



Acid-catalyzed oxidation of carboxymethyl cellulose. Kinetics and mechanism of permanganate oxidation of carboxymethyl cellulose in acid perchlorate solutions

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ABSTRACT

The kinetics of oxidation of carboxymethyl cellulose (CMC) by permanganate ion in aqueous perchloric acid at a constant ionic strength of 2.0 mol dm^{-3} has been investigated, spectrophotometrically. The reaction time curves of the pseudo first-order plots were of inverted S-shape throughout the entire course of reaction. The initial rates were found to be relatively slow in the early stages, followed by an increase in the oxidation rates over longer time periods. The experimental results indicated first-order kinetics in permanganate and fractional second-order dependence with respect to CMC concentration in either the induction or autoacceleration periods. Kinetic evidences for the formation of 1:2 intermediate complexes were revealed in both stages. The influence of the $[\text{H}^+]$ on the reaction rates showed that the oxidation reactions are acid-catalyzed in both stages. Added salts indicated that Mn^{III} and/or Mn^{IV} play an important role in the reaction kinetics. The kinetic parameters have been evaluated and a reaction mechanism consistent with the experimental kinetics is suggested.

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1. Introduction

Although, a great attention has been focused on the kinetics of oxidation of alginate [1,2], pectate [3,4], carboxymethyl cellulose [5,6] and ethylcellulose [7] by alkaline permanganate at higher pH's ≥ 12 , the literature survey is still scarce from kinetic studies on those carbohydrates by this oxidant in acidic solutions [8]. One possible reason may be attributed to the complexity arisen from generation of unstable manganese intermediates of various oxidation states through the reduction of permanganate ion from heptavalent state to the divalent state in acidic medium. This fact may not allow a plausible mechanistic conclusion.

In view of the foregoing aspects and our interesting in the oxidation of carbohydrates by this oxidant, the present study is of great significant to gain some information on the role of the medium on the kinetics and mechanistics of oxidation in these redox systems. Again, the results which obtained may shed some lights on the aqueous chemistry of carbohydrates.

2. Experimental

2.1. Materials

A stock solution of CMC was prepared 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 [8–11].

2.2. Kinetic procedure

The kinetic measurements were performed under pseudo-first-order conditions where CMC was present in a large excess over that of permanganate concentration in order to minimize the possible further reaction of Mn^{2+} produced with the excess of permanganate ion. The procedure of the kinetic measurements was performed as described elsewhere [9–11]. The spectral changes during the redox reaction are shown in Fig. 1.

2.3. Stoichiometry and product analysis

Reaction mixtures containing different initial concentrations of the reactants in $1.0 \text{ mol dm}^{-3} \text{ HClO}_4$ adjusted to a constant ionic

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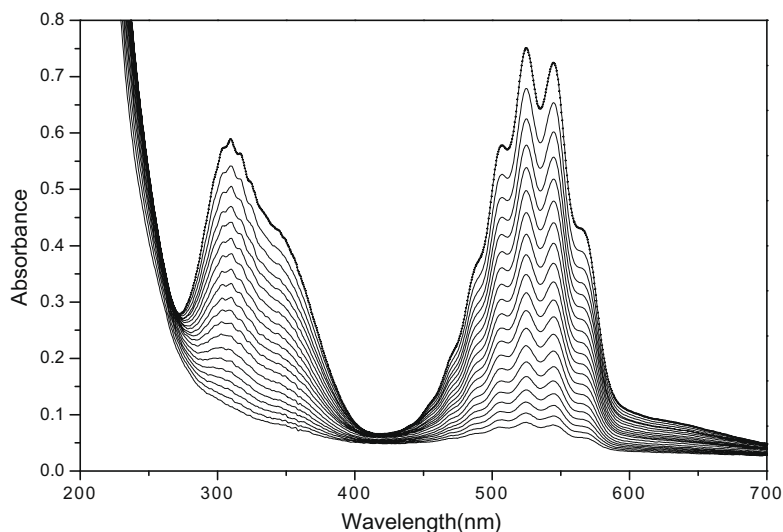
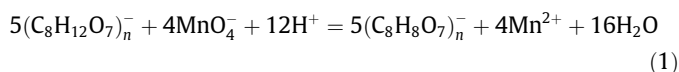


Fig. 1. Spectral changes (200–700 nm) in the oxidation of carboxymethyl cellulose by permanganate ion in aqueous perchlorate solutions. $[\text{MnO}_4^-] = 5 \times 10^{-4}$, $[\text{CMC}] = 0.025$, $[\text{H}^+] = 2.0$ and $l = 2.0 \text{ mol dm}^{-3}$ at 25°C (scanning time intervals = 2.0 min).

strength of 2.0 mol dm^{-3} were equilibrated in dark. The unreacted $[\text{MnO}_4^-]$ was estimated periodically until it reached a constant value ($\sim 24 \text{ h}$). A stoichiometric ratio ($[\text{MnO}_4^-]_{\text{consumed}}/[\text{CMC}]_0$) of 0.8 ± 0.1 was obtained. This result conforms to the following stoichiometric equation:



where $(\text{C}_8\text{H}_{12}\text{O}_7)_n^-$ and $(\text{C}_8\text{H}_8\text{O}_7)_n^-$ are CMC and its *diketo* oxidation product, respectively. The products were identified by the spectral data and microanalysis as described earlier [12,13].

2.4. Polymerization test

The possibility of formation of free-radicals was examined by adding 10% (v/v) of acrylonitrile to the partially oxidized reaction mixtures. The results indicate the initiation of free-radicals during the entire course of the present oxidation reaction.

3. Results

3.1. 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 process obeys the rate-law expression $-(A_\infty - A_t) = B_0 e^{-k_s t} + P_0 e^{-k_f t}$ [11,13–15] where k_s and k_f are the pseudo first-order rate constants for the slow and fast reactions. A_t and A_∞ 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. A typical plot is shown in Fig. 2. The pseudo first order rate constants were calculated from the gradients of the linear portions in these plots.

3.2. Dependence of reaction rate on $[\text{MnO}_4^-]$ and $[\text{CMC}]$

The independence of the pseudo-first-order rate constants obtained from the linear portions of $\ln(\text{absorbance}) - \text{time}$

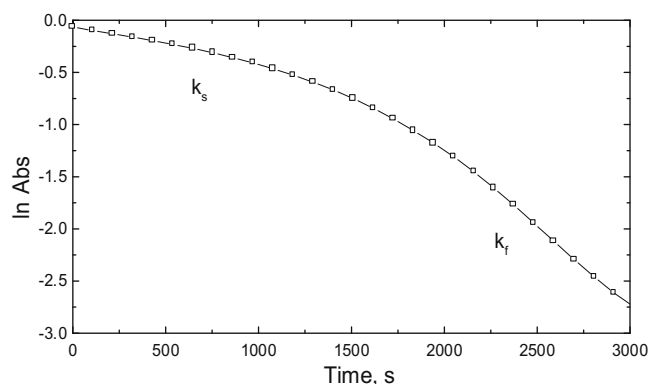


Fig. 2. A plot of $\ln \text{Abs}$ versus time in the oxidation of carboxymethyl cellulose by permanganate ion in aqueous perchlorate solutions. $[\text{MnO}_4^-] = 5 \times 10^{-4}$, $[\text{CMC}] = 0.025$, $[\text{H}^+] = 2.0$ and $l = 2.0 \text{ mol dm}^{-3}$ at 25°C .

plots at various permanganate concentration ($2 \times 10^{-4} - 6 \times 10^{-4} \text{ mol dm}^{-3}$) may confirm that the reaction is first-order with respect to the permanganate ion concentration. The average value of k_s was found to be $(4.75 \pm 0.14) \times 10^{-4} \text{ s}^{-1}$.

The non-constancy obtained for the second-order rate constants, Table 1, derived from dividing the rate constant by $[\text{CMC}]_0$ indicates that the reaction rate is of fractional-order in CMC concentration. When the values of $1/\text{rate}$ ($1/k_s$ or $1/k_f$) were plotted against $1/[\text{CMC}]^2$, straight lines with positive intercept on $1/k_s$ or $1/k_f$ axis were obtained as shown in Fig. 3. This dependence of the pseudo first-order rate constants on the carboxymethyl cellulose concentration was found to follow Michaelis–Menten kinetics [16] for the formation of an intermediate complex between the substrate and the oxidant.

At relatively high concentrations of $\text{CMC} > 5 \times 10^{-2} \text{ mol dm}^{-3}$, 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 $[\text{CMC}]$ decreases the rate. Again, the increase in viscosity with increasing the CMC concentration may also play a role in a such behavior where increasing the viscosity will tend to slow down the movement of the reactant species and, hence, a decrease in the reaction rate should be occurred as was experimentally

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