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The thesis entitled "STUDIES ON KINETICS OF CRYSTALLIZATION OF SOME CARBOHYDRATES AND THEIR OXIDATIONS" is being submitted to the Dr.Babasaheb Ambedkar Marathwada University, Aurangabad, for the award of degree of Doctor of Philosophy.

The thesis is divided into two parts:

I) STUDIES ON KINETICS OF CRYSTALLIZATION OF SOME CARBOHYDRATES.

AND

II) KINETICS AND MECHANISM OF OXIDATION OF SOME CARBOHYDRATES BY ACIDIFIED PERMANGANATE.

I) STUDIES ON KINETICS OF CRYSTALLIZATION OF SOME CARBOHYDRATES:

It is divided into three chapters.

The first chapter deals with the Introduction and the importance and role of crystallization in sugar industries. It also describes up-to-date literature survey of the rate of crystallization of carbohydrates under different experimental conditions. It also includes research plan and its objective.
The second chapter explains the experimental procedure including the materials, apparatus, reagents etc. The following different experimental methods for studying the rate of crystallization are described.

1. Refractrometric method
2. Miniature crystallizer method
3. Polarimetric method
4. Thermometric method
5. Batchwise operating crystallizer method.

In the investigation of kinetics of crystallization, Refractrometric method has been used while studying the rate of crystallization of the following carbohydrates.

1. Sucrose,
2. Maltose,
3. D-xylose,
4. D-mannose,
5. D-Galactose
6. Raffinose Pentahydrate.
The crystallization rates are investigated at constant temperature, time, Refractive Index being experimental variables.

The measurements of Refractive Index are carried out at different constant temperature. The plots of $\log (n_t - n_\infty)$ versus time being linear indicating that order of reaction is unity.

The third chapter describes the experimental results such as –

1. Effect of temperature on rate of crystallization
2. Effect of non-sugars for example
   (a) Starch
   (b) Gum-arabic
   (c) Potassium chloride
3. Effect of amino acids,
   (i) Glycine,
   (ii) Glutamic acid
4. Effect of salts on the rate of crystallization of sucrose.
(i) Nickel sulphate,
(ii) Zinc sulphate,
(iii) Manganese sulphate,
(iv) Cobalt sulphate

From the values of rate constants at different temperature, the activation energy $E_{\text{Act}}$ associated with process growth and constant $K_0$ are calculated. The kinetic parameters like Enthalpy of activation, Free energy of activation and Entropy of activation are calculated and results are discussed. The kinetic results of rate of crystallization leads to important conclusion that under certain conditions, the desired crystal size with minimum economy can be obtained.

II) KINETICS AND MECHANISM OF OXIDATION OF SOME CARBOHYDRATES BY ACIDIFIED PERMANGANATE:

This part is divided into four chapters:

The first chapter deals with Introduction, Literature survey and properties of potassium permanganate as an oxidising agent and research plan.

The oxidation properties of potassium permanganate, its
decomposition in sulphuric acid medium are also described. Spectral properties of potassium permanganate such as U.V. and visible are discussed. The literature survey reveals that potassium permanganate is used for oxidation of Aliphatic hydrocarbons, Olefins and acetylenes, Alcohols, Aldehyde, Phenols, Ketones, Carboxylic acids, Esters, Amines etc. whereas the oxidation of carbohydrates by various oxidants for example Vanadium (V), Cerium (IV), Chromium (VI), Bromamine T, Chloramine T, Chromium Peroxyperridichromate, Potassium bromate etc. have been studied by different workers. However careful survey of the literature reveals that oxidation of carbohydrates by potassium permanganate in presence of sulphuric acid and acetic acid has not been investigated. Therefore systematic study of kinetics and mechanism of oxidation of some carbohydrates by permanganate is undertaken.

The second chapter deals with the instrumental techniques such as use of UV-160A, UV-VIS, RECORDING SPECTROPHOTOMETER (P/N 204.04550) SHIMADZU MODEL, ERMA Photo electric Calorimeter Model SN-68, Thermostat etc.
The third chapter includes the kinetic measurements of the oxidation of 1) D-Xylose 2) D-Mannose, 3) Raffinose Pentahydrate, 4) D-Galactose, 5) Maltose, 6) D-Arabinose by acidified permanganate using Spectrophotometric techniques.

The following factors with affect the rate of oxidation of above substrates by acidified permanganate have been investigated.

i) Variation of concentration of oxidant,

ii) Variation of concentration of substrates,

iii) Variation of concentration of Sulphuric acid,

iv) Variation of concentration of Acetic acid in presence of constant concentration of Sulphuric acid.

v) Variation of Salts,

vi) Variation of temperature.

The Bunnett’s hypothesis and its application for the study of oxidation of carbohydrates is investigated. The following graphs are plotted for each substrates.

i) Log K Vs. Log [H₂SO₄]

ii) Log K Vs. -H_o where H_o is the Hammett’s
Acidity function.

iii) [Log $K + H_0$] Vs. Log $a_w$ where $a_w$ is the activity of water.

The rate constants from the results obtained were calculated. The thermodynamic Parameters such as $\Delta E^\pm$, $\Delta G^\dagger$, $\Delta H^\dagger$, $\Delta S^\mp$ and frequency factory have been evaluated. The product analysis has been carried out.

The chapter four describes results and discussions of Kinetics and Mechanism of oxidation of substrates and the product analysis. The formation of the radicals is also explained. Based on the experimental results rate law and probable mechanism for oxidation of substrate is proposed and confirm by application of study state conditions.

$$\frac{d\chi}{dt} \propto [MnO_4^-] \ [\text{substrates}] \ [H^+].$$