



KINETIC STUDY OF THE REDOX REACTION OF MALACHITE GREEN AND METABISULPHITE ION IN AQUEOUS ACIDIC MEDIUM

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ABSTRACT Kinetic investigations of the redox reaction of malachite green (MG^+) and metabisulphite ion were carried out under pseudo first order conditions in aqueous acidic medium at $28 \pm 1^\circ\text{C}$, $[\text{H}^+] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$ (NaCl) and $\lambda_{\text{max}} = 620 \text{ nm}$. A first order dependence in both reactants was indicated and the result of the stoichiometric investigation revealed that one mole of malachite green consumed one mole of metabisulphite ion. The rate equation for the reaction has been proposed as;

$$\frac{-d[\text{MG}^+]}{dt} = k_2[\text{MG}^+][\text{S}_2\text{O}_5^{2-}]$$

where $k_2 = (38.04 \pm 0.30) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Reaction rate retardation was observed from increasing $[\text{H}^+]$. The acid dependent rate constant can be represented by the equation

$$k_2 = (a + b [\text{H}^+]^{-1})$$

Hence two parallel pathways were indicated for the reaction. An increasing dielectric constant of the reaction medium greatly supported the positive ionic strength effect observed. These assertions together with the result of Michaelis-Menten plot suggest an outer-sphere mechanism for the reaction.

Key Words: Kinetics, metabisulphite, stoichiometry, rate constant, ionic strength.

Introduction

Reduction-Oxidation (Redox) reaction is a key to life on earth. It plays a vital role in many inorganic chemical revolutions and the natural geochemical cycles (Cutter *et al.*, 2018). Examples include the cycles of Carbon, Nitrogen, Sulfur, Iron, and Manganese, as well as those of redox-sensitive trace elements such as Chromium, Copper, Arsenic, and Uranium. The regime shifts which occur in parameter ranges relevant to these cycles is a direct consequence of the presence of oxidative and reductive species in the environment (Bush *et al.*, 2015).

Malachite Green (MG^+), is a highly water soluble triphenylmethane dye with a large scale utilization owing to its low cost. It is widely used as a biocide in the aquaculture industry because of its effectiveness against important protozoal and fungal organisms (Teimouri *et al.*, 2018). It is a basic dye used to colour silk, wool, jute, cotton, paper and leather products. It is also used as an intestinal anthelmintic, a medical disinfectant and

therapeutic agent (Latona and Adegoke, 2017).

Regardless of the inclusive applications of this dye, its presence in water poses deleterious effects to aquatic beings and human health due to its toxic characteristics. It acts as a tumor-promoting agent in mammalian liver cells (Ullah *et al.*, 2021). It also acts as a respiratory enzyme poison. Post-exposure effects include; delayed blood coagulation, leukocytosis, and dyscrasia (Sartape *et al.*, 2014).

Owing to these hazardous effects, several kinetic studies have been reported to unfold the oxidation and reduction reactions on this dye in various reacting medium such as aqueous, acidic, basic, mixed aqueous/surfactants, fenton-like and so on (Tanimu *et al.*, 2012; Hashemian, 2013; Hameed and Ewais, 2014; Bamgbose *et al.*, 2015; Idris *et al.*, 2015; Bañuelos *et al.*, 2016; Latona and Adegoke, 2017; Imam *et al.*, 2018; Hu *et al.*, 2018; Ghime *et al.*, 2019). However the kinetic study of the redox reaction of MG^+ with metabisulphite ion ($\text{S}_2\text{O}_5^{2-}$) has not been reported. Hence this

prompted this research with the view to determining a mechanistic pathway for the reaction.

Materials and Methods

All chemical reagents used were of analytical grade. Malachite green was obtained from M&B Laboratory Chemicals in the laboratory grade and used without further purification. Distilled water was used to prepare all solutions. A stock solution of $\text{Na}_2\text{S}_2\text{O}_5$ and MG^+ were prepared by dissolving the required amount in distilled water. Sodium chloride solution was used to maintain the strength of the ions in the reaction medium.

Stoichiometry

The stoichiometry of the reaction was probed by spectrophotometric titration using the mole ratio method. Excess MG^+ was determined by measuring the absorbance of the solutions at 620 nm (λ_{max} of MG^+). The stoichiometry was evaluated from the plot of absorbance against mole ratio (Imam *et al.*, 2018).

Kinetics studies

The kinetic studies were carried out under pseudo-first order conditions with the $[\text{S}_2\text{O}_5^{2-}]$ in excess over the $[\text{MG}^+]$ at 620 nm. The pseudo-first order rate plots of $\log(A_t - A_\infty)$ versus time were made (where A_∞ and A_t are the absorbance at the end of the reaction and at time, t) and from the slopes of the plots, the pseudo-first order rate constants (k_1) were determined (Idris *et al.*, 2014).

Effect of hydrogen ion concentration $[\text{H}^+]$, ionic strength of reaction medium (I) and added ions on the rate of reaction

The effect of changes in $[\text{H}^+]$ on the reaction rate was studied by varying the $[\text{H}^+]$ in the range $(5.0 - 12.0) \times 10^{-3} \text{ mol dm}^{-3}$ while keeping the concentration of all other reactants constant. At $T = 28 \pm 1^\circ\text{C}$ and constant concentration of other reactants, the effect of ionic strength on the rate of reaction was studied in the range $(0.05 - 0.5) \text{ mol dm}^{-3}$. Similarly, for $[\text{X}] = (10 - 80) \times 10^{-4} \text{ mol dm}^{-3}$, the effect of added ions ($\text{X} = \text{NH}_4^+$ and NO_3^-) at constant $[\text{MG}^+]$, $[\text{S}_2\text{O}_5^{2-}]$, $[\text{H}^+]$ and ionic strength was studied.

Test for intermediate complex and free radical formation

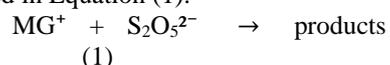
The spectrum of the reaction mixture was obtained over a wavelength range of (480–700) nm shortly after the initiation of the reaction. This was carried out in order to

determine whether there is significant shift in λ_{max} or enhancement of peak as reaction progressed. Michaelis-Menten plot of $1/k_1$ versus $1/[\text{S}_2\text{O}_5^{2-}]$ was made (Ibrahim and Hamza, 2016). To a partially oxidized solution of the reaction mixture, about 5cm^3 of acrylamide was added followed by large excess of methanol to initiate free radical polymerization. A control experiment was carried out by adding acrylamide to each of the reactants separately (Idris *et al.*, 2015).

Results and Discussion

Stoichiometry:

The result of the stoichiometric investigation indicates that one mole of MG^+ consumed one mole of metabisulphite ion (Fig. 1), and is represented in Equation (1).



This agrees with the stoichiometries observed in the reactions of $\text{S}_2\text{O}_5^{2-}$ with crystal violet (Abdulsalam and Idris, 2016) and rosaniline monochloride (Onu and Iyun, 2001). However, stoichiometry of 1:3 was established for the reduction of methylene blue with metabisulphite (Babatunde *et al.*, 2013).

Kinetics studies

From the kinetic studies, plots of $\log(A_t - A_\infty)$ versus time were linear to about 80% extent of the reaction. The linearity of these plots indicates that these reactions are first order with respect to $[\text{MG}^+]$. Typical pseudo-first order plot is shown (Fig. 2) and the rate constants, k_1 calculated are reported (Table 1). Least square plot of $\log k_1$ versus $\log[\text{S}_2\text{O}_5^{2-}]$ for the determination of order of reaction gave a slope of 0.99 (Fig. 3).

Consequently, the reaction is second order overall and rate equation can thus be written as;

$$\frac{-d[\text{MG}^+]}{dt} = k_2 [\text{MG}^+][\text{S}_2\text{O}_5^{2-}] \quad (2)$$

where $k_2 = (38.04 \pm 0.30) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Results of effect of changing $[\text{H}^+]$, ionic strength of reaction medium (I) and added ions on the rate of reaction

The rate of reaction was found to decrease with increasing $[\text{H}^+]$ (Table 1). Least square plot of k_2 versus $[\text{H}^+]^{-1}$ had an intercept (Fig.

4) indicating that two parallel reaction pathways are available for the reaction: the acid independent and the inverse acid dependent pathways. The inverse acid pathway shows that there is a pre-equilibrium step before the rate determining step in which a proton is lost. This means that the two rate-controlling steps are preceded by a rapid equilibrium for which the equilibrium constant is small, and both forms (i.e the protonated and deprotonated forms) are reactive (Abdulsalam *et al.*, 2020). From Table 1, it is clear that rate of reaction increases with increase in ionic strength of reaction medium. A straight line graph with a slope of +1 obtained from the plot of $\log k_2$ versus \sqrt{I} (Fig. 5), suggests a positive salt effect. This is consistent with interaction between two liked charged species at the rate determining step (Imam *et al.*, 2018). The positive salt effect was further supported by the observed increase in reaction rate with increase in dielectric constant of reaction medium (Table 2). A plot of k_2 versus $1/D$ is

Reaction mechanism

presented (Fig. 6). Added ions inhibited the rate of the reaction. The inhibitive effect of these ions suggested that the reaction might be operating via the outer-sphere mechanism (Myek *et al.*, 2020).

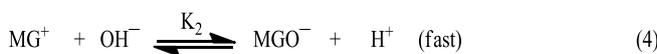
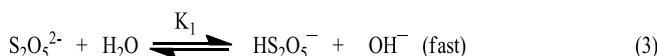
Test for intermediate complex and free radical formation

Neither a shift in λ_{max} (620 nm) nor enhanced absorbance was observed when the spectrum of MG^+ was compared with that of the reaction mixture. Similarly, no intercept was recorded from michaelis-menten plot of $1/k_1$ versus $1/[S_2O_5^{2-}]$ (Fig 7). These observations both spectrophotometrically and kinetically eliminate the formation of intermediate complex in the reaction.

A gelatinous precipitate was observed when the radical scavenger (acrylamide) was added to a partially oxidized solution of the reaction mixture followed by large excess of methanol. This shows that the participation of free radicals in this reaction system is likely.

On the basis of the above results, the scheme in equation (3) - (11) is thus proposed for the reaction which

occurred via the outer sphere mechanism.



Equation 5 and 6 are the rate determining steps. Therefore:

$$\text{Rate} = k_3 [MGO^-] [HS_2O_5^-] + k_4 [MG^+] [S_2O_5^{2-}] \quad (7)$$

$$\text{From equation 4, } [MGO^-] = K_2 [MG^+] [OH^-] [H^+]^{-1} \quad (8)$$

$$\text{Also from equation 3, } [HS_2O_5^-] = K_1 [S_2O_5^{2-}] [OH^-]^{-1} \quad (9)$$

Substituting equations 8 and 9 in 7, we have,

$$\text{Rate} = K_1 K_2 k_3 [MG^+] [S_2O_5^{2-}] [H^+]^{-1} + k_4 [MG^+] [S_2O_5^{2-}] \quad (10)$$

$$= k^{II} [MG^+] [S_2O_5^{2-}] \quad (11)$$

where $k^{II} = k_4 + K_1 K_2 k_3 [H^+]^{-1}$

This is analogous to equation 2 where $k^{II} = k_2 = (38.04 \pm 0.30) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

Conclusion

The redox reaction of malachite green and metabisulphite ion in acidic medium revealed a stoichiometry of 1:1. The reaction is second order overall. It also displayed a positive Bronsted-Debye salt effect. Both kinetic and spectroscopic investigations showed no evidence of intermediate complex formation.

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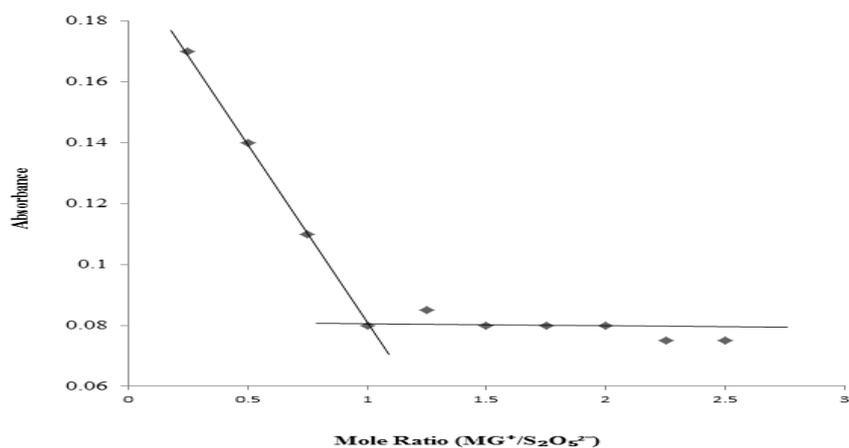


Fig. 1: Plot of absorbance versus mole ratio for the redox reaction of malachite green with metabisulphite ion at $[MG^+] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[H^+] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$ and $T = 28 \pm 1^\circ\text{C}$

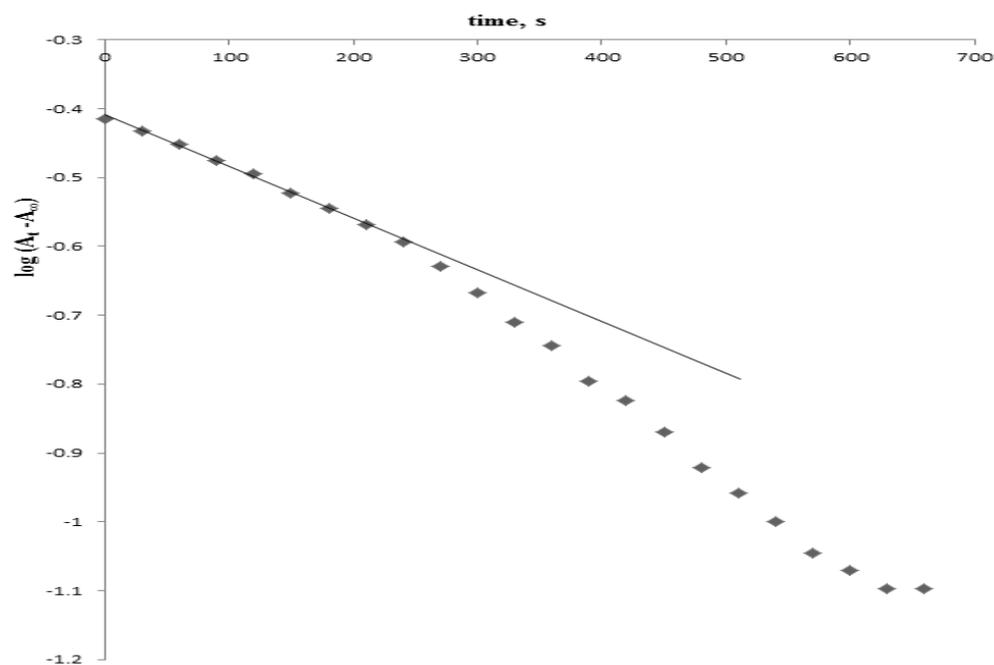


Fig. 2: Typical pseudo-first order plot for the redox reaction of malachite green with metabisulphite ion at $[MG^+] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[S_2O_5^{2-}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[H^+] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$ and $T = 28 \pm 1^\circ\text{C}$

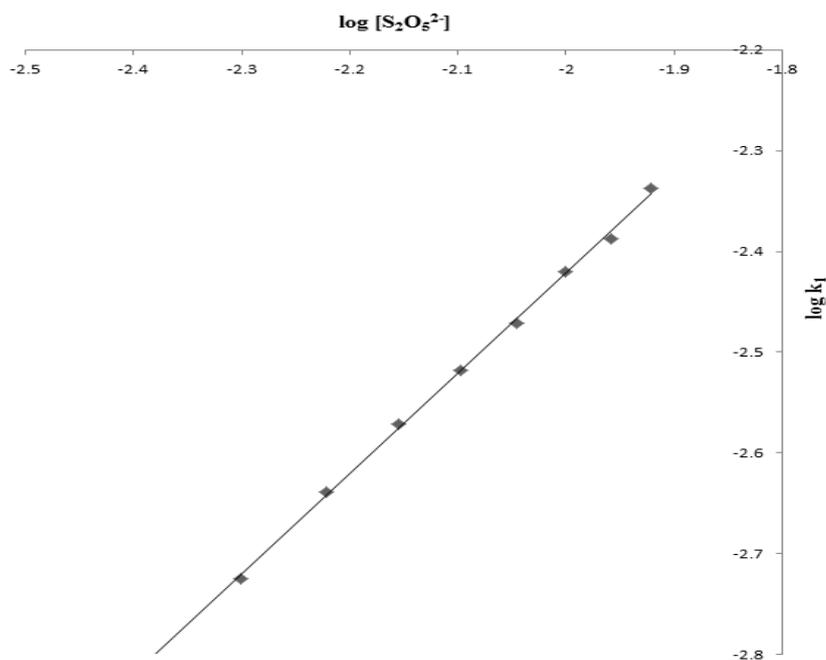


Fig. 3: Pseudo-first order plot of $\log k_1$ versus $\log [S_2O_5^{2-}]$ for the redox reaction of malachite green with metabisulphite ion at $[MG^+] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[H^+] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 620 \text{ nm}$ and $T = 28 \pm 1 \text{ }^\circ\text{C}$

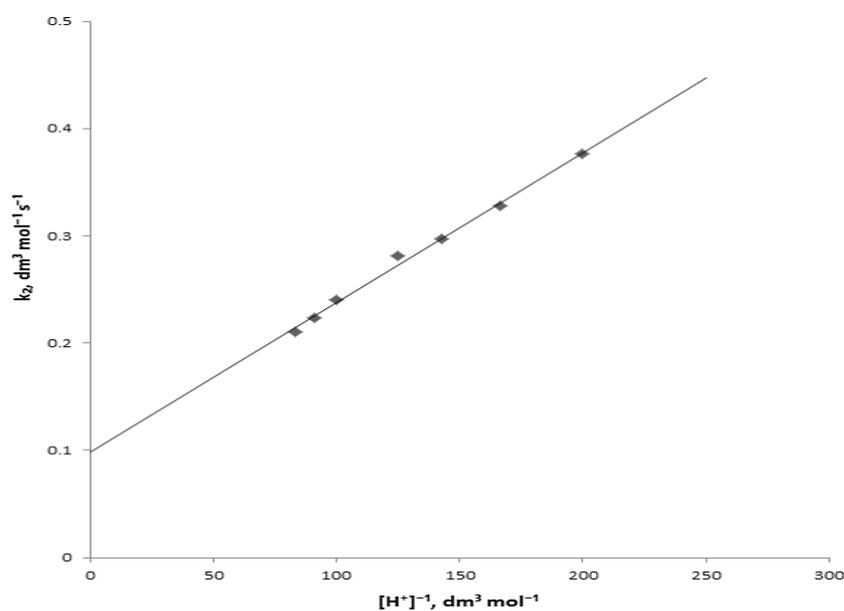


Fig. 4: Plot of k_2 versus $\log [H^+]^{-1}$ for the redox reaction of malachite green with metabisulphite ion at $[MG^+] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[S_2O_5^{2-}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$ and $T = 28 \pm 1 \text{ }^\circ\text{C}$

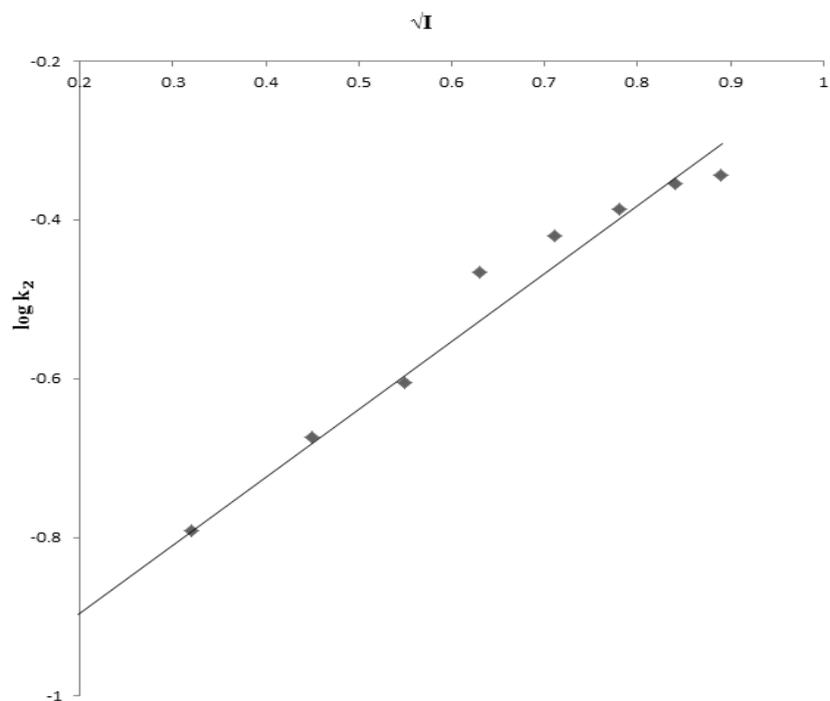


Fig. 5: Plot of $\log k_2$ versus \sqrt{I} for the redox reaction of malachite green with metabisulphite ion at $[MG^+] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[S_2O_5^{2-}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[H^+] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $T = 28 \pm 1 \text{ }^\circ\text{C}$

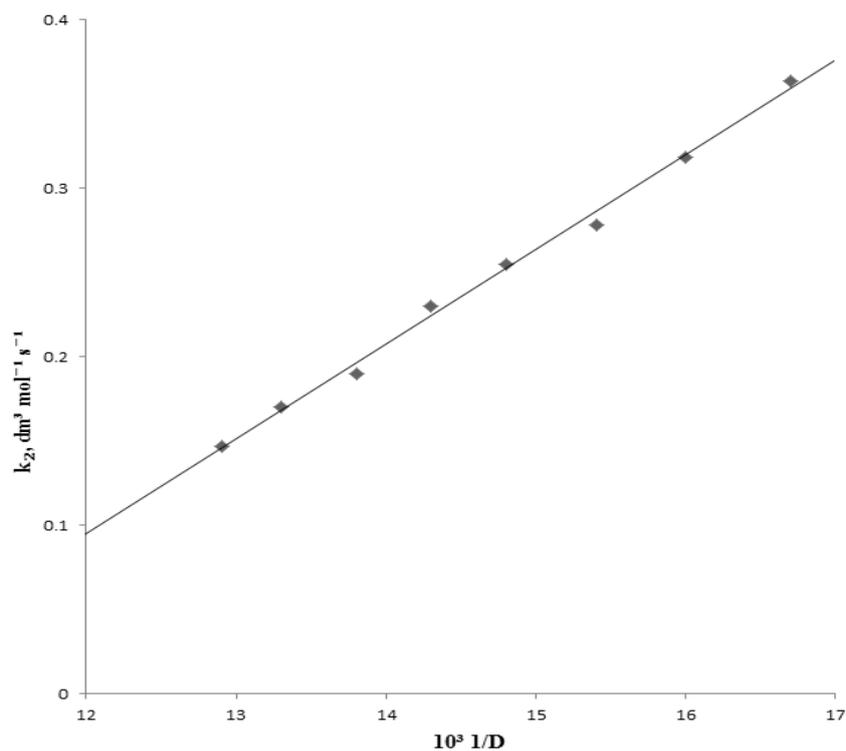


Fig. 6: Plot of k_2 against $1/D$ for redox reaction of malachite green with metabisulphite ion at $[\text{MG}^+] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{S}_2\text{O}_5^{2-}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$ and $T = 28 \pm 1^\circ\text{C}$

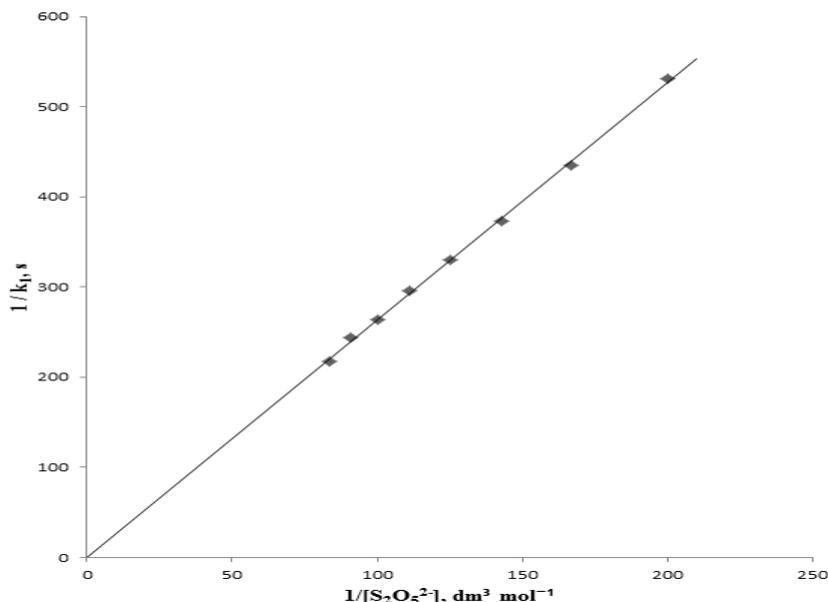


Fig. 7: Michaelis-Menten plot of $1/k_1$ versus $1/[S_2O_5^{2-}]$ for the redox reaction of malachite green with metabisulphite ion at $[MG^+] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[H^+] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$ and $T = 28 \pm 1 \text{ }^\circ\text{C}$

Table 1: Pseudo-first order and second order rate constants for the redox reaction of malachite green with metabisulphite ion in aqueous HCl medium at $[MG^+] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $T = 28 \pm 1 \text{ }^\circ\text{C}$ and $\lambda_{\text{max}} = 620 \text{ nm}$

$10^3[S_2O_5^{2-}],$ mol dm ⁻³	$10^3[H^+],$ mol dm ⁻³	$I, \text{ mol dm}^{-3}$	$10^3 k_1, \text{ s}^{-1}$	$10^1 k_2,$ dm ³ mol ⁻¹ s ⁻¹

5.00	5.00	0.50	1.88	3.77
6.00	5.00	0.50	2.30	3.83
7.00	5.00	0.50	2.68	3.84
8.00	5.00	0.50	3.03	3.79
9.00	5.00	0.50	3.38	3.76
10.00	5.00	0.50	3.80	3.80
11.00	5.00	0.50	4.10	3.81
12.00	5.00	0.50	4.60	3.83
10.00	5.00	0.50	3.77	3.77
10.00	6.00	0.50	3.28	3.28
10.00	7.00	0.50	2.97	2.97
10.00	8.00	0.50	2.82	2.82
10.00	10.00	0.50	2.40	2.40
10.00	11.00	0.50	2.23	2.23
10.00	12.00	0.50	2.10	2.10
10.00	5.00	0.10	1.62	1.62
10.00	5.00	0.20	2.12	2.12
10.00	5.00	0.30	2.48	2.48
10.00	5.00	0.40	3.42	3.42
10.00	5.00	0.50	3.80	3.80
10.00	5.00	0.60	4.10	4.10
10.00	5.00	0.70	4.42	4.42
10.00	5.00	0.80	4.53	4.53

Table 2: Pseudo-first order and second order rate constants for the effect of changes in dielectric constant on the rate of redox reaction of malachite green with metabisulphite ion at $[MG^+] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[S_2O_5^{2-}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$ and $T = 28 \pm 1^\circ\text{C}$

D	10³1/D	10³ k₁, s⁻¹	10¹ k₂, dm³ mol⁻¹ s⁻¹
77.57	12.9	1.47	1.47
75.05	13.3	1.70	1.70
72.52	13.8	1.90	1.90
70.00	14.3	2.30	2.30
67.47	14.8	2.55	2.55
64.94	15.4	2.78	2.78
62.42	16.0	3.18	3.18
59.89	16.7	3.63	3.63