



## Base-catalyzed oxidation: Kinetics and mechanism of hexacyanoferrate (III) oxidation of methyl cellulose polysaccharide in alkaline solutions

R.M. Hassan<sup>a,\*</sup>, S.M. Ibrahim<sup>a</sup>, I.A. Zaafarany<sup>b</sup>, A. Fawzy<sup>a,b</sup>, H.D. Takagi<sup>c</sup>

<sup>a</sup> Chemistry Department, Faculty of Science, Assiut University, Assiut 71516, Egypt

<sup>b</sup> Chemistry Department, Faculty of Applied Sciences, Umm Al-Qura University, Makkah Al-Mukarramah 13401, Saudi Arabia

<sup>c</sup> Chemistry Department, School of Science, Research Center for Physical Inorganic Science, Nagoya 464-01, Japan

### ARTICLE INFO

#### Article history:

Received 21 December 2010

Received in revised form 7 May 2011

Accepted 9 May 2011

Available online 17 May 2011

#### Keywords:

Catalysis

Methyl cellulose

Polysaccharides

Natural polymers

Hexacyanoferrate (III)

Oxidation

Kinetics

Mechanisms

### ABSTRACT

The kinetics of oxidation of methyl cellulose polysaccharide as a natural polymer by alkaline potassium ferricyanide at a constant ionic strength of 1.0 mol dm<sup>-3</sup> have been studied, spectrophotometrically. The experimental results showed complex kinetics where the pseudo first-order plots were found to be straight lines up to 60% of reaction completion, and then deviated from linearity. A first-order dependence in Fe(CN)<sub>6</sub><sup>3-</sup> and fractional first-order kinetics with respect to the methyl cellulose concentration was observed. The oxidation reaction was found to be base catalyzed. Again, addition of Fe(CN)<sub>6</sub><sup>4-</sup> product to the reaction mixture leads to a remarkable retardation of the oxidation rates. A kinetic evidence for the formation of 1:1 intermediate complex was revealed. The activation parameters have been evaluated and a tentative reaction mechanism in good consistency with the kinetic results is discussed.

© 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

Kinetics of oxidation of methyl cellulose macromolecule as a natural polymer by alkaline permanganate have been reported elsewhere [1]. The oxidation process was found to proceed through non-free-radical mechanism of two distinct stages. The first stage was relatively fast involving the formation of green manganate (VI) and/or blue hypomanganate (V) intermediate complexes, followed by slow decomposition of these formed intermediates to give rise to the oxidation product in the second stage of reaction.

Although, hexacyanoferrate (III) ion is considered as a weak oxidant with a redox potential of 0.36 V for Fe(CN)<sub>6</sub><sup>3-</sup>/Fe(CN)<sub>6</sub><sup>4-</sup> couple [2], it has been widely used for oxidation of many organic [3–7] and inorganic [8–10] substrates. A survey on earlier literature indicates that no attention was paid to the oxidation of macromolecules by this oxidant. This may be attributed to the complexity of the reaction kinetics.

In view of the aforementioned aspects and our interesting in the oxidation of macromolecules by multi-equivalent oxidants such as permanganate [11,12] and chromate ion [13] as well as by one-equivalent oxidants such as cerium (IV) ion [14], the present work

has been undertaken with a view at shedding some light on the influence of the nature of both the oxidant and the media on the kinetics and mechanistics of the redox reactions as well as on the nature of oxidation products. Moreover, the results obtained may gain some information on the chemistry of these macromolecules in aqueous solutions.

### 2. Experimental

#### 2.1. Materials

All materials employed in the present work were of reagent grade. Doubly distilled conductivity water was used in all preparations. The temperature was controlled within ±0.05 °C.

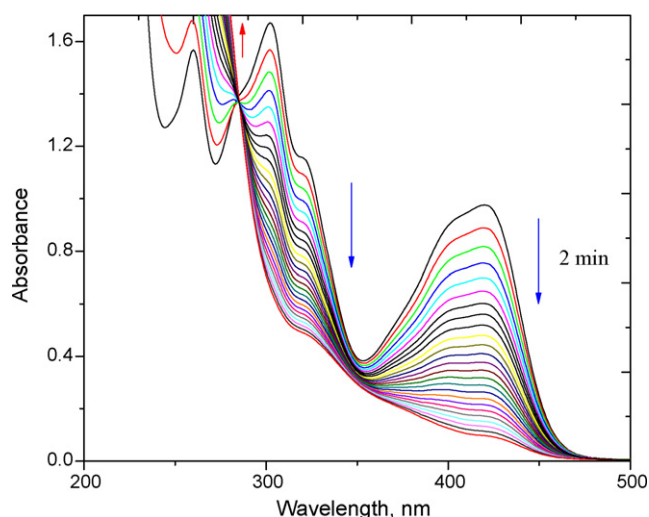
Methyl cellulose (MC) used in this paper is one of the (MP Biomedicals, LLC) and was used without further purification.

#### 2.2. Preparation of [MC] sols

A stock solution of MC was prepared by stepwise addition of the reagent powder to bidistilled water whilst rapidly stirring the solution to avoid the formation of lumps, which swell with difficulty. The preparation and standardization of K<sub>3</sub>Fe(CN)<sub>6</sub> (Mallinckrodt chemical works) were the same as described earlier [2,10]. All other

\* Corresponding author. Tel.: +2 127319979; fax: +20 882342708.

E-mail address: [rmhassan2002@yahoo.com](mailto:rmhassan2002@yahoo.com) (R.M. Hassan).



**Fig. 1.** Spectral changes (200–500 nm) during the formation of intermediate complexes in the oxidation of methyl cellulose by alkaline hexacyanoferrate (III).  $[\text{Fe}(\text{CN})_6^{3-}] = 7 \times 10^{-4}$ ,  $[\text{MC}] = 4 \times 10^{-2}$ ,  $[\text{OH}^-] = 0.3$  and  $I = 1.0 \text{ mol dm}^{-3}$  at  $40^\circ\text{C}$  (scanning time intervals = 2 min).

reagents were prepared by dissolving the requisite amount of the reagent in bidistilled water.

The ionic strength was maintained constant at  $1.0 \text{ mol dm}^{-3}$  by adding  $\text{NaClO}_4$  as a non-complexing agent.

### 2.3. Kinetic measurements

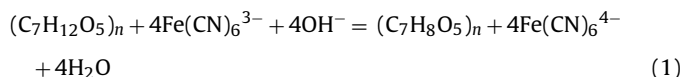
Preliminary experiments indicated that the oxidation reaction is of such a rate to be measured by a conventional spectrophotometer. To maintain pseudo first-order conditions, a large excess of  $[\text{MC}]$  was present over that of hexacyanoferrate (III) concentration in all kinetic measurements. The reaction was initiated by mixing the thermostated solutions of the reactants which containing the required concentrations of  $\text{NaOH}$  and  $\text{NaClO}_4$  into the reaction cell. The zero time was taken when half of  $\text{Fe}(\text{CN})_6^{3-}$  solution had been added to  $\text{MC}$  solution into the reaction cell. The progress of the reaction was followed by monitoring the decrease in absorbance of  $\text{Fe}(\text{CN})_6^{3-}$  at the wavelength of 420 nm, its absorption maximum (whereas the other constituents of the reaction mixture do not absorb significantly at this wavelength), as a function of time. The applicability of Beer's law for  $\text{Fe}(\text{CN})_6^{3-}$  at 420 nm has been verified giving  $\epsilon = (1040 \pm 20) \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  in good agreement with the values reported elsewhere [2,10]. The absorbance measurements were made in a thermostated cell compartment at the desired temperature within  $\pm 0.05^\circ\text{C}$  on a Shimadzu UV-2101/3101 PC automatic scanning double beam spectrophotometer fitted with a wavelength program controller using cells of a pathlength 1 cm. The spectral changes during the progress of the oxidation reaction are shown in Fig. 1.

## 3. Results

### 3.1. Stoichiometry and product analysis

The stoichiometry of the overall reaction of  $\text{MC}$  with slightly excess of  $\text{Fe}(\text{CN})_6^{3-}$  in  $0.3 \text{ mol dm}^{-3}$   $\text{NaOH}$  and  $1.0 \text{ mol dm}^{-3}$  ionic strength was determined at room temperature, spectrophotometrically. The unreacted  $\text{Fe}(\text{CN})_6^{3-}$  was estimated periodically until it reached a constant value. The results for various ratios of the equilibrated reactants indicated that 4.0 mol of  $\text{Fe}(\text{CN})_6^{3-}$  consumed 1.0 mol of  $\text{MC}$  ( $\pm 0.1$ ). This result indicates that the stoichiometry of

the oxidation reaction conforms to the following equation:



where  $\text{C}_7\text{H}_{12}\text{O}_5$  and  $\text{C}_7\text{H}_8\text{O}_5$  represent the methyl cellulose and its corresponding diketo derivative, respectively. The reaction product was identified by the IR spectra and elemental analysis as described elsewhere [10,15,16]. The recorded IR spectra of  $\text{MC}$  and its oxidation product showed a decay of the band at  $3450 \text{ cm}^{-1}$  and disappearance of the band at  $1700 \text{ cm}^{-1}$  of  $\text{MC}$  indicating the interconversion of secondary hydroxyl groups ( $\text{OH}$ ) to the keto ( $\text{C}=\text{O}$ ) groups.

### 3.2. Reaction time curves

Reaction time curves were found to be of complexity where plots of  $\ln(\text{absorbance})$  against time gave straight lines up to 60%, and then it deviates from linearity. This deviation may be attributed to the interference of  $\text{Fe}(\text{CN})_6^{4-}$  product.

The pseudo first-order rate constants,  $k_{\text{obs}}$ , were evaluated from the slopes of the linear portions of such plots. Again, some results were calculated from the tangents of the initial rates of reaction to avoid such complexity (from the remaining  $[\text{Fe}(\text{CN})_6^{3-}]$  vs time plots at initial stages). The results were found to be reproducible to each other within experimental errors of about  $\pm 5\%$ . Therefore,  $k_{\text{obs}}$  values were used to interpret the results throughout the present study. These values were calculated by the method of least-squares.

### 3.3. Dependence of reaction rate on $[\text{Fe}(\text{CN})_6^{3-}]$ and $[\text{MC}]$

The effect of hexacyanoferrate (III) on the reaction rates was examined by keeping all other concentrations fixed. It was found that the change in  $[\text{Fe}(\text{CN})_6^{3-}]$  ( $6\text{--}11 \times 10^{-4} \text{ mol dm}^{-3}$ ), at  $[\text{MC}] = 4 \times 10^{-2}$ ,  $[\text{OH}^-] = 0.3$ ,  $I = 1.0 \text{ mol dm}^{-3}$  at  $40^\circ\text{C}$  has no effect on the oxidation rate. This independency confirms that the reaction is first-order in hexacyanoferrate (III) concentration. Again, the linearity obtained from plots of the initial rates vs  $[\text{Fe}(\text{CN})_6^{3-}]$  may also indicate that the reaction is first-order in  $[\text{Fe}(\text{CN})_6^{3-}]$ .

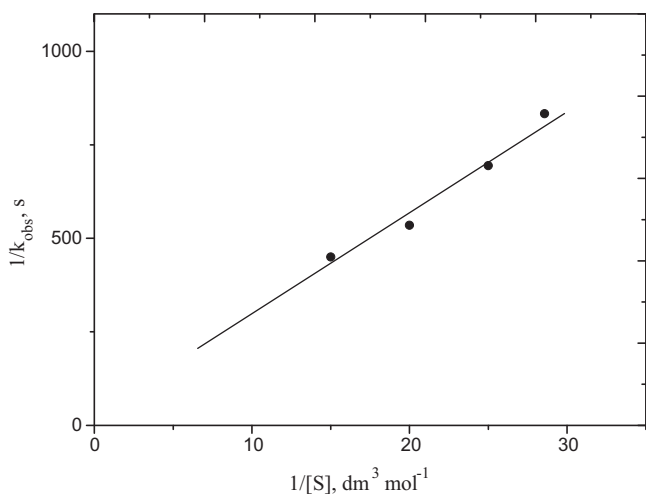
The dependence of  $k_{\text{obs}}$  on  $[\text{MC}]$  was deduced from the measurement of the observed first-order rate constants at various  $[\text{MC}]_0$  and fixed of all other reagents concentration. A fractional first-order dependence in  $[\text{MC}]_0$  was observed ( $\log k_{\text{obs}} - \log [\text{MC}]_0$  plots). Again the double reciprocal plots of  $k_{\text{obs}} - [\text{MC}]$  were found to be linear with positive intercepts on  $1/k_{\text{obs}}$  axis. This behavior seems to obey Michaelis–Menten kinetics for the formation of 1:1 intermediate complex. A typical plot is shown in Fig. 2.

### 3.4. Dependence of reaction rate on $[\text{OH}^-]$

In order to clarify the influence of  $[\text{OH}^-]$  on the rate of reaction and to elucidate a reaction mechanism, kinetic measurements were conducted at various  $[\text{OH}^-]$  keeping all other reagents concentration fixed. The values of  $k_{\text{obs}}$  were found to increase with increasing  $[\text{OH}^-]$  up to  $0.6 \text{ mol dm}^{-3}$  after that a turbidity in the tested solution had appeared which made any spectrophotometric measurements very difficult. Therefore, all the experimental measurements were performed at  $[\text{OH}^-] < 0.6 \text{ mol dm}^{-3}$ . A fractional first-order dependence with respect to  $[\text{OH}^-]$  ( $\log k_{\text{obs}} - \log [\text{OH}^-]$  plots) was observed.

### 3.5. Dependence of reaction rate on ionic strength

To shed some light on the reactive species in the rate determining step, kinetic runs were performed at constant  $[\text{OH}^-] = 0.3 \text{ mol dm}^{-3}$  as  $\text{NaClO}_4$  concentration was increased

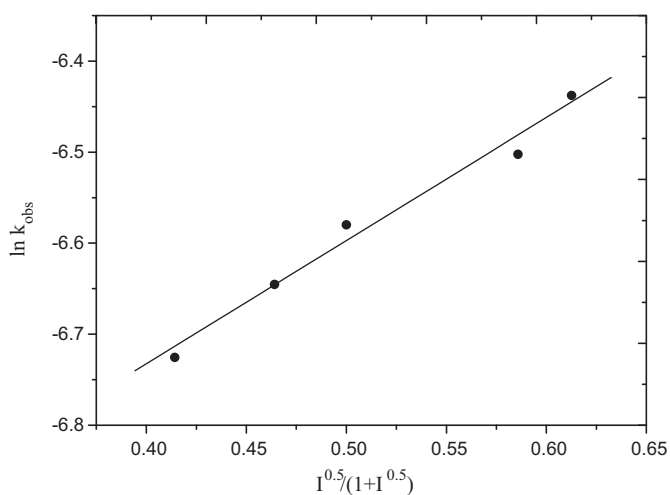


**Fig. 2.** A reciprocal plot of Michaelis–Menten kinetics in the oxidation of methyl cellulose by alkaline hexacyanoferrate (III).  $[\text{Fe}(\text{CN})_6^{3-}] = 7 \times 10^{-4}$ ,  $[\text{OH}^-] = 0.3$  and  $I = 1.0 \text{ mol dm}^{-3}$  at  $40^\circ\text{C}$  at various  $[\text{MC}]$ .

to  $2.5 \text{ mol dm}^{-3}$ . The values of  $k_{\text{obs}}$  were found to increase with increasing the ionic strength. A plot of  $\log k_{\text{obs}}$  vs  $I^{0.5}/(1+I^{0.5})$  according to extended Brönsted–Debye–Hückel equation was found to be linear with positive slope as shown in Fig. 3. However the present measurements lie far outside the Brönsted–Debye–Hückel region covering a range over which the activity coefficients of many electrolytes are known to be fairly dependent on ionic strength. The ionic strength dependence of the rate constants is qualitatively as expected when considering the charges involved [17].

### 3.6. Dependence of reaction rate on $[\text{Fe}(\text{CN})_6^{4-}]$

The effect of the initially added  $\text{Fe}(\text{CN})_6^{4-}$  product on the rate of reaction was also examined in the range  $(0.7\text{--}2) \times 10^{-3} \text{ mol dm}^{-3}$  at constant of all other reagents concentration at  $40^\circ\text{C}$ . The added  $\text{Fe}(\text{CN})_6^{4-}$  was found to decrease the reaction rates, i.e. it retarded the oxidation process (Table 1). A similar behavior has been observed in some redox reactions involving the formation of similar intermediates [18–20].



**Fig. 3.** Ionic strength-dependence of the rate constants in the oxidation of methyl cellulose by alkaline hexacyanoferrate (III).  $[\text{Fe}(\text{CN})_6^{3-}] = 7 \times 10^{-4}$ ,  $[\text{MC}] = 4 \times 10^{-2}$  and  $[\text{OH}^-] = 0.3 \text{ mol dm}^{-3}$  at  $40^\circ\text{C}$ .

**Table 1**

Influence of  $[\text{Fe}(\text{CN})_6^{4-}]$  on the observed first-order rate constant in the oxidation of methyl cellulose by alkaline hexacyanoferrate (III).  $[\text{Fe}(\text{CN})_6^{3-}] = 7 \times 10^{-4}$ ,  $[\text{MC}] = 4 \times 10^{-2}$ ,  $[\text{OH}^-] = 0.3$  and  $I = 1.0 \text{ mol dm}^{-3}$  at  $40^\circ\text{C}$ .

$10^4 [\text{Fe}(\text{CN})_6^{4-}]$ , $\text{mol dm}^{-3}$	0.0	7.0	9.0	11	12
$10^3 k_{\text{obs}}$ , $\text{s}^{-1}$	1.43	1.37	1.26	1.21	1.16

### 3.7. Dependence of reaction rate on temperature

In order to evaluate the kinetic parameters, kinetics runs were performed at various temperatures. The experimental results were found to fit the Arrhenius and Eyring equations. The kinetic parameters were evaluated from the slopes and intercepts of such plots using the least squares method.

### 3.8. Polymerization test

Since the reaction seems to be of a non-complementary type, the intervention of free-radicals during the course of reaction was examined. This was tested by adding 10% (v/v) acrylonitrile to the partially oxidized reaction mixture. After a lapse of 30 min mixing (on warming) a copious precipitate was observed. Black experiments from which either MC or  $[\text{Fe}(\text{CN})_6^{3-}]$  were excluded gave no detectable polymerization. This result indicates that the oxidation reaction of the present work proceeds via the intervention of free-radical mechanism as contrary to that observed for oxidation of MC by alkaline permanganate [10].

## 4. Discussion

The experimental observations indicated that the reaction kinetics of oxidation of methyl cellulose by alkaline hexacyanoferrate was of complexity. The deviation of  $\log(\text{absorbance}) - t$  plots from linearity after 60% linearity may attributed to the intervention of one of the oxidation products,  $\text{Fe}(\text{CN})_6^{4-}$ , through the formation of an intermediate complex between the oxidant and the substrate [21] or to a secondary salt effect [22].

The retardation effect observed in the rate constants on adding  $\text{Fe}(\text{CN})_6^{4-}$  to the reaction mixture (Table 1) may support this suggestion [2,8,12,23]. Again obeying the  $[\text{MC}]$  dependence of the rate constants to the Michaelis–Menten kinetics suggests the formation of an intermediate complex. The formation of such intermediate is not only confirmed by the reciprocal plots of Michaelis–Menten kinetics but also by the increase in the initial absorbance of the reaction mixture observed on mixing in particularly at lower temperature and reactant concentration. Again, the appearance of an isobestic point in the UV range at 284 nm may suggest an equilibrium state between the oxidant and the intermediates which confirm our proposal mechanism. Furthermore, the positive slope obtained with  $\log k_{\text{obs}} - I^{0.5}/(1+I^{0.5})$  plot refers to the fact that the oxidation process occurs between two similar charge ions.

In view of these interpretations and the experimental observations, the most likely reaction mechanism which may be suggested

**Table 2**

The apparent rate constants ( $k'$  and  $k''$ ) and the deprotonation constants  $K_1$  in the oxidation of methyl cellulose by alkaline hexacyanoferrate (III) at various temperatures.  $[\text{Fe}(\text{CN})_6^{3-}] = 7 \times 10^{-4}$ ,  $[\text{MC}] = 4 \times 10^{-2}$  and  $I = 1.0 \text{ mol dm}^{-3}$ .

Constants	Temp, $^\circ\text{C}$	
	35 $^\circ\text{C}$	45 $^\circ\text{C}$
$k'$ , $\text{dm}^9 \text{ mol}^{-3} \text{ s}^{-1}$	0.16	0.23
$10^2 k''$ , $\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$	2.90	7.10
$K_1$ , $\text{dm}^3 \text{ mol}^{-1}$	5.56	3.16

Experimental errors  $\pm 3\%$ .

**Table 3**  
The kinetic parameters of the second-order rate constant ( $k_n$ ), apparent rate constant ( $k'$  and  $k''$ ) and the deprotonation constant ( $K_1$ ) in the oxidation of methyl cellulose by alkaline hexacyanoferrate (III).

Constants	Parameters				
	$\Delta H^\ddagger$ , kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ , J mol <sup>-1</sup> K <sup>-1</sup>	$\Delta G^\ddagger_{298}$ , kJ mol <sup>-1</sup>	$E_a^\ddagger$ , kJ mol <sup>-1</sup>	A, mol <sup>-1</sup> s <sup>-1</sup>
$k$	25.12	-178.80	78.40	27.76	$8.24 \times 10^3$
$k''$	70.45	-46.16	84.21	73.04	$6.85 \times 10^4$
$k_n^a$	62.55	-72.93	84.28	65.23	$2.81 \times 10^7$

Constants	Parameters		
	$\Delta H^\ddagger$ , kJ mol <sup>-1</sup>	$\Delta S^\ddagger_{313}$ , J mol <sup>-1</sup> K <sup>-1</sup>	$\Delta G^\ddagger_{313}$ , kJ mol <sup>-1</sup>
$K_1$	-44.70	-27.83	-35.99

Experimental errors  $\pm 4\%$ .

<sup>a</sup> Second-order rate constant measured at  $[\text{OH}^-] = 0.3 \text{ mol dm}^{-3}$ .

involves a fast deprotonation of the substrate by the alkali to form the more reactive alkoxide:



followed by the formation of an intermediate complex ( $C_1$ ) between the oxidant (Ox) and the formed alkoxide ( $S^-$ ):



Then, the formed complex ( $C_1$ ) is slowly decomposed in the rate determining step to give rise to the initial oxidation products as the substrate radical (S) and  $\text{Fe}(\text{CN})_6^{4-}$  reductant (Red).



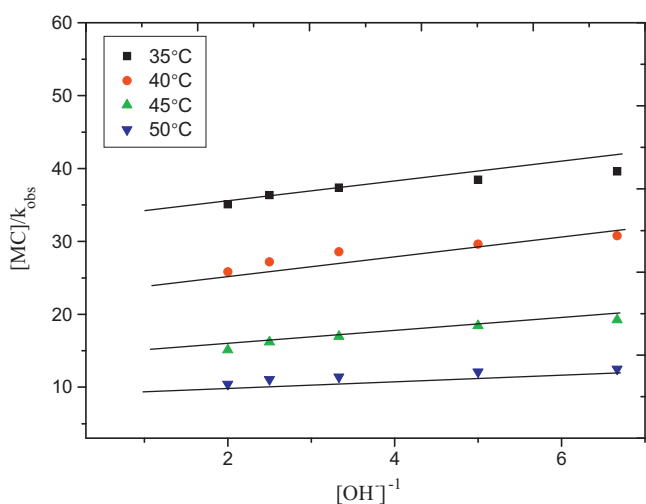
The change of the rate constant with the change in the hydroxide ion and substrate concentrations can be expressed by the following rate-law equation:

$$\text{Rate} = -\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{kK_1K_2[\text{OH}^-][S]_T[\text{Ox}]}{1 + K_1[\text{OH}^-] + K_1K_2[\text{OH}^-][\text{Ox}]} \quad (5)$$

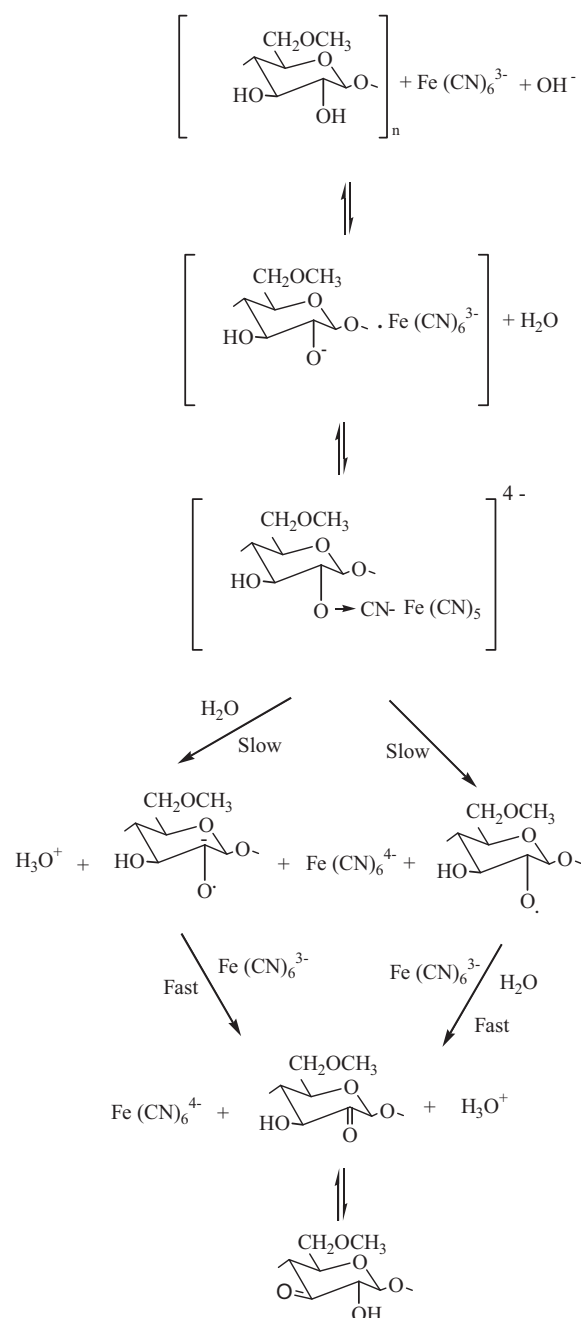
where  $[S]_T$  denotes the analytical concentration of the substrate. When the substrate is present in a large excess over that of the  $[\text{Ox}]$  (pseudo first order conditions) and rearrangement, Eq. (5) can be rewritten in the form:

$$\frac{1}{k_{\text{obs}}} = \left( \frac{1}{kK_1K_2[\text{OH}^-]} + \frac{1}{kK_2} \right) \frac{1}{[S]} + K', \quad (6)$$

where  $K' = [\text{Ox}]/k[S]$ .



**Fig. 4.** Plots of  $[S]/k_{\text{obs}}$  against  $[\text{OH}^-]^{-1}$  in the oxidation of methyl cellulose by alkaline hexacyanoferrate (III).  $[\text{Fe}(\text{CN})_6^{3-}] = 7 \times 10^{-4}$ ,  $[\text{MC}] = 4 \times 10^{-2}$  and  $I = 1.0 \text{ mol dm}^{-3}$  at various of both temperatures and  $[\text{OH}^-]$ .



**Scheme 1.** Mechanism of oxidation of methyl cellulose by alkaline hexacyanoferrate (III).

According to Eq. (6), at constant  $[\text{OH}^-]$  plots of  $1/k_{\text{obs}}$  against  $1/[\text{S}]$  should be linear with positive intercept or  $1/k_{\text{obs}}$  axis as was experimentally observed (Fig. 2). Again, plots of  $1/k_{\text{obs}}$  against  $1/[\text{OH}^-]$  at constant  $[\text{S}]$  should be linear with positive intercepts on  $1/k_{\text{obs}}$  axis. The experimental results satisfied this requirement. The small intercept observed in Fig. 2 may lead us to simplify Eqs. (6) to (7):

$$\frac{[\text{S}]_T}{k_{\text{obs}}} = \frac{1}{k_n} = \frac{[\text{OH}^-]}{kK_1K_2} + \frac{1}{kK_2} \quad (7)$$

According to Eq. (7), plots of  $[\text{S}^-]/k_{\text{obs}}$  against  $[\text{OH}^-]$  were found to be linear with positive intercepts on  $[\text{S}]/k_{\text{obs}}$  from whose slopes and intercepts, the apparent rate constants ( $kK_1K_2$  and  $kK_2$ ) and the deprotonation constant  $K_1$  can be evaluated. These values were calculated by the method of least-squares and are summarized in Table 2.

An alternative reaction mechanism may also be suggested. It involves a fast complexation between the reactants prior to rate determining step:



followed by releasing the water molecules to give a more reactive intermediate ( $\text{C}_2$ ) prior to the electron transfer process:



Then, the formed complex ( $\text{C}_2$ ) is slowly decomposed in the rate determining step to give the substrate radical and reductant as the initial oxidation products:



In a similar manner to that followed in the former mechanism, the change of the rate constant with the change in the  $[\text{OH}^-]$  and substrate concentrations leads to the following relationship:

$$\frac{1}{k_{\text{obs}}} = \left( \frac{[\text{OH}^-]^{-1}}{kK_3K_4} + \frac{[\text{Ox}]}{kK_4} \right) \frac{1}{[\text{S}]_T} + K' \quad (11)$$

Plots of either  $1/k_{\text{obs}}$  against  $1/[\text{S}]$  at constant alkali concentration or  $1/k_{\text{obs}}$  against  $1/[\text{OH}^-]$  at constant substrate were found to be linear with positive intercepts on  $1/k_{\text{obs}}$  axes as required by Eq. (11). The small intercept observed in Fig. 2, may also lead us to simplify Eqs. (11) to (12):

$$\frac{[\text{S}]_T}{k_{\text{obs}}} = \frac{1}{k_n} = \frac{[\text{OH}^-]}{k'} + \frac{[\text{Ox}]}{k''} \quad (12)$$

where  $k'$  and  $k''$  are the apparent rate constants and equal to  $kK_3K_4$  and  $kK_4$ , respectively. Plots of  $[\text{S}]/k_{\text{obs}}$  against  $1/[\text{OH}^-]$  gave good straight lines with positive intercepts (Fig. 4) from whose slopes and intercepts the apparent rate constants ( $k'$  and  $k''$ ) and the formation constant ( $K_3$ ) can be evaluated. The values of the formation constants obtained were found to be very small ( $\sim 10^{-3} \text{ dm}^6 \text{ mol}^{-2} \text{ dm}^6$ ) and, hence, cannot be considered as the formation constants for this redox reaction. Therefore, this later mechanism is excluded and, hence, the former mechanism is considered as the sole mechanism for the cited reaction.

Unfortunately, the values of the rate constant of the elementary reaction ( $k$ ) could not be calculated because of the non-availability of the formation constants ( $K_2$ ). Therefore, the apparent rate constants are considered to be composite quantities of the rate constants, deprotonation constants and the formation constants, respectively.

The activation and thermodynamic parameters of the apparent rate constants ( $k'$  and  $k''$ ) and the deprotonation constant ( $K_1$ ),

respectively, were calculated from the dependence of those constants on temperature using Arrhenius and Eyring equations by the least squares method. These values are summarized in Table 3.

It is well known that redox reactions involving  $\text{Fe}(\text{CN})_6^{3-}$  as an inert oxidant are proceeding by a variety of reaction mechanistics. Some of these reactions proceed by either inner or outer sphere mechanisms for the electron transfer processes. Other reactions occur by both outer- and inner-sphere mechanisms or free-radical mechanism. However, the present rate laws provide no information on whether electron transfer of inner- or outer sphere nature, some information may be expected by examining the magnitude of the rate constants of the elementary reactions.

Again, it has been reported previously [24–27] that the entropy of activation tends to be more negative for reactions of inner-sphere nature, whereas the reactions of positive  $\Delta S^\ddagger$  values proceed via outer-sphere mechanism. In view of the large negative entropy of activation obtained (Table 3), the inner-sphere mechanism is the more probable and acceptable one.

Moreover, the formation of intermediate complex in which one cyanide ion from the inert  $\text{Fe}(\text{CN})_6^{3-}$  may act as a bridging ligand suggests that one-electron transfer of inner-sphere nature is the more plausible mechanism for oxidation of methyl cellulose by alkaline hexacyanoferrate (III). This suggested mechanism can be illustrated by Scheme 1. The decrease of the magnitude of deprotonation constants ( $K_1$ ) with temperature indicates that the deprotonation process is an exothermic process. The large positive value of  $\Delta G^\ddagger$  is indicative to the enhanced formation of the intermediate with increasing temperature as well as to the non-spontaneity of the complex formation in the rate determining step as represented by the proposed mechanism. Again, the lower activation energy obtained indicated the lower energy barrier required for the formation of the activated complex in the transition state.

Although the behavior of the ionic strength dependence of the rate constant (Fig. 3) is as expected for the charges involved. The ionic pairing between  $\text{K}^+$  and  $\text{Fe}(\text{CN})_6^{3-}$  [2,28,29] may be suggested to affect the magnitude of the slope obtained from the ionic strength–rate constants plot.

Addition of  $[\text{K}^+]$  ions was found to has no influence on the rate constants and, hence, the possibility of existing an ion-pairing mechanism was excluded.

## References

- [1] R.M. El-Khatib, Carbohydr. Polym. 47 (2002) 377–385; A.M. Shaker, R.M. El-Khatib, H.S. Mahran, J. Appl. Polym. Sci. 106 (2007) 2668–2674.
- [2] T.P. Jose, S.T. Nandibewoor, S.M. Tuwar, J. Solution Chem. 35 (2006) 51–61; G. Milazzo, S. Carroll, Tables of Standard Electrode Potential, Wiley, New York, 1978.
- [3] P.S. Radhakrishnamurti, B. Sahu, Indian J. Chem. 16 (1978) 95–98.
- [4] S.K. Upadhyay, M.C. Agrawal, Indian J. Chem. 16 (1978) 39–42.
- [5] H.S. Singh, S.P. Singh, S.M. Singh, R.K. Singh, A.K. Sisodia, J. Phys. Chem. 79 (1975) 1920–1924.
- [6] W.A. Skinner, P. Alaupovic, Science 140 (1963) 803–805.
- [7] B. Singh, S. Sakena, S.P. Singh, J. Indian Chem. Soc. LX (1983) 795–797.
- [8] S.K. Upadhyay, M.C. Agrawal, J. Indian Chem. Soc. LVIII (1981) 871–873.
- [9] B.T. Reagor, D.H. Huchital, Inorg. Chem. 21 (1982) 703–705.
- [10] R.M. Hassan, T. Kojima, H. Fukutomi, Bull. Res. Lab. Nucl. React. Jpn. 5 (1980) 41–47.
- [11] R.M. Hassan, J. Polym. Sci. A 31 (1993) 51–59; R.M. Hassan, J. Polym. Sci. A 31 (1993) 1147–1151; R.M. Hassan, Polym. Int. 30 (1993) 5–9; R.M. Hassan, S.A. El-Gaiar, A.M. El-Summan, Polym. Int. 32 (1993) 39–42.
- [12] R.M. Hassan, A. Fawzy, G.A. Ahmed, I.A. Zaafarany, B.S. Asghar, K.S. Khairou, J. Mol. Catal. A 309 (2009) 95–102; R.M. Hassan, D.A. Abdel-Kader, S.M. Ahmed, A. Fawzy, I.A. Zaafarany, B.H. Asghar, H.D. Takagi, Catal. Commun. 11 (2009) 184–190; G.A. Ahmed, K.S. Khairou, R.M. Hassan, Chem. Res. 182 (2003) 2003–2008.
- [13] I.A. Zaafarany, K.S. Khairou, R.M. Hassan, J. Mol. Catal. 302 (2009) 112–118; R.M. Hassan, S.M. Ahmed, A. Fawzy, D.A. Abdel-Kader, Y. Ikeda, H.D. Takagi, Catal. Commun. 11 (2010) 611–615; M.I. Abdel-Hamid, G.A. Ahmed, R.M. Hassan, Eur. Polym. J. 37 (2001) 2201–2206.



- [14] R.M. Hassan, A. Alaraifi, A. Fawzy, I.A. Zaafarany, K.S. Khairou, Y. Ikeda, H.D. Takagi, *J. Mol. Catal. A* 332 (2010) 138–144.
- [15] M.A. Malik, M. Ilyas, Z. Khan, *Indian J. Chem.* 48A (2009) 189–193.
- [16] J.K. Beattie, *Pure Appl. Chem.* 62 (1990) 1145–1146.
- [17] K. Laidler, *Chemical Kinetics*, Mc Graw-Hill, New York, 1965.
- [18] M.A. Malik, S.A. Al-Thabaiti, Z. Khan, *Colloids Surf. A: Physicochem. Eng. Aspect.* 337 (2009) 9–14.
- [19] F. Freeman, J.C. Kappos, *J. Org. Chem.* 54 (1989) 2730–2734.
- [20] R.M. Naik, A. Srivastava, A.K. Verma, *Turk. J. Chem* 32 (2008) 495–503.
- [21] S.K. Upadhyay, M.S. Agrawal, *Indian J. Chem.* 15A (1977) 709–715.
- [22] J.H. Swinehart, *J. Inorg. Nucl. Chem.* 29 (1967) 2313–2320;  
S.A. Farokhi, S.T. Nandibewoor, *Tetrahedron* 59 (2003) 7595–7602.
- [23] M.A. Malik, F.M. Al-Nowaiser, N. Ahmed, Z. Khan, *Int. J. Chem. Kinet.* 42 (2010) 704–712.
- [24] K.W. Hicks, D.L. Toppen, R.G. Linck, *Inorg. Chem.* 11 (1972) 310–315;  
F.M. Moore, K.W. Hicks, *Inorg. Chem.* 14 (1975) 413–416;  
K.W. Hicks, G.A. Chappelle, *Inorg. Chem.* 19 (1980) 1623–1631.
- [25] N. Sutin, *Acc. Chem. Res.* 1 (1968) 225–231.
- [26] F. Freeman, *J. Am. Chem. Soc.* 103 (1981) 1154–1158.
- [27] R.M. Hassan, *J. Coord. Chem.* 27 (1992) 255–266.
- [28] W.A. Eaton, P. George, G.I.H. Hanania, *J. Phys. Chem.* 71 (1967) 2016–2021.
- [29] H.S. Singh, V.P. Singh, J.M. Singh, P.N. Srivastava, *Inorg. Chim. Acta* 43 (1977) 24–33.