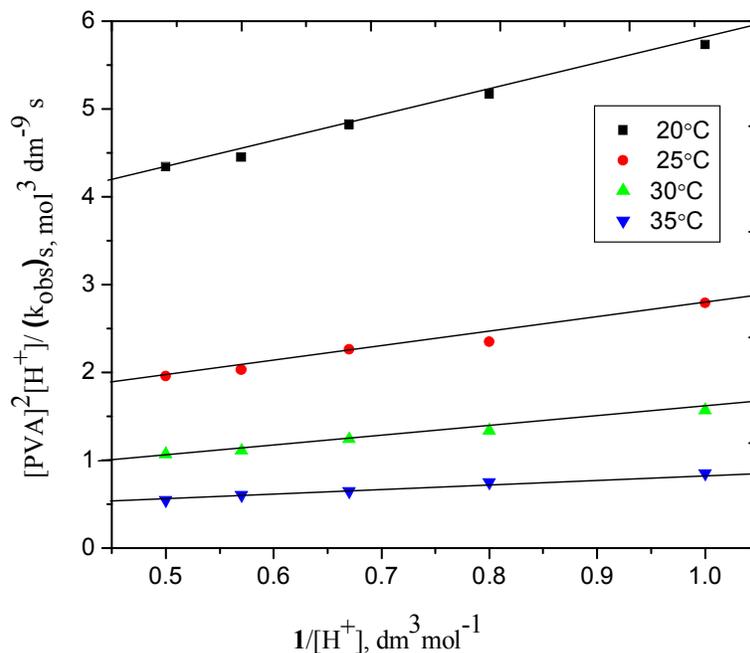
**Figure 3.** A plot of  $\ln \text{Abs}$  versus time in the oxidation of poly (vinyl alcohol) by permanganate ion in aqueous perchlorate solutions.  $[\text{MnO}_4^-] = 5 \times 10^{-4}$ ,  $[\text{PVA}] = 4 \times 10^{-2}$ ,  $[\text{H}^+] = 2.0$  and  $I = 2.0 \text{ mol dm}^{-3}$  at  $25^\circ \text{C}$ .



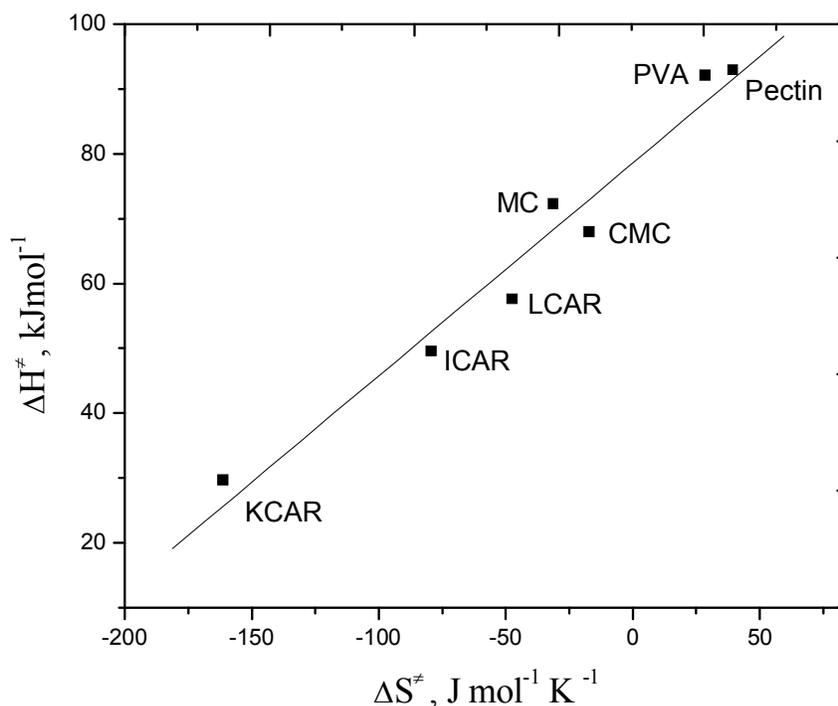
**Figure 4.** Reciprocal of Michaelis-Menten plots in the oxidation of poly (vinyl alcohol) by permanganate ion in aqueous perchlorate solutions.  $[\text{MnO}_4^-] = 3.1 \times 10^{-4}$ ,  $[\text{H}^+] = 2.0$  and  $I = 2.0 \text{ mol dm}^{-3}$  at  $20^\circ \text{C}$ .



**Figure 5.** Reciprocal plots for the  $[H^+]$  -dependence of the observed pseudo first-order rate constants in the oxidation of poly (vinyl alcohol) by permanganate ion in aqueous perchlorate solutions.  $[MnO_4^-] = 3.1 \times 10^{-4}$ ,  $[PVA] = 4 \times 10^{-2}$  and  $I = 2.0 \text{ mol dm}^{-3}$  at  $20^\circ\text{C}$ .



**Figure 6.** Plots of  $1/k_s$  versus  $1/[H^+]$  in the oxidation of poly (vinyl alcohol) by permanganate ion in aqueous perchlorate solutions.  $[MnO_4^-] = 3.1 \times 10^{-4}$ ,  $[PVA] = 4 \times 10^{-2}$  and  $I = 2.0 \text{ mol dm}^{-3}$  at : (■):  $20^\circ\text{C}$ ; (●):  $25^\circ\text{C}$ ; (▲):  $30^\circ\text{C}$ ; (▼):  $35^\circ\text{C}$ .



**Figure 7.** Isokinetic relationship plot in the oxidation of poly (vinyl alcohol) by permanganate ion in aqueous perchlorate solutions.

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11/12/2013