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Base-catalyzed oxidation of sulfated kappa-carrageenan by alkaline hexacyanoferrate(III): A mechanistic approach of electron-transfer process

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ABSTRACT

The oxidation of kappa-carrageenan (KCAR) as sulfated anionic polyelectrolyte by alkaline hexacyanoferrate(III) has been investigated spectrophotometrically. Pseudo-first-order plots showed complex kinetics where slightly upward curvatures at the initial absorbance changes were appeared, followed by linearity portions for about two-half-lives of reaction completion, and then it deviates from linearity at longer time periods. The oxidation process was found to be of base-catalyzed and free-radical intervention nature. Formation of 1:1 intermediate complex was revealed kinetically. Addition of $[\text{Fe}(\text{CN})_6]^{4-}$ to the reaction mixtures was found to inhibit the reaction rates. The activation parameters have been evaluated and a tentative reaction mechanism consistent with the kinetic results is suggested and discussed.

Keywords: Catalysis, Kappa-carrageenan, Hexacyanoferrate(III), Oxidation, Kinetics, Mechanism.

1.Introduction

Redox reactions which involving sulfur-containing compounds such as carrageenan showed a remarkable kinetic complexity [1] which is highlighted by either autocatalysis and / or free-radical intervention.

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