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KINETICS AND OXIDATION OF THE REACTIONS BETWEEN DITHIONITE ION AND NITROCELLULOSE IN ACIDIC PHASE

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ABSTRACT

Kinetics and oxidation of the reactions between dithionite ion and nitrocellulose was studied in acidic phase under the condition of excess [$S_2O_4^{2-}$] at T = 29 ± 1°C, [H+] = 1.0 × 10^{-2} mol dm^{-3}, I = 1.0 mol dm^{-3} (Na_2SO_4) and λ_{max} = 360 nanometer. The oxidation-reduction result for NC^+ with dithionite ion displayed a 1:2 mole ratio. The reaction showed first order in terms of the oxidant [NC^+] as well as first order in terms of the reductant [$S_2O_4^{2-}$]. The rate of reaction indicated a first order relationship in terms of acid ion concentration. The reaction rate law is given as: $k_2 = a + b [H^+]$, where a = Intercept, b = Slope. The rate of reaction increased with an increase in the moles of sulphuric acid added. This implies great stability of NC^+ in an aqueous acidic medium. The rate decreased with an increase in sodium sulphate concentration. The spectroscopic investigation gave no signal for the formation of an intermediate complex. Based on the results obtained for the non-formation of intermediate complex, a plausible mechanism that favoured the outer-sphere mechanism was proposed for the studied reaction.

Keywords: Oxidation, Nitrocellulose, Dithionite ion

INTRODUCTION

Nitrocellulose (NC^+) is a non-toxic but highly flammable compound made from cellulose, nitric acid, or other heavy nitrate gas (Chai *et al.,* 2020). It is a key ingredient in smokeless gunpowder. With applicable in the: military, medical field, and industries. In the military NC^+ present in gun powder increases its stability and burn rate (Sullivan *et al.,* 2020). In the medical field, nitrocellulose is used in the application of biosensor and chips that can detect different antibodies, proteins, serums and other chemicals that affect the homeostasis of the body. Industrially, NC^+ is important in water filtration, electricity generation, and coating. Dithionite has successfully been used in the treatment of plumes of Cr (vi) (Ludwig *et al.*, 2007). It is also used for bleaching paper pulp, manufacturing chemicals, as a biochemical reductant; as a compound of sodium ($Na_2S_2O_4$). It is used in industrial dyeing processes for sulphur and vat dyes, for water treatment, gas purification, as a decolorizing agent in organic reactions, as a sulphonating agent as a source of sodium ion, and used in industries concerned with leather, foods, polymers, photography (Katherine *et al.*, 2019; Hamza *et al.*, 2012). Much work has not been reported on NC^+ in the literature which has promoted the kinetic and mechanistic pathways of NC^+ and dithionite ion in an aqueous acidic medium.

MATERIALS AND METHODS

Sulphuric acid and sodium sulphate were used to investigate the impact of added hydrogen ion and to maintain the ionic strength of the medium respectively. The stock solutions of nitrocellulose and sodium dithionite were prepared by dissolving appropriate amounts of the reagents in distilled water and making up the solution to a known volume. Analar grade reagents were employed without further purification.

Stiochiometric Determination

The stoichiometry of the reaction was investigated by keeping the concentration of nitrocellulose at 2.0 × 10^{-5} mol dm^{-3} while that of the dithionite ion were varied at (1.0 – 6.0) × 10^{-5} mol dm^{-3}, [H^+] = 1.0 × 10^{-2} mol dm^{-3}. The reaction mixture was kept for 24 hours until the absorbance value became constant. The graph of absorbance versus concentration was ploted to determine the mole ratio of the reaction (Mamman and Iyun, 2004).

Kinetics Experiment

Pseudo-first-order condition was applied for the kinetics experiment with $S_2O_4^{2-}$ concentration prepared at least 50 % greater than that of [NC^+]. Log (A_t - A_∞) against t were plotted (where A_t and A_∞ are the absorbance at a time, t and at the end of the reaction respectively). The rate constant (k_1) was calculated from the slope of the graph. The second- order rate constant (k_2) was obtained from k_1 as k_1/[$S_2O_4^{2-}$]. The reaction rate was supervised on a UV-visible spectrophotometer at 29 ± 1°C, [Hydrogen ion] = 1.0 × 10^{-2} mol dm^{-3}, I = 1.0 mol dm^{-3} (Na_2SO_4), [NC^+] = 2.0 × 10^{-5} mol dm^{-3}, [$S_2O_4^{2-}$] = (1.0 – 5.0) × 10^{-3} mol dm^{-3}. (Umoru and Udoh, 2022)

Change in Hydrogen Ion Concentration

Change in hydrogen ion concentration was investigated in the range of (0.5 – 3.0) × 10^{-2} mol dm^{-3} sulphuric acid, [NC^+] = 2.0 × 10^{-5} mol dm^{-3}, T = 29 ± 1°C, [$S_2O_4^{2-}$] = 2.0 x 10^{-3} mol dm^{-3} and I = 1.0 mol dm^{-3} (Na_2SO_4). Graph of k_2 versus [H^+] was plotted (Figure 4).

Impact of Change in Ionic Strength Concentration

The impact of ionic strength concentration was varified in the range of (0.5 – 3.0) mol dm^{-3} Na_2SO_4 at [NC^+] = 2.0 × 10^{-5} mol dm^{-3}, T = 29 ± 1°C, [$S_2O_4^{2-}$] = 2.0 x 10^{-3} mol dm^{-3} and [H^+] = 1.0 × 10^{-2} mol dm^{-3}. Log of k_2 versus √I was plotted (Figure 5.0).

Added Ions Impact

Added ions impact were studied as X = (0.5 – 2.5) × 10^{-2} mol dm^{-3} (X = Mg^{2+}, NH_4^+, NO_3^- and Cl^-) and the concentration of other reactants were kept constant at [NC^+] = 2.0 × 10^{-5} mol dm^{-3}, T = 29 ± 1°C, I = 1.0 mol dm^3, [$S_2O_4^{2-}$] = 2.0 x 10^{-5} mol dm^{-3} and [H^+] = 1.0 × 10^{-2} mol dm^{-3} (Table 2).

Polymerization Studies

Acrylonitrile solution was added to the partially oxidized reaction mixture containing all the reactants and excess of methanol was further added to ascertain if free radicals were initiated in the course of the reaction.

Determination of Intermediate Complex Formation

The electronic spectra of the reaction mixtures and that of nitrocellulose alone were compared within a range of 200 –

850 nm. Michaelis – Mentens plot of $1/k_1$ versus $1/[S_2O_4^{2-}]$ was achieved (Figure 6).

RESULTS AND DISCUSSION

Stoichiometry

A mole ratio of 1:2 was observed for $NC^+ : S_2O_4^{2-}$ respectively (Figure 1). Similar result was reported by Idris *et al.*, (2015). The rate equation is given as:

$$NC^+ + 2S_2O_4^{2-} \longrightarrow \text{Products} \qquad (1)$$

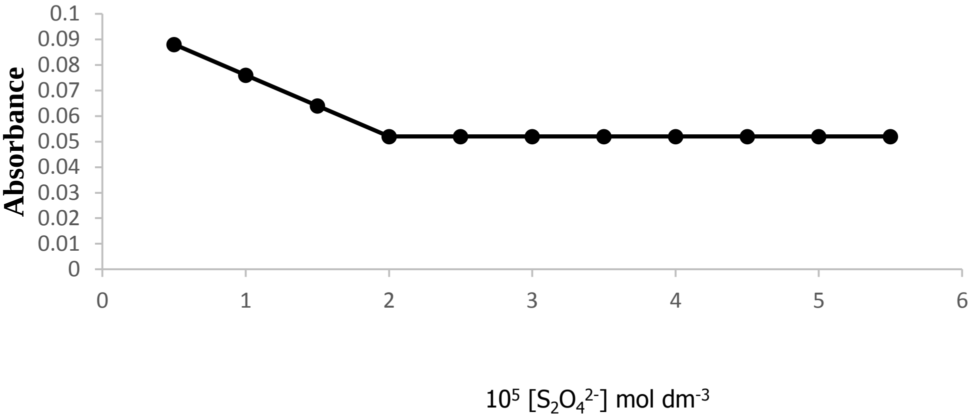

Figure 1: Stoichiometry Plot for the reduction of NC^+ by $S_2O_4^{2-}$ at $[NC^+] = 2 \times 10^{-5}$ mol dm^{-3}, $[S_2O_4^{2-}] = (1.0 – 6.0) \times 10^{-5}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-2}$ mol dm^{-3}, T = 29 ± 1°C, λ_{max} = 360 nm and I = 1.0 mol dm^{-3}.

Kinetics Experiment

The log of $(A_t - A_\infty)$ against time (mins) was linear to over 90% of the reaction (Figure 2.0). The linearity of this plot suggests that the reaction is the first order concerning $[NC^+]$. The plot of log k_1 versus log $[S_2O_4^{2-}]$ (Figure 3.0) was also linear with a slope of 1.0026, implying that the reaction is the first order concerning $[S_2O_4^{2-}]$. This is evident in the consistent values of k_2 (Table 1). Thus, the reaction is the second-order at constant $[H^+]$ and the rate equation for the reaction is:

$$-\frac{d}{dt}[NC^+] = k_2[NC^+][S_2O_4^{2-}] \qquad (2)$$

The order of one each for NC^+ and $S_2O_4^{2-}$ concentration in the reaction confirms to results reported by other authors regarding kinetic reactions involving dithionite and other oxidants: Onu and Iyun, (2000) oxidation of monomethyl fuschin by dithionite ion in aqueous hydrochloric acid; Hamza *et al.* 2012) oxidation of toluidine blue by dithionite ion in aqueous acidic medium; Idris *et al.* 2015) reaction of malachite green and dithionite ion.

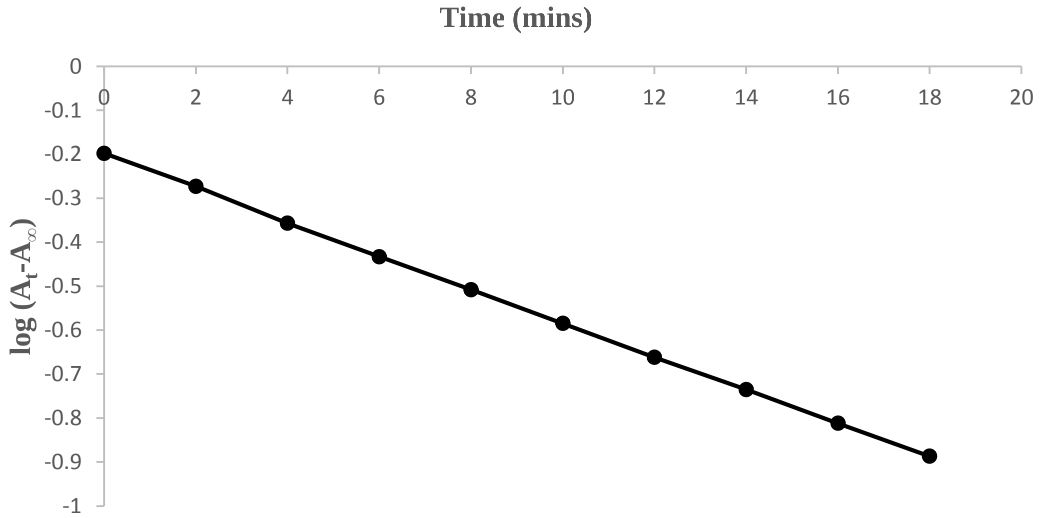

Figure 2: Plot for the Reaction of Nitrocellulose with Dithionite Ion. $[NC^+] = 2.0 \times 10^{-5}$ mol dm^{-3}, $[S_2O_4^{2-}] = (1.0 – 5.0) \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-2}$ mol dm^{-3}, I = 1.0 mol dm^{-3}, λ_{max} = 360 nm and T = 29 ± 1°C.

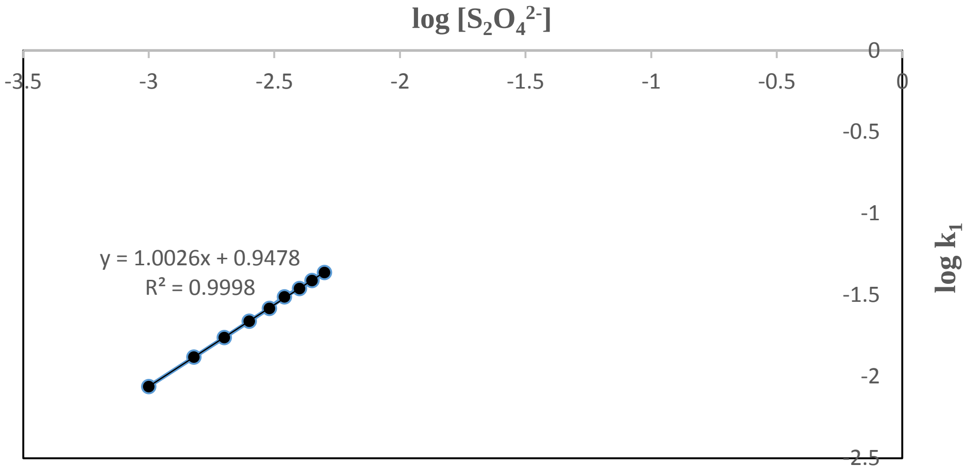

Figure 3: Plot of log k_1 versus log [$S_2O_4^{2-}$] for the Reaction of $S_2O_4^{2-}$ and NC^+ at [NC^+] = 2.0 x 10^{-5} mol dm^{-3}, I = 1.0 mol dm^{-3}, [H^+] = 1.0 x 10^{-2} mol dm^{-3}, λ_{max} = 360 nm and T = 29 ± 1°C.

Table 1: Rate Constants k_1 and k_2 for the Reaction of $S_2O_4^{2-}$ and NC^+. [NC^+] = 2.0 × 10^{-5} mol dm^{-3}, λ_{max} = 360 nm, T = 29 ± 1°C, [$S_2O_4^{2-}$] = (1.0 -5.0) x 10^{-3} mol dm^{-3}, [H^+] = 1.0 x 10^{-2} mol dm^{-3}, I = 1.0 mol dm^{-3} (Na_2SO_4).

10^3 [$S_2O_4^{2-}$] mol dm^{-3}	10^2 [H^+] mol dm^{-3}	I (Na_2SO_4) mol dm^{-3}	10^2 k_1 min^{-1}	k_2 dm^3 mol^{-1} min^{-1}
1.0	1.0	1.0	0.87	8.70
1.5	1.0	1.0	1.31	8.73
2.0	1.0	1.0	1.75	8.75
2.5	1.0	1.0	2.19	8.76
3.0	1.0	1.0	2.63	8.76
3.5	1.0	1.0	3.06	8.74
4.0	1.0	1.0	3.50	8.75
4.5	1.0	1.0	3.93	8.73
5.0	1.0	1.0	4.37	8.74
2.0	0.5	1.0	1.20	6.00
2.0	1.0	1.0	1.75	8.75
2.0	1.5	1.0	2.34	11.70
2.0	2.0	1.0	2.93	14.67
2.0	2.5	1.0	3.54	17.69
2.0	3.0	1.0	4.16	20.78
2.0	1.0	0.5	2.12	10.60
2.0	1.0	1.0	1.75	8.74
2.0	1.0	1.5	1.45	7.41
2.0	1.0	2.0	1.29	6.46
2.0	1.0	2.5	1.12	5.62
2.0	1.0	3.0	1.01	5.05

Change in Hydrogen Ion Concentration

The rate constants of the reactions were found to increase with increase in [H^+]. The plot of k_2 versus [hydrogen ion] was linear with a positive slope and intercept (Figure 4). The rate law agrees with the equation:

$$k_2 = a + b\,[H^+] \qquad (3)$$

where a = 3.03 dm^3 mol^{-1} min^{-1}, b = 5.83 dm^6 mol^{-2} min^{-1}.

Substituting equation (3) into equation (2), the rate of the reaction become:

$$-\frac{d}{dt}[NC^+] = (a + b\,[H^+])[NC^+][S_2O_4^{2-}] \qquad (4)$$

Similar results were reported in the oxidation reaction of adipato bridged iron(iii)-salen complex with dithionite ion in an acidic medium by Ukoha *et al.* 2015).

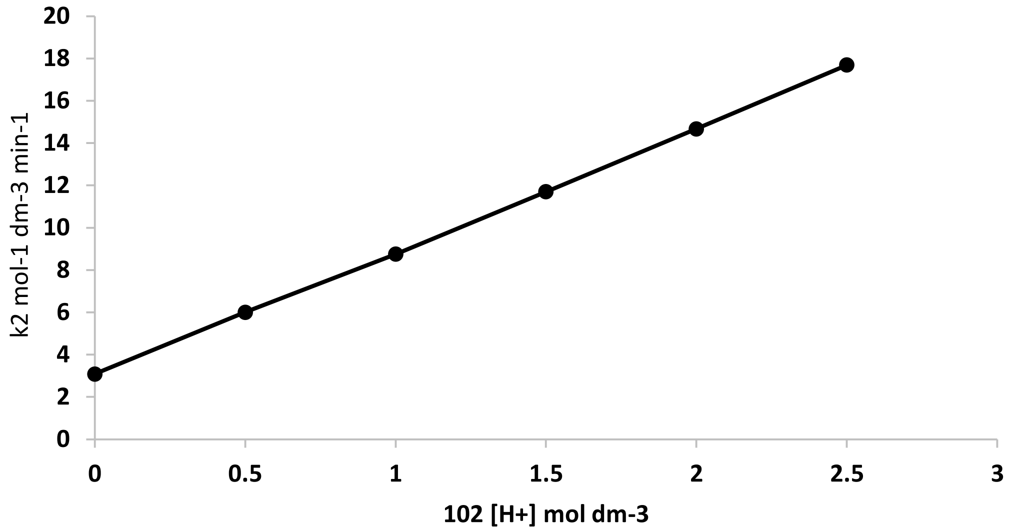

Figure 4: Plot of k_2 versus $[H^+]$ for the Reaction of NC^+ and $[S_2O_4^{2-}]$ at $[NC^+] = 2.0 \times 10^{-5}$ mol dm^{-3}, $[S_2O_4^{2-}] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-2}$ mol dm^{-3}, I = 1.0 mol dm^{-3}, λ_{max} = 360 nm and T = 29 ± 1°C.

Impact of Change in Ionic Strength

Change in ionic strength (Table 1) indicate that the rate decreased by an increase in the concentration of sodium sulphate. This trend suggests negative Bronsted – Debye salt effect, implying no formation of an activated complex during a reaction. A graph of k_2 versus √I (Figure 5.0) was linear with a slope of -0.3235 ($R^2 = 0.9995$). This result is consistent with the report given by Meyek *et al*., (2014), for the Oxidation of Naphthol Green B by Peroxydisulphate Ion in Acidic Medium; Ismaila *et al.* 2016), for the Redox Reaction of Neutral Red with Nitrite Ion in Aqueous Acidic Medium; Bugaje *et al.* 2021), for the Oxidation of Safranin – O by Permanganate Ion in Acidic Medium.

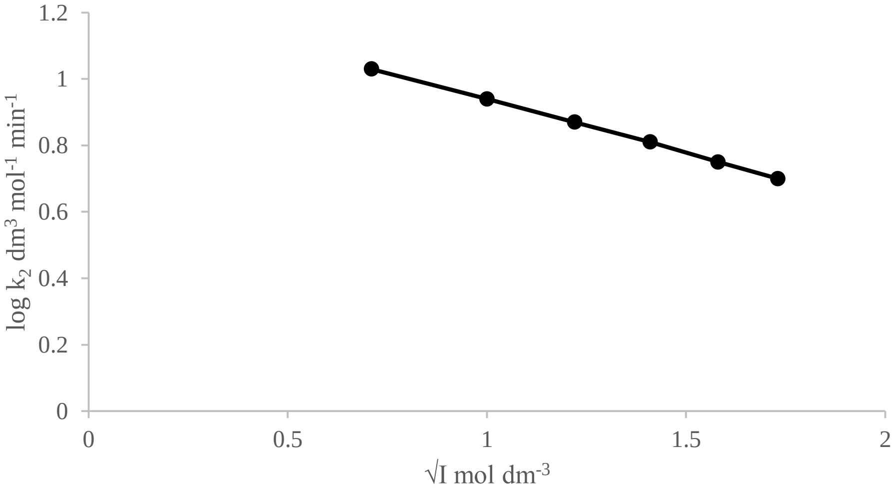

Figure 5: Graph of log k_2 versus √I for the Reaction of Dithionite Ion and Nitrocellulose at $[NC^+] = 2.0 \times 10^{-5}$ mol dm^{-3}, $[S_2O_4^{2-}] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-2}$ mol dm^{-3}, I = (0.5 – 3.0) mol dm^{-3}, T = 29 ± 1°C and λ_{max} = 360 nm.

Added Ions Impact

The addition of (Mg^{2+} and NH_4^+) to the reaction mixtures showed no significant increase in the rate of reaction. The rate of the reaction slightly decreased with an increase in the $[NO_3^-]$ to the reaction mixture. Increased concentration of the added Cl^- ion decreased the reaction rate (Table 2). This is in agreement with the results reported by (Hamza *et al.*, 2012) for the oxidation of toluidine blue by dithionite ion in an acidic medium; by (Onu and Iyun, 2000) oxidation of monomethyl fuschin by dithionite ion aqueous hydrochloric acid

Polymerization Studies

Added acrylonitrile solution to the reacting mixture even in excess of methanol did not form gelatinous precipitate. This indicates the absence of free radical in the reaction mixture, Umoru and Faruruwa, (2014), for the kinetics analysis of the oxidation of nitrate ion by methylthioninium chloride in an acidic medium.

Determination of Intermediate Complex Formation

The results for the spectroscopic test for intermediate complex formation showed no significant shift from the absorption maxima of 360 nm for nitrocellulose. The plot of $1/k_1$ against $1/[S_2O_4]$ gave a straight line graph passing through the origin

(Figure 6). This further suggests the absence of the formation of intermediate complex.

Table 2: Impact of Added Ions on the Second Order Rate Constants for Nitrocellulose and Dithionite Ion Reaction. $[NC^+] = 2.0 \times 10^{-5}$ mol dm^{-3}, $[S_2O_4^{2-}] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-2}$ mol dm^{-3}, I = 1.0 mol dm^{-3} (Na_2SO_4), T = 29 ± 1°C, and λ_{max} = 360 nm.

Ion	10^{-2}	10^2 k_1 min^{-1}	k_2 dm^3 mol^{-1} min^{-1}
Mg^{2+}			
	0.5	2.25	1.95
	1.0	2.27	1.95
	1.5	2.30	1.95
	2.0	2.30	1.97
	2.5	2.33	1.98
NH_4^+			
	0.5	1.38	0.80
	1.0	1.39	0.80
	1.5	1.40	0.81
	2.0	1.41	0.81
	2.5	1.41	0.82
NO_3^-			
	0.5	1.51	2.53
	1.0	1.52	2.51
	1.5	1.53	2.51
	2.0	1.54	2.50
	2.5	1.55	2.50
Cl^-			
	0.5	1.14	0.49
	1.0	1.17	0.45
	1.5	1.17	0.41
	2.0	1.19	0.37
	2.5	1.19	0.37

Product Analysis

The UV-visible spectra of the product gave no absorbance at 360 nm. In addition, the product of the reaction system was quantitatively identified. $BaCl_2$ solution of 2 ml was added to the reaction mixture followed by drops of dilute HCl, a white precipitate was formed which was insoluble in excess dilute HCl acid. This confirmed the presence of SO_4^{2-} ions as the product of analysis.

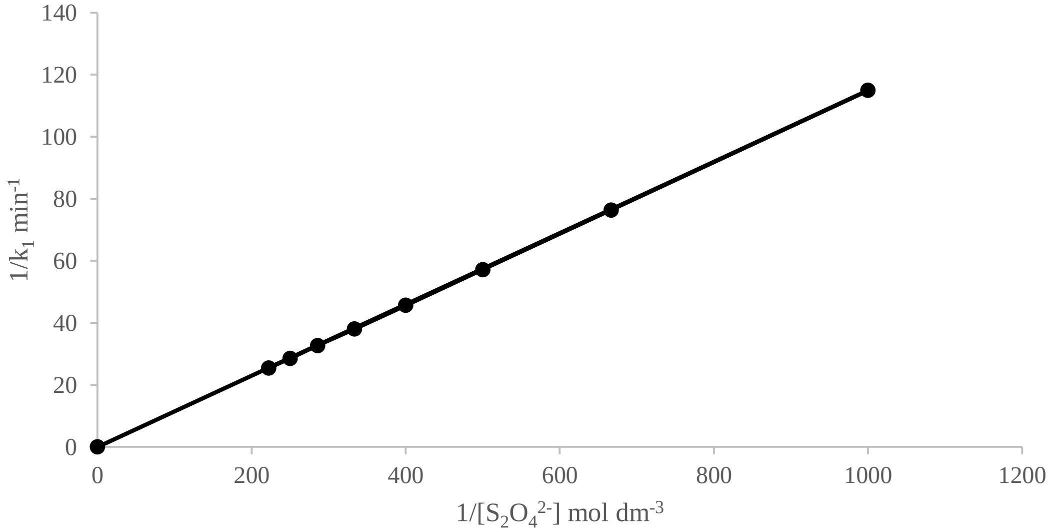

Figure 6: Plot of $1/k_1$ versus $1/[S_2O_4^{2-}]$ for the Reaction of NC^+ and $[S_2O_4^{2-}]$ ion at $[NC^+] = 2.0 \times 10^{-5}$ mol dm^{-3}, $[S_2O_4^{2-}] = (1.0 - 5.0) \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-2}$ mol dm^{-3}, T = 29 ± 1°C , I = 1.0 mol dm^{-3} (Na_2SO_4) and λ_{max} = 360 nm.

CONCLUSION

A mole ratio of 1:2 was obtained for nitrocellulose and dithionite ions respectively. The redox reaction was first-order concerning $[NC^+]$ and first-order concerning $[S_2O_4^{2-}]$, giving a second-order overall. The rate of reaction increased with an increase in [hydrogen ion]. This is an indication of the stability of NC^+ in acidic medium. The rate of reaction decreased with an increase in the concentration of Na_2SO_4. There was no positive polymerization in the reaction. The investigation of spectroscopic and Michaelis – Mentens studies did not indicate any intermediate complex formation during the reaction. An outer-sphere mechanism is proposed for the reaction.

Mechanism

A plausible mechanism has been established in support of the observed experimental data as follows:

$$S_2O_4^{2-} + H^+ \overset{K}{\rightleftharpoons} HS_2O_4^- \qquad (5)$$

$$HS_2O_4^- + NC^+ \xrightarrow{k_1} [HSO_4^-//NCS^+] \qquad (6)$$

$$S_2O_4^{2-} + H^+ \xrightarrow{k_2} HS_2O_4^- \qquad (7)$$

$$HS_2O_4^- + H_2O \xrightarrow{k_3} SO_4^{2-} + H_3SO^+ \qquad (8)$$

From equation (5)

$$[HS_2O_4^-] = K[S_2O_4^{2-}][H^+] \qquad (9)$$

$$Rate = k_1[HS_2O_4^-][NC^+] + k_2\,[S_2O_4^{2-}][H^+] \qquad (10)$$

Substituting equation (9) into equation (10)

$$Rate = k_1K[H^+][S_2O_4^{2-}][NC^+] + k_2[S_2O_4^{2-}][H^+] \qquad (11)$$

$$Rate = k_2 + k_1K[H^+][NC^+][S_2O_4^{2-}] \qquad (12)$$

Equation 12 is similar to equation 4

Where k_2 = ‘a’ is the intercept of 3.03 $dm^3\ mol^{-1}\ min^{-1}$ and k_1K = ‘b’ is the slope of 5.83 $dm^6\ mol^{-2}\ min^{-1}$.

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