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 [H+] on the reaction rates showed that the oxidation reactions are acid-catalyzed in both stages. Added salts indicated that MnIII and/or MnIV 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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