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KINETIC APPROACH TO THE REDUCTION OF TOLUIDINE BLUE BY DITHIONATE ION IN AQUEOUS ACIDIC MEDIUM

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Kinetic Approach to the Reduction of Toluidine Blue by Dithionate Ion in Aqueous Acidic Medium

Babatunde O.A ^α & Ajayi J.O ^σ

Abstract- The kinetics of redox reduction of Toluidine blue (hereafter referred to as TB⁺) by dithionate ion have been studied in acidic medium under pseudo-first order condition of excess [S₂O₆²⁻] at 31 ± 1°C, [H⁺] = 1 × 10⁻² mol dm⁻³, ionic strength (I) = 0.5 mol dm⁻³ (NaCl) and λ max 600 nm. The redox reaction displays a 1:1 stoichiometry and the reaction was found to be first order and 3/2 order in the oxidant and the reductant respectively. The reaction is also catalyzed by hydrogen ion with the empirical rate law as:

$$-d[TB^+] = (a + b [H^+])[TB^+][S_2O_6^{2-}]^{3/2}$$

dt

Where a = 0.52 × 10⁻¹ dm³ mol⁻¹s⁻¹, b = 7.2 dm⁶ mol⁻²s⁻¹

The rate of reaction decreases with increase in ionic strength while it increases with increase in dielectric constant of the reaction mixture. Added anions and cations catalyzed the reaction. The result of kinetic studies, spectroscopic investigations and Michealis-Mentens plot did not suggest the formation of intermediate complex. Outer - sphere mechanism is therefore postulated for this reaction.

Keywords: kinetics, reduction, toluidine blue dye, dithionate.

I. INTRODUCTION

Toluidine blue dye (3-amino-7-(dimethylamino)-2-methyl phenothiazine chloride) is a coloured dye which is a phenothiazine that is mainly used as biological stains most especially in medical laboratory [1]. It has many uses, among the uses of this dye are: to detect oral cancer or pre-cancer, confirm the cells in rape victims [2, 3, 4, 5], as breast localization marker [6]. It also has antimicrobial property [7, 8]. Recently toluidine blue is used to study pneumocystis carinii pneumonia (pcp), a frequent and potentially life – threatening complication of the acquired immune deficiency syndrome (AIDS) [9,10]. It is also useful in chemistry as a redox indicator for many redox reactions such as Nitrite ion, Dithionite ion [11, 12] and Bromate ion [13] which has earlier been reported. As a dye, it is also very useful in the textile industry [14].

Dithionate is an important ion in inorganic chemistry [15, 16]. Strong oxidants oxidize dithionate to sulphate and strong reducing agents reduce them to sulphite and dithionite [17, 18].

In this paper, we report on the kinetics of reduction of TB⁺ and dithionate ion with the aim of providing relevant data to help gain a deep insight into the nature and reaction of both reactants so as to enhance the applicability of this dye in biological sciences, medicine, and industry.

II. EXPERIMENTAL

a) Materials

Stock solutions of TB⁺ were prepared by dissolving known quantities in distilled water and the observed λ max = 600 nm which agrees with literature value. Sodium dithionate (BDH), sodium chloride (BDH) and other reagents were used as supplied.

b) Stoichiometric studies

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method [19] and keeping the concentration of the dye constant at 1 × 10⁻³ mol dm⁻³, [H⁺] = 1 × 10⁻² mol dm⁻³, I = 0.5 mol dm⁻³, λ max = 600 nm, T = 31 ± 1°C and varying the concentration of S₂O₆²⁻ from (1 – 6) × 10⁻³ mol dm⁻³. The absorbance of the reacting mixture was obtained after the reaction had gone to completion by the steady readings recorded after 24 hours. The stoichiometry was then evaluated from the plot of absorbance against different concentrations of S₂O₆²⁻.

c) Kinetic Measurements

The kinetics of the reaction was monitored under various conditions by following decrease in the absorbance of TB⁺ at λ max = 600 nm on a colorimeter 252. All measurements were made under pseudo - first order conditions with [S₂O₆²⁻] in large excess over [TB⁺]. The pseudo-first order plots of log(A_t A_∞) versus time were made, where A_t and A_∞ are the absorbance at time (t) and at the end of the reaction respectively. From the slope of the plots, the pseudo-first order rate constants (k_o) were determined and second order rate constant

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(k_2) were obtained from k_0 as $k_0 / [S_2O_6^{2-}]$. The results were presented in table 1.

d) Effect of $[H^+]$

The effect of $[H^+]$ on the rate of reaction was studied within the range of $(0.5 - 3.0) \times 10^{-2} \text{ mol dm}^{-3}$ while $[TB^+]$ and $[S_2O_6^{2-}]$ were kept constant at $T = 31 \pm 1^\circ\text{C}$, $\lambda_{\text{max}} = 600 \text{ nm}$ and $I = 0.5 \text{ mol dm}^{-3}$ (NaCl). The results are presented in Table 1.

e) Effect of ionic strength

The effect of ionic strength on the rate of reaction was investigated in the range of $(0.5 - 2.4) \text{ mol dm}^{-3}$ (NaCl) while the concentration of other reactants were kept constant at $31 \pm 1^\circ\text{C}$. The result are presented in table 1.

f) Effect of Dielectric Constant

The effect of medium dielectric constant, D , on the rate of reaction was investigated by adding $0.1 - 0.6 \text{ cm}^3$ (accounting for 2 - 12%) of 10% mixture of water and acetone to the mixture, while keeping all other parameters constant.

g) Test for added ion

The effect of added cation and anion were investigated for $X = (0.5 - 2.0) \times 10^{-3} \text{ mol dm}^{-3}$ where $X = \text{Ca}^{2+}$, Mg^{2+} , NO_3^- and SO_4^{2-} while the concentration of other reagents were kept constant.

h) Test for intermediate complex formation

The spectrophotometric test was carried out by comparing the electronic spectra of the reaction mixture and that of TB^+ alone within 400 - 700 nm. Michealis - Mentens plot of $1/k_0$ versus $1/[S_2O_6^{2-}]$ was made Fig. 3.

i) Test for free Radical

The detection of free radicals in the reaction mixture was by Acrylamide polymerization studies.

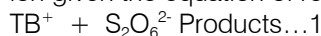
j) Product Analysis

This was carried out by reacting equimolar amount of the dye and dithionate at $31 \pm 1^\circ\text{C}$, $[H^+] = 1 \times 10^{-2} \text{ mol dm}^{-3}$ and $I = 0.5 \text{ mol dm}^{-3}$. After the completion of the reaction a colorless solution was obtained. This indicates the destruction of the quinoid (chromophore) group. BaCl_2 solution and HCl was then used to test for the inorganic product of the reaction.

III. RESULTS AND DISCUSSION

a) Stoichiometry

A stoichiometric study showed that one mole of the dye was consumed by one mole of the dithionate ion given the equation of reaction shown below:



The stoichiometry agrees with the consumption ratio obtained for dithionate and Triaminotolydiphenyl

The stoichiometry agrees with the consumption ratio obtained for dithionate and Triaminotolydiphenyl methane chloride [20].

b) Kinetics

The pseudo-first order plot of $\log (A_t - A_\infty)$ versus time for the reaction were linear to greater than 80% of the reaction indicating that the reaction is first order with respect to $[TB^+]$. A plot of $\log k_0$ (pseudo - first order rate constant) versus $\log [S_2O_6^{2-}]$ were linear with a slope of 1.5 showing that the reaction is 3/2 order with respect to $[S_2O_6^{2-}]$ (Fig.1). The second order rate constants k_2 were calculated as $k_0 / [S_2O_6^{2-}]$ and the reading were found to be fairly constant, the results are presented in Table 1. Thus the overall order of the reaction is 5/2 at constant $[H^+]$ and the rate equation for the reaction is:

$$- \frac{d[TB^+]}{dt} = k_2 [TB^+] [S_2O_6^{2-}]^{3/2} \dots 2$$

$$\text{where } k_2 = 1.19 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Similar fractional order has been reported for redox reaction of TB^+ with dithionite ion, stannous ion and phenylhydrazine (pz) [12, 21, 23] respectively.

c) Effect of $[H^+]$

The value of the reaction rate constant of the reaction increases with increasing $[H^+]$ (Table 1). The plot of k_2 versus $[H^+]$ was linear with an intercept on k_2 axis. The acid dependence rate constant is therefore given as:

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

Based on the above observations, the rate equation for the reaction can then be written as:

$$- \frac{d[TB^+]}{dt} = (a + b [H^+]) [TB^+] [S_2O_6^{2-}]^{3/2} \dots 4$$

Where $a = 0.52 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $b = 7.2 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$

From equation 4 it is evident that the reaction proceeds through two pathways i.e acid dependent and acid independent reaction pathways. Similar trend has been reported in the reaction of TB^+ with ascorbic acid by [24].

The positive $[H^+]$ dependence on the rate of oxidation of dithionate has been explained in terms of its protonation to form HS_2O_6 which subsequently reacts with the substrate in a slow step to give the product [25].

d) Effect of ionic strength

The rate of reduction of TB^+ by $S_2O_6^{2-}$ decreases with increasing ionic strength (Table 1), this suggest that activated complex is formed from two ions of unlike charges. A plot of k_2 versus $\sqrt{I}$ gave a slope of 0.07 (Fig.3). This suggests that some other interactions

must be taking place to account for this non- integral value of the slope for the product species at the transition state.

e) Effect of Dielectric Constant

The rate of the reaction increases with increase in dielectric constant Table 2. This suggests that both positively and negatively charged species are participating in the rate determining step.

f) Effect of added species

Addition of Mg^{2+} , Ca^{2+} , NO_3^- and SO_4^{2-} ions to the reaction mixture catalyzes the rate of reaction Table 3. The enhancing effects suggest that there is interference of these ions in the transition state, which shows that an outer-sphere mechanism might be in operation [26, 27].

g) Free radical test

Acrylamide, a radical scavenger was added to the partially reacted mixture in the presence of excess of methanol, there was no formation of gelatinous precipitate - an indicator of the absence of free radical in the reaction.

h) Test for intermediate complex

Spectroscopic results indicate no significant shift from the absorption maxima of 600nm which is characteristic of Toluidine blue dye. This suggests that the formation of an intermediate complex during the reaction is very unlikely [28].

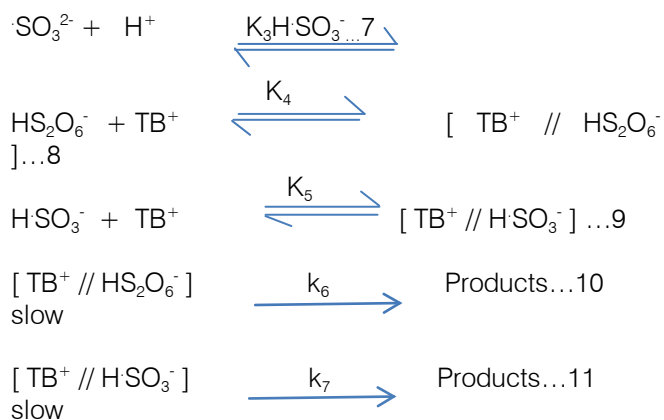
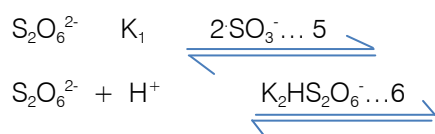
Michealis- Menten's plots of $1/k_o$ versus $1/[S_2O_6^{2-}]$ gave a straight line which passes through the origin fig. 4. This further suggests the absence of formation of intermediate complex thereby supporting the outer - sphere mechanism for this reaction Babatunde [19].

IV. PRODUCT ANALYSIS

After the completion of the reaction, a colourless solution was obtained. The UV visible spectra of the product showed no absorption peak at λ_{max} of 600 nm. This indicates the destruction of the quinoid (chromophore) group. In addition $BaCl_2$ solution was added to the complete reaction mixture of $TB^+ / S_2O_6^{2-}$ followed by dilute HCl; a white precipitate was obtained which was insoluble in excess dilute HCl indicating the presence of SO_4^{2-} ions.

a) Reaction mechanism

The mechanism proposed below accommodates all the experimental findings for the reaction of Toluidine blue dye with dithionite ion.



Equations 10 and 11 are the rate determining steps.

$$\text{Rate} = k_6 [TB^+ // HS_2O_6^{\cdot-}] + k_7 [TB^+ // HSO_3^-] \dots 12$$

From equation 8

$$[TB^+ // HS_2O_6^{\cdot-}] = K_4 [HS_2O_6^{\cdot-}] [TB^+] \dots 13$$

And from equation 6

$$[HS_2O_6^{2-}] = K_2 [S_2O_6^{2-}] [H^+] \dots 14$$

From equation 9

$$[TB^+ // HSO_3^-] = K_5 [HSO_3^-] [TB^+] \dots 15$$

From equation 7

$$[HSO_3^-] = K_3 [SO_3^{2-}] [H^+] \dots 16$$

From equation 5

$$[SO_3^{2-}] = K_1^{1/2} [S_2O_6^{2-}]^{1/2} \dots 17$$

$$\text{Rate} = K_2 K_4 k_6 [S_2O_6^{2-}] [TB^+] [H^+] + K_1^{1/2} K_3 K_5 k_7 [S_2O_6^{2-}] [TB^+] [H^+] \dots 18$$

Rearrange equation

$$(K_2 K_4 k_6 + K_1^{1/2} K_3 K_5 k_7) [H^+] [TB^+] [S_2O_6^{2-}]^{3/2} \dots 1$$

$$(a + b [H^+])^2 [TB^+] [S_2O_6^{2-}]^{3/2}$$

Where $a = 0.52 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $b = 7.2 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$

V. CONCLUSION

Redox reaction of toluidine blue dye with Dithionite ion showed a stoichiometry of 1:1 and the reaction involve two independent pathways, one directly dependent on $[H^+]$ and the other indirectly independent on $[H^+]$.

The evidence for the formation of intermediate complex was neither detected nor identified by the spectroscopic method suggesting an outer - sphere mechanism [28].

Table 1 : Pseudo-first order and second order rate constants for the reduction of TB⁺ by dithionate ions in aqueous acidic medium at [TB⁺] = 1 x 10⁻³ mol dm⁻³, λ max = 600 nm, T = 31 ± 1°C.

[S ₂ O ₆ ²⁻] x 10 ⁻³ x 10 ⁻² mol dm ⁻³	[H ⁺] mol dm ⁻³ mol dm ⁻³	I(NaCl) x 10 ⁻³	k ₀ k ₂ x 10 ⁻¹	s ⁻¹ dm ³ mol ⁻¹ s ⁻¹
20	1.0	0.5	2.0	1.00
30	1.0	0.5	3.7	1.26
40	1.0	0.5	4.40	1.11
50	1.0	0.5	6.15	1.23
60	1.0	0.5	8.00	1.33
30	0.5	0.5	3.02	1.01
30	1.0	0.5	3.68	1.23
30	1.5	0.5	5.64	1.88
30	2.0	0.5	6.92	2.31
30	2.5	0.5	7.35	2.45
30	3.0	0.5	8.42	2.81
30	1.0	0.5	3.68	1.23
30	1.0	1.0	3.53	1.18
30	1.0	1.6	3.41	1.14
30	1.0	2.0	3.35	1.12
30	1.0	2.5	3.291.10	

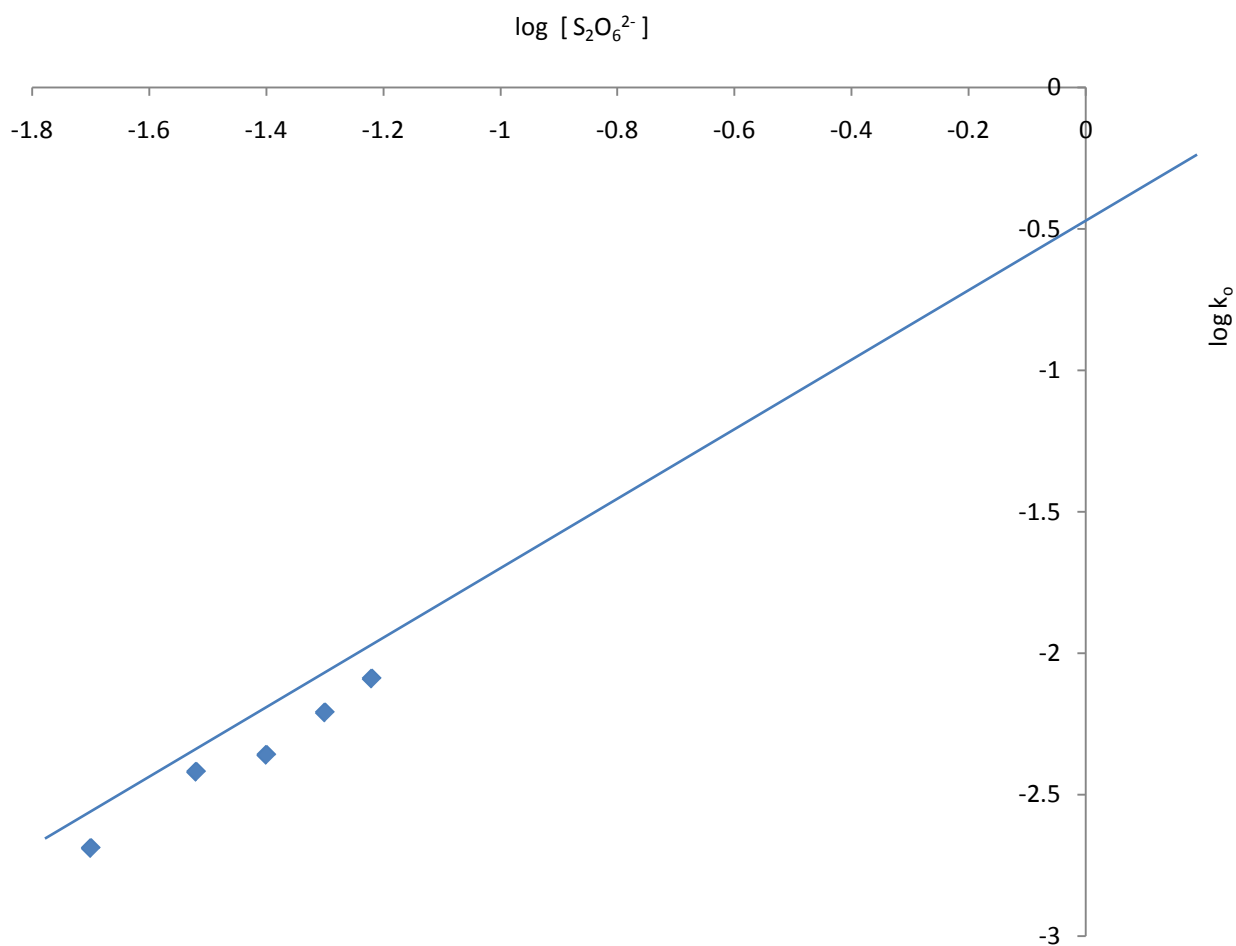


Fig.1 : Pseudo – first order plot of $\log k_o$ versus $\log [S_2O_6^{2-}]$ for reduction of TB^+ by $S_2O_6^{2-}$ at $[TB^+] = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $[H^+] = 1 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 600 \text{ nm}$, $T = 31 \pm 1^\circ\text{C}$.

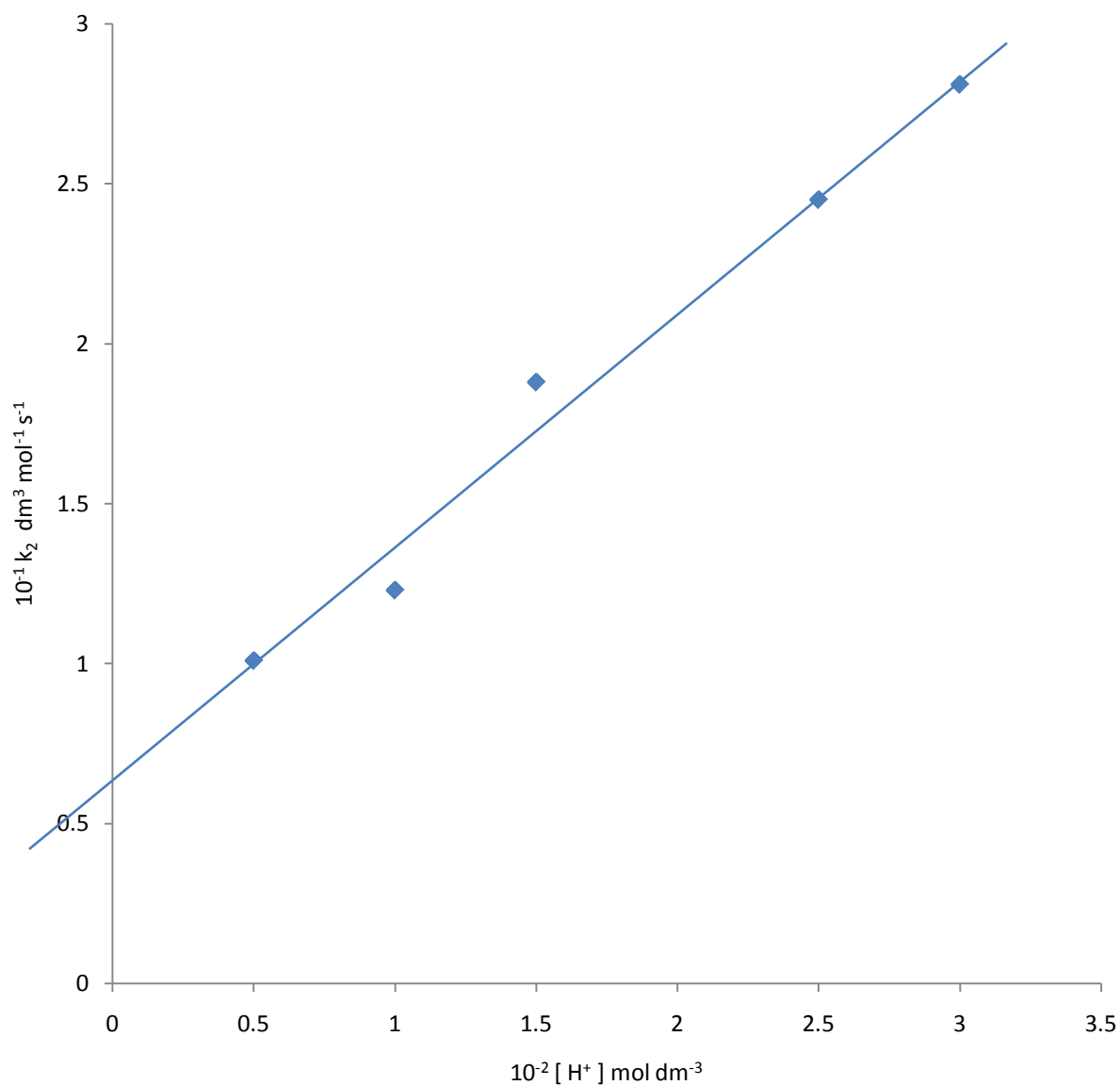


Fig. 2: Pseudo – first order plot of k_2 versus $[\text{H}^+]$ for the reduction of dithionite ion at $[\text{S}_2\text{O}_6^{2-}] = 30 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{TB}^+] = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 600 \text{ nm}$, $T = 31 \pm 1^\circ\text{C}$.

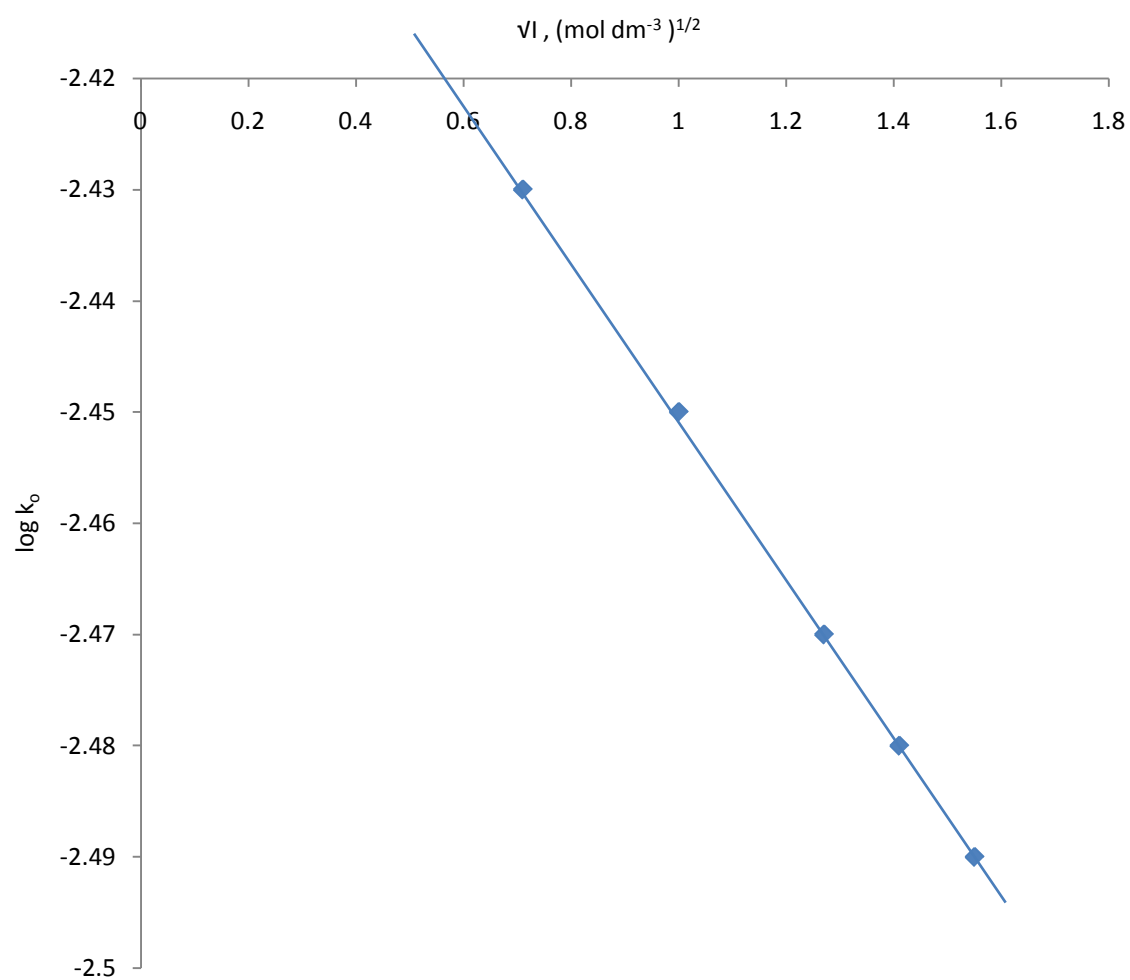


Fig.3 : Plot of $\log k_0$ versus $\sqrt{I}$ for the reduction of TB^+ by dithionate ion.

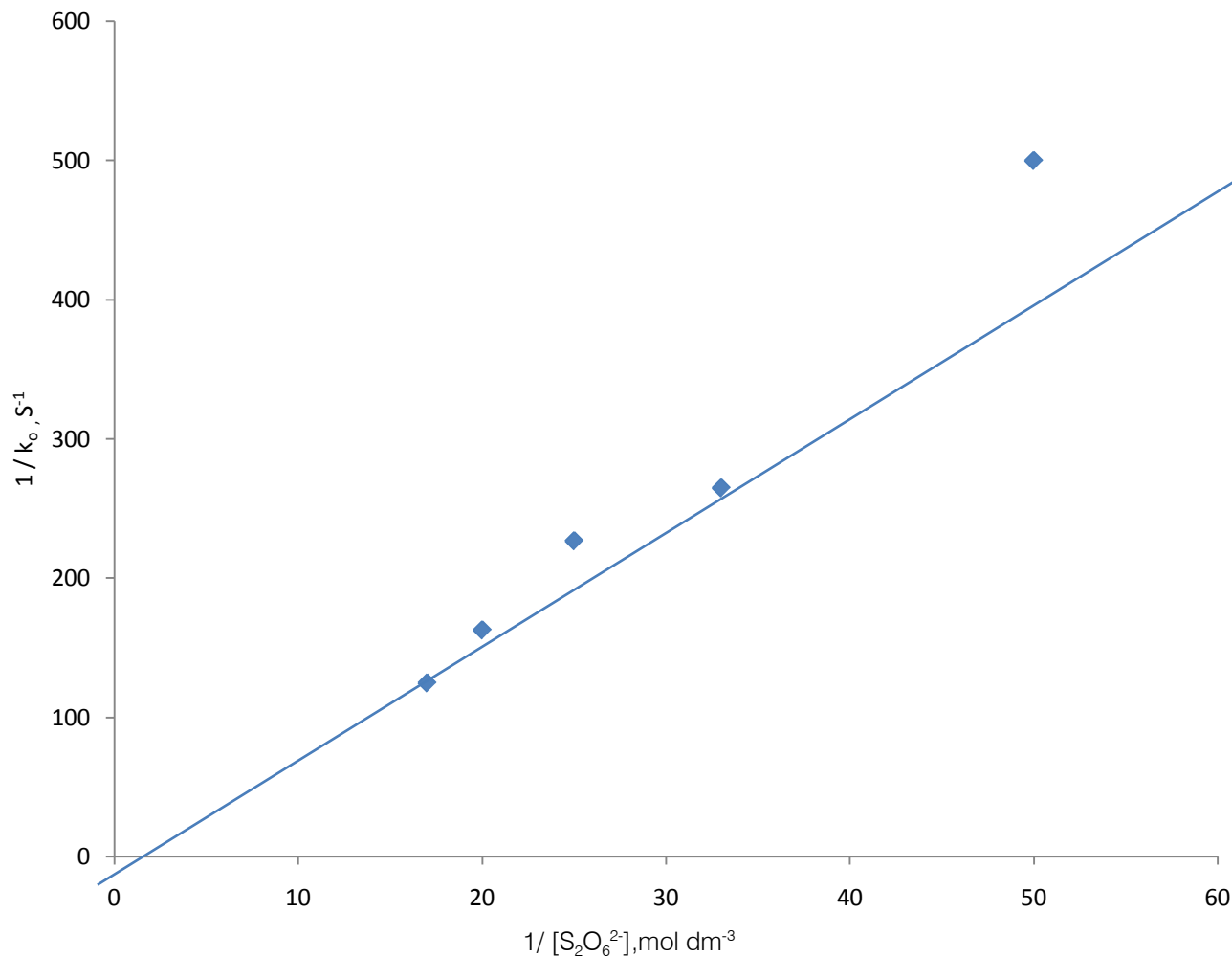


Fig. 4 : Michealis – Menten's plot for the reduction of TB^+ with $S_2O_6^{2-}$ ion at $[TB^+] = 1 \times 10^{-3} \text{mol dm}^{-3}$, $[S_2O_6^{2-}] = 30 \times 10^{-3} \text{mol dm}^{-3}$, $[H^+] = 1 \times 10^{-2} \text{mol dm}^{-3}$, $I = 0.5 \text{mol dm}^{-3}(\text{NaCl})$, $\lambda_{\text{max}} = 600 \text{nm}$, $T = 31 \pm 1^\circ\text{C}$.

Table 2 : Pseudo – first order and second order rate constants for the effect of change in dielectric constant of the medium on the toluidine blue oxidation by dithionate ion at $[TB^+] = 1 \times 10^{-3} \text{mol dm}^{-3}$, $[H^+] = 1 \times 10^{-2} \text{mol dm}^{-3}$, $[S_2O_6^{2-}] = 30 \times 10^{-3} \text{mol dm}^{-3}$, $I = 0.5 \text{mol dm}^{-3}(\text{NaCl})$, $\lambda_{\text{max}} = 600 \text{nm}$, $T = 31 \pm 1^\circ\text{C}$.

D $\text{s}^{-1} \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	k_o $\times 10^{-2}$	k_2 $\times 10^{-1}$
0.2	0.893.00	
0.3	1.51	5.00
0.4	1.73	5.77
0.5	1.88	6.25
0.6	2.05	6.83

Table 3: Pseudo-first order and second order rate constants for the effect of added

ions on the reaction of TB⁺ with dithionate ions at [TB⁺] = 1 x 10⁻³ mol dm⁻³, [S₂O₆²⁻] = 30 x 10⁻³ mol dm⁻³, [H⁺] = 1 x 10⁻² mol dm⁻³, I = 0.5 mol dm⁻³ (NaCl), λ_{max} = 600 nm, T = 31 ± 1°C.

X	10 ⁻³ [X], mol dm ⁻³	10 ⁻² k _o s ⁻¹	k ₂ , dm ³ mol ⁻¹ s ⁻¹
SO ₄ ²⁻	0.5	1.50	0.50
	1.0	1.52	0.51
	1.5	1.55	0.52
	2.0	1.60	0.53
	2.5	1.63	0.54
	3.0	1.66	0.55
NO ₃ ⁻	0.5	1.79	0.59
	1.0	1.82	0.61
	1.5	1.86	0.62
	2.0	1.89	0.63
	2.5	1.92	0.64
	3.0	1.93	0.63
Mg ²⁺	0.5	3.64	1.21
	1.0	3.42	1.14
	1.5	3.34	1.11
	2.0	3.29	1.10
	2.5	3.19	1.06
	3.0	3.16	1.05
Ca ²⁺	0.5	1.15	0.38
	1.0	1.17	0.39
	1.5	1.19	0.40
	2.0	1.20	0.40
	2.5	1.23	0.41
	3.0	1.24	0.41

REFERENCES RÉFÉRENCES REFERENCIAS

- Elderfield, R.C. (1957). *Heterocyclic compounds*. Chpman and Hall Limited London 6:722.
- Kiese, M. and Waller, H.D. (1951). Reduction of hemoglobin and oxygen for reversibly reducible dyes in red cells. *Naunyn-Schmiedebergs Arch Pharmacology*.213:44(German).
- Jeffrey, S. B. and Jones J. S. (2004). Significant of toluidine blue positive findings after speculum examination for sexual assault. *The American journal of emergency medicine*.22(3): 201 – 203.
- Epstein, J.B. and Guneri, P. (2009). The adjunctive role of toluidine blue in detection of oral premalignant and malignant lesions. *Curr Opin Otolaryngol Head Neck Surg*. 17:79-87.
- Carson, F. L. and Hladik, C. (2009). *Histotechnology: A Self-Instructional Text* (3 ed.). Hong Kong: American Society for Clinical Pathology Press. Pp 188.
- David, L. M. and Barbara, C.(1999). Fluorescent Tissue Site- Selective Lanthanide Chelate, Tb-PCTMB for Enhanced Imaging of Cancer. *Anal. Chem*. 71(14) :2607-2615.
- Ko" merik,N.; Nakanishi,H.;Mac, R.; ,A.J. Henderson, A.J.; Speight, B. and Wilson, M.(2003). In vivo killing of porphyromonasgingivalis by toluidine blue –mediated photosensitization in an animal model. *Antimicrob . Agents chemother* .47(3): 932.
- Williams, J. A.; Pearson;Colles, G. J. and Wilson,M.J.M.(2004).The photo activated antibacterial action of toluidine blue in a collagen matrix and in carious dentine. *Caries Res*.38 : 530-6.
- Metersky M. L., Colt H. G., Olson L. K. and Shanks T. G. (1995). AID – related spontaneous pneumothorax, risk factors and treatment. *Chest*.108(4): 946 – 51.
- Chakaya J. M., Bii C., Ng'ang'a L., Amukoye E., Ouko T., Muita L., Gitau J., Odongo I., Kabanga J. M., Nagai K., Suzumura S., SugiuraY. (2003). Pneumocystis carinii pneumonia in HIV/AIDS patients at an urban district hospital in Kenya. *East Afr. Med. J*. 80(1):30-5.
- Hamza, S. A., Iyun, J. F. and Idris, S. O. (2012). Kinetics and mechanism of the redox reaction of toluidine blue and nitrite ions in aqueous acidic medium. *Archives of Applied Science Research*.4(1): 10 – 18.
- Hamza S.A., Iyun J.F. and Idris S.O.(2012). Kinetics and Mechanism of Toluidine blue Reduction by Dithionite Ion in Aqueous Acidic Medium. *Journal of Chemical and Pharmaceutical Research*,4(1): 6-13.
- Zenovia M. (2011). Kinetic – spectrophotometric determination of nitrite by its accelerating effect on the oxidation of toluidine blue by bromate. *Revue Roumaine de Chimie*. 56(1): 39 – 46.

14. Cizek Z. and Studlova V. (1984). Kinetics and Mechanisms of Toluidine Blue Reduction by Dithionite Ion in Aqueous Acidic Medium. *Talanta*.31:547 – 562.
15. Baran, M. P., Bugay, O. A., Kolesnik, S. P., Maksimenko, V. M., Teslenko, V. V., Petrenko, T. L. and Desrosiers, M. F. (2006). Barium dithionate as a EPR dosimeter. *Radiation Protection Dosimetry*.120: 202.
16. Ishii, M. (2001). Structure of Some Copper (II) Complexes Containing $S_2O_6^{2-}$ Ion. *Bulletin of the Yamagata University* 5(1):7.
17. Greenwood, N. and Earn Shaw, A. (1997). Chemistry of the Elements (2nd Edn.), Oxford: Butterworth-Heinemann. ISBN 0-7506-3365-4.
18. Murthy, G. S. Eager, R. L. and McCallum, K. J. (1971). Radiation Chemistry of Dithionates. *Can. J. Chem.* 49(22): 3733.
19. Babatunde O. A. (2008). A study of the kinetics and mechanism of oxidation of L-ascorbic acid by permanganate ion in acidic medium. *World J. of Chem.*, 3(1):27-31.
20. Babatunde, O. A. (2007). Mechanism of the reduction of Triamino/dimethane chloride by dithionate in acidic medium – kinetic approach. *The Academy Journal of Research and Defence Studies*. 14Pp 232 – 239.
21. Jonnalagada S.B. and Dumba M. (1993). Reduction of toluidine blue by stannous ion at low pH: Kinetics and simulations. *International Journal of Chemical Kinetics*. 25(9): 745-753.
22. Jonnalagada, S B. and Gollapalli, N. R. (2000). Kinetics of reduction of TB^+ with sulfite- kinetic salt effect in elucidation of mechanism. *J Chem. Educ.*, 77, 4 506.
23. Jonnalagada, S.B. and Nattar, K. (1999). A kinetics and mechanism of autocatalysed reaction between phenyl hydrazine and toluidine blue in aqueous solution. *Int. J. Chem. Kinet.*, 31, 83.
24. Hamza, S.A. (2012). Kinetic and mechanism of the redox reactions of toluidine blue with some oxyanions and ascorbic acid in Aqueous Acidic Medium. *Archives of Applied Science Research*. 4(1):10-18
25. Grases, F., Genester, C. and Amat, E. (1986). Kinetic studies on the oxidation of ascorbic acid by technetium(VII). *International Journal of Chemical Kinetics* 18(8): 899–905.
26. Pryztas T.J. and Sutin, N. (1973). Kinetic studies of anion assisted outer-sphere electron transfer reaction. *J. Am. Chem. Soc.*, 95: 5595.
27. Babatunde, O. A. (2009). Kinetics and Mechanism of reduction of parafuchsin by nitrite ions in aqueous acid medium. *World J. of Chem.*, 4(1),39-44.
28. Iyun, J.F., Peters, A.O. and Babatunde, O.A. (2002). Kinetics of reduction of triaminotolydiphenylmethane chloride (rosanilinehydrochloride) by hydroxide ions in aqueous medium. *Indian Journal of Chemistry*.41A: 967 – 969.