Influence of Ionic Strength on Thionine Degradation by UV/Visible Radiation With Maltose

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ABSTRACT

Degradation of thionine (Th) was observed with UV/visible spectrophotometer at $\lambda_{\max}$ 599 nm using maltose as a reductant in aerobic conditions. A significant role of ionic strength by changing the concentration of nitrate ions was observed, leading to more rapid degradation of dye at increasing concentration than low concentration, which was confirmed by measuring the optical density of the reaction mixture. Rate constant at elevated temperature showed that reaction depends upon ionic strength and temperature that follows pseudo-first-order kinetics. Activation parameters like E_a , ΔG° , ΔS° and ΔH° were computed, and a mechanism of reduction of dye was proposed.

Keywords: Thionine, maltose, ionic strength, activation parameters

1. INTRODUCTION:

Thionine is a purple dye having singly protonated form ThH^+ that exists as a monochloride in the pH range of 2-10. The doubly protonated cation ThH_2^{++} is blue and appears in 2.5 mol.dm³ HCl or H₂SO₄. But doubly and triply protonated forms also exist in highly acidic conditions on photoreduction. Thionine dye gets reduced partly or entirely, but it depends upon the power of the reductant and the pH of the medium.

Double protonated thionine

Guha *et al.* [1] reported the reduction of thionine by H , e_{aq}^- and radicals derived from methanol, ethanol, isopropanol, using the technique of nanosecond pulse radiolysis and kinetic spectrophotometry. The rate constants for the transfer of electrons from these radicals to thionine and the one-electron reduction potential of thionine were directly determined from the pseudo-first-order kinetics of the product, semi thionine. Hatchard and Parker [2] observed the kinetics of reducing thionine with FeSO_4 in 0.1 N H_2SO_4 using flash photolysis and monitored it at various wavelengths. Somer and Temizer [3] used a scheme applied earlier work on the photoreduction of methylene blue and observed the photoreduction of thionine by water. A long-lived excited intermediate for thionine and methylene blue (MB) formed was finally converted into a reduced molecule. Hatchard and Parker [2], Parker [4] examined the dilute solutions of methylene blue in 0.1N H_2SO_4 by flash photolysis with orange-red light in the presence of 0.1 M FeSO_4 . The rate constant for the dismutation of the semiquinone radical was in the order of $1.5 \times 10^{-9} \text{ s}^{-1}$. Kamat *et al.* [5] studied the oxidation of leuco thionine by Fe^{+3} in an aqueous medium with a cross-beam illumination kinetic spectrophotometry technique. The specific rate of oxidation of leucothionine by Fe^{+3} monitored as photobleaching recovery follows pseudo 1st order kinetics. This specific rate attains a limiting value with increasing Fe^{+3} concentrations. The influence of varying concentrations of Fe^{+2} and thionine is marginal. The observed results support a complex formation between leucothionine and Fe^{+3} .

The redox reaction of thiazine dyes often occurs on a time scale of a few seconds to minutes. They may be followed usually for quantitative interpretation and spectrophotometrically for quantitative determination [6]. In alkaline solutions, glucose is oxidized to D-gluconic acid according to the following reaction[7, 8].

The kinetics of reduction of dye and the kinetics of oxidation of carbohydrates have been studied widely, using various organic and inorganic compounds [4-7]. The reaction was the first order for the concentration of MB, and the observed rate constants increased with glucose (GH) concentration [9].

The oxidation of leuco thionine by Fe^{+2} chelate was also examined. The physicochemical studies of some metal complexes such as vanadium, niobium (Nb), and tantalum (Ta) with dyes such as Erichrome cyanine-R and methylene blue have been examined by Awadallah *et al.* [10]. Conductometric and spectrophotometric methods were applied to investigate the complexation processes of metal with methylene blue. The measurements were used to investigate stoichiometry, formation constants, and thermodynamics parameters like enthalpy change ΔH^* , free energy changes ΔG^* and entropy change ΔS^* of the complexes. The effect of pH on absorption spectra of complexes, time, and temperature on the stability of metal chelates was also studied. Matsumoto [11] found the effect of pH on the quantum yield of photoreduction of methylene blue in the pH range 5.0-10.5. He also noted the effect of buffer solutions and a possible change in the ionic species of N-phenyl glycine with the pH value. N-Phenylglycine behaved as a monobasic acid of PK_a 4.3 to base titration so that it existed solely as univalent anion $\text{C}_6\text{H}_5\text{NH}.\text{CH}_2\text{COO}^-$ in this pH range. The lifetime of methylene blue was found to be dependent on the pH value [12]. The Detailed literature survey [5-14] revealed that thionine degradation with maltose under the influence of ionic strength had not been studied yet. Therefore, this study was planned to monitor the influence of ionic strength on thionine degradation. The influence of ionic strength in aerobic conditions on thionine degradation with maltose in an alkaline medium has been monitored by recording the change in optical density. Various parameters like the effects of concentrations of maltose, Th, and ionic strength of the medium and activation parameters were computed; a mechanism was proposed based on the above investigations.

2. MATERIALS AND METHODS

An aqueous solution of maltose, sodium hydroxide, thionine (E-Merck) was prepared by dissolving the known amounts of samples in doubly distilled conductivity water. Potassium nitrate (E-Merck) was used to maintain the ionic strength of the medium. Kinetics measurements were made by preparing three sets of reaction mixtures in which one species was varied while the other two were kept constant at given concentrations. The three contents were mixed, and the progress of the (inlet) reaction was monitored by recording the change in optical density at $\lambda_{\text{max}} = 599 \text{ nm}$ during the reaction on a UV-Visible spectrophotometer (Shimadzu 1601). The reaction order at different operational parameters and activation parameters was evaluated by measuring the specific reaction rate at various temperatures and different ionic strengths. Percentage decrease in absorbance was calculated using $\% \text{ of the decrease in absorption} = \frac{(A_i - A_f)}{A_i} \times 100$, where A_i and A_f represent initial and final absorption, respectively. The UV/Visible spectrophotometer (Shimadzu 1601) was used throughout the experiments.

3. RESULT AND DISCUSSION

The effect of ionic strength concentration on the rate constant was studied at different concentrations of potassium nitrate ranging from 0.05 mol dm^{-3} to 0.2 mol dm^{-3} shown in Tables 1-5. The pH of the reacting solution was kept constant, and the temperature was maintained at 303K-323K. The effect of change in concentration of potassium nitrate was studied, and it is revealed that there is a significant change in the rate constant. Results indicate that the rate constant of dye reduction with potassium nitrate increases with the increase in ionic strength. The plots of $\log A_0 - A_\infty / A_t - A_\infty$ Vs t were shown in Figures 1, 2, 3, 4, and 5. It was observed through the graph that the reaction followed a first-order kinetics reaction with respect to salt concentration.

Moreover, it was observed that with a decrease in salt concentration, the values of rate constant decrease. The plots of $\ln A$ vs time are shown in Figures 6, 7, 8, 9, and 10. The values of the rate of reduction at different concentrations of reductants are calculated from the graph of absorbance versus time and are shown in Figures 11, 12, 13, 14, and 15. Results showed that rate constant and % decolorization also depends upon the concentration of salt.

3.1 Effect of Change in Ionic Strength on Reduction of Thionine

The ionic strength of the medium was changed by the addition of KNO_3 to check whether a charged species is involved in the rate-determining step or not. As the reaction rate between two uncharged molecules or between an ion and a molecule is usually only slightly affected by the addition of salt, as shown in Table 1-5. This indicates that primary and secondary salt effects are operative in opposite directions. The reaction was followed by experiments with a varying initial

concentration of KNO_3 at constant concentrations of thionine and maltose at different temperatures. The ionic strength was varied 0.05 to 0.2 mol dm^{-3} . Since ionic strength influences the reaction rate between charged species, the rate of bleaching increases with time by varying concentration of KNO_3 , which may be attributed to that the dye reduction is more favorable in the presence of NO_3^- . Results showed that the apparent rate constant of dye decoloration increased at different ionic strengths at a temperature from 303 K to 323 K, but higher temperature and increased ionic strength resulted in the decreased rate constant. That may be due to self-quenching of $\text{OH}^\cdot$ radicals by added NO_3^- .

3.2 Effect of Temperature on Reduction of Thionine

The effect of temperature on dye reduction has been shown in Table 6. Thermodynamics activation parameters like E_a (42.30 kJ mol^{-1}) were computed and presented in that Table-7, support the initially slow reaction process as compared to that the literature value 15.78 [15], 5.73 kJ mol^{-1} [16] reported the rapid decoloration of thiazine dye. The value of entropy change of activation ($\Delta S^\ddagger$) for reducing thionine with maltose (-22.18 J/K.mol) showed a highly solvated state of the activated complex. The negative value of $\Delta S^\ddagger$ indicates a decrease in the degree of freedom due to the formation of a rigid activation complex resulting in an extensive reorientation of solvent molecules. It may also be indicated that the solvent molecules are highly held to the $\text{OH}^\cdot$ bond, which is the site of oxidation. The reasonably high values of enthalpy change or activation $\Delta H^\ddagger$, free energy change of activation $\Delta G^\ddagger$, and energy of activation (E_a) indicate that the transition state is highly saturated. It also reveals that the rate-determining state is less disorderly oriented relative to the reactants. The positive value of $\Delta H^\ddagger$ (61.01 kJ/mol) showed that enthalpy was not the driving force for the formation of complex, and entropy was responsible for forming the complex that involves one charged species and solvent molecules for the reduction of dye. The present value of $\Delta S^\ddagger$ (-22.18 J/K.mol) is comparable with the literature values of 39.24 [17], 33.7 and 34.6 J/K.mol [18]. These values integrated that the same but slow rate of reduction was operating during the reduction of thionine with maltose as observed by earlier researchers [17-21]. The values of other parameters like $\Delta H^\ddagger$ and $\Delta G^\ddagger$ also support the initially slow reaction and then immediate bleaching of the dye. The value of $\Delta G^\ddagger$ (61.01 kJ/mol) is compared with the literature 8.18 kJ/mol [22] and $\Delta H^\ddagger$ 56.75 kJ/mol with 15.56 [21] and 18.4 kJ/mol [19-22].

Table 1: Influence of ionic strength on rate constant of photochemical reduction of thionine.

[Th] = $5.54 \times 10^{-5} \text{ mol.dm}^{-3}$

[Maltose] = $1.43 \times 10^{-2} \text{ mol.dm}^{-3}$

Temperature = 303 K

[NaOH] = 1.27 mol.dm^{-3}

Confidence Interval = 0.050

[KNO ₃] $\times 10^2 \text{ mol. dm}^{-3}$	$-v \times 10^4$ [dx/dt] $\text{mol. dm}^{-3} \cdot \text{s}^{-1}$	Apparent Rate Constant (k_{app}) $\times 10^3$	Specific Rate Constant (k_{sp}) $10^3 \cdot \text{s}^{-1}$	% Decoloration	% Decoloration At fixed time
5	14	14.6	4.3 ± 0.002	94.37	94.37
8.75	15	15.5	4.8 ± 0.003	94.78	94.78
12.5	16	15.6	5.6 ± 0.005	93.77	93.77
16.25	15	16.7	5.5 ± 0.001	95.23	95.23
20	16	18.2	5.7 ± 0.002	96.47	96.47

Table 2: Influence of ionic strength on rate constant of photochemical reduction of thionine.

[Th] = $5.54 \times 10^{-5} \text{ mol.dm}^{-3}$

[Maltose] = $1.43 \times 10^{-2} \text{ mol.dm}^{-3}$

Temperature = 308 K

[NaOH] = 1.27 mol.dm^{-3}

Confidence Interval = 0.028

[KNO ₃] $\times 10^2 \text{ mol. dm}^{-3}$	$-v \times 10^4$ [dx/dt] $\text{mol. dm}^{-3} \cdot \text{s}^{-1}$	Apparent Rate Constant (k_{app}) $\times 10^3$	Specific Rate Constant (k_{sp}) $10^3 \cdot \text{s}^{-1}$	% Decoloration	% Decoloration At fixed time
5	21	26.6	13.5 ± 0.009	95.92	95.92
8.75	21	25.5	13.2 ± 0.008	95.02	95.02
12.5	23	27.5	11.5 ± 0.008	97.11	97.11
16.25	23	30.1	13.4 ± 0.002	97.51	97.51
20	23	35.5	13.3 ± 0.007	99.17	99.17

Table 3: Influence of ionic strength on rate constant of photochemical reduction of thionine.

[Th] = $5.54 \times 10^{-5} \text{ mol.dm}^{-3}$

[Maltose] = $1.43 \times 10^{-2} \text{ mol.dm}^{-3}$

Temperature = 313 K

[NaOH] = 1.27 mol.dm^{-3}

Confidence Interval = 0.019

[KNO ₃] x 10 ² mol. dm ⁻³	- ν x 10 ⁴ [dx/dt] mol. dm ⁻³ . s ⁻¹	Apparent Rate Constant (k _{app}) x 10 ³	Specific Rate Constant (k _{sp}) 10 ³ . s ⁻¹	% Decoloration	% Decoloration At fixed time
5	28	37.5	26.5± 0.002	95.17	95.17
8.75	30	40.1	23.9± 0.006	96.23	96.23
12.5	31	40.2	19.2± 0.004	96.70	96.70
16.25	30	40.3	19.8± 0.004	96.62	96.62
20	32	49.9	20.0± 0.001	98.79	98.79

Table 4: Influence of ionic strength on rate constant of photochemical reduction of thionine.[Th] = 5.54 × 10⁻⁵ mol.dm⁻³[Maltose] = 1.43 x 10⁻² mol.dm⁻³

Temperature = 318 K

[NaOH] = 1.27 mol.dm⁻³

Confidence Interval = 0.0045

[KNO ₃] x 10 ² mol. dm ⁻³	- ν x 10 ⁴ [dx/dt] mol. dm ⁻³ . s ⁻¹	Apparent Rate Constant (k _{app}) x 10 ³	Specific Rate Constant (k _{sp}) 10 ³ . s ⁻¹	% Decoloration	% Decoloration At fixed time
5	34	42.3	15.3± 0.001	96.17	96.17
8.75	34	42.5	17.5± 0.002	95.78	95.78
12.5	36	45.6	17.9± 0.005	96.72	96.72
16.25	37	51.7	16.4± 0.002	98.37	98.37
20	38	56.9	19± 0.003	98.79	98.79

Table 5: Influence of ionic strength on rate constant of photochemical reduction of thionine.[Th] = 5.54 × 10⁻⁵ mol.dm⁻³[Maltose] = 1.43 x 10⁻² mol.dm⁻³

Temperature = 323 K

[NaOH] = 1.27 mol.dm⁻³

Confidence Interval = 0.090

[KNO ₃] x 10 ² mol. dm ⁻³	- ν x 10 ⁴ [dx/dt] mol. dm ⁻³ . s ⁻¹	Apparent Rate Constant (k _{app}) x 10 ³	Specific Rate Constant (k _{sp}) 10 ³ . s ⁻¹	% Decoloration	% Decoloration At fixed time
5	38	62	41.0± 0.008	96.50	96.50
8.75	40	64	38.4± 0.002	97.09	97.09
12.5	42	69.1	36.4± 0.006	98.06	98.06
16.25	42	95.7	40.5± 0.005	99.61	99.61
20	43	97.7	43.1± 0.003	99.61	99.61

strength (5-20x 10⁻² mol. dm⁻³) **Figure 1:** A plot of $\log \frac{A_0 - A_\alpha}{A_t - A_\alpha}$ Vs time (S) of reduction of Th with different ionic strength (5-20x 10⁻² mol. dm⁻³)

Figure 2: A plot of $\log \frac{A_o - A_\alpha}{A_t - A_\alpha}$ Vs time (S) of reduction of Th with different ionic strength ($5-20 \times 10^{-2} \text{ mol. dm}^{-3}$)

Figure 3: A plot of $\log \frac{A_o - A_\alpha}{A_t - A_\alpha}$ Vs time (S) of reduction of Th with different ionic strength ($5-20 \times 10^{-2} \text{ mol. dm}^{-3}$)

Figure 4: A plot of $\log \frac{A_o - A_\alpha}{A_t - A_\alpha}$ Vs time (S) of reduction of Th with different ionic strength ($5-20 \times 10^{-2} \text{ mol. dm}^{-3}$)

Figure 5: A plot of $\log \frac{A_o - A_\alpha}{A_t - A_\alpha}$ Vs time (S) of reduction of Th with different ionic strength ($5-20 \times 10^{-2} \text{ mol. dm}^{-3}$)

Figure 6: A plot of $\ln A$ Vs time (S) of reduction of Th with different ionic

Figure 7: A plot of $\ln A$ Vs time (S) of reduction of Th with different ionic strength ($5-20 \times 10^{-2} \text{ mol. dm}^{-3}$)

Figure 8: A plot of $\ln A$ Vs time (S) of reduction of Th with different ionic strength ($5-20 \times 10^{-2} \text{ mol. dm}^{-3}$)

Figure 9: A plot of $\ln A$ Vs time (S) of reduction of Th with different ionic strength ($5-20 \times 10^{-2} \text{ mol. dm}^{-3}$)

Figure 10: A plot of $\ln A$ Vs time (S) of reduction of Th with different ionic strength ($5-20 \times 10^{-2} \text{ mol. dm}^{-3}$)

Figure 11: A plot of Absorbance Vs time (S) of reduction of Th with different ionic strength ($5-20 \times 10^{-2} \text{ mol. dm}^{-3}$)

Figure 12: A plot of Absorbance Vs time (S) of reduction of Th with different ionic strength ($5-20 \times 10^{-2} \text{ mol. dm}^{-3}$)

Figure 13: A plot of Absorbance Vs time (S) of reduction of Th with different ionic strength ($5-20 \times 10^{-2} \text{ mol. dm}^{-3}$) **Figure 14:** A plot of Absorbance Vs time (S) of reduction of Th with different ionic strength ($5-20 \times 10^{-2} \text{ mol. dm}^{-3}$) **Figure 15:** A plot of Absorbance Vs time (S) of reduction of Th with different ionic strength ($5-20 \times 10^{-2} \text{ mol. dm}^{-3}$)**Table 6:** variation of percnet decoloration of thionine with different reductant with respect to different temperature
 $[\text{Th}] = 5.54 \times 10^{-5} \text{ mol. dm}^{-3}$ $[\text{Maltose}] = 1.43 \times 10^{-2} \text{ mol. dm}^{-3}$
 $[\text{NaOH}] = 1.27 \text{ mol. dm}^{-3}$

	Change in Temperature	303 K	308 K	313 K	318 K	323 K
Reductants	Time (s)	% Decoloration				
Maltose	60	4.95	6.63	78.54	88.35	98.79

Table 7: Parameters of reduction of thionine with maltose

Temperature	$E_a \text{ kJmol}^{-1}$	$\Delta H^* \text{ kJmol}^{-1}$	$\Delta G^* \text{ kJmol}^{-1}$	$\Delta S^* \text{ J.K}^{-1} \text{ mol}^{-1}$
303K	42.30	49.12	61.01	-22.18

4. CONCLUSIONS:

The present investigation deals with reducing thionine kinetics by reducing sugars in doubled distilled water with maltose. Experimental results are obtained under different parameters i.e., concentration of dye and reductant, the acidity of the reaction mixture, and different temperatures. It was concluded that the reaction rate depends upon ionic strength. A mechanism has been drawn from the analysis of the reaction mixture. It has been concluded that the mechanism of the reaction shows the following necessary steps of photoreduction.

Reduction of thionine is taking place through enediol species of reducing sugars.

Oxidation of sugars gives respective acid according to following equation

Thermodynamic study of reduction of thionine reveals that reaction between thionine and maltose is fast reactions. The rate of reduction of dye also depends upon the concentration of dye. Photoreduction of thionine follows 1st order kinetics with respect to dye and reductant.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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