Global Journal of Science Frontier Research
Chemistry
Volume 13 Issue 8 Version 1.0 Year 2013
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

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GJSFR-B Classification : FOR Code: 250000

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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 $[S_2O_6^{2-}]$ at 31± 1°C, $[H^+] = 1 \times 10^{-2}$ 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:

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

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

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 coloureddyewhich is a phenothiazinethat 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 pneumocysticscarinii 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 =600nm whichagrees 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 constantat 1×10^{-3}mol dm^{-3}, $[H^+] = 1 \times 10^{-2}$mol dm^{-3}, I= 0.5mol dm^{-3}, λ max=600nm, T= 31± 1°C and varying the concentration of $S_2O_6^{2-}$from $(1 - 6) \times 10^{-3}$moldm^{-3}. The absorbance of the reacting mixture was obtained after the reaction had gone to completion by the steady readings recorded after 24hours. The stoichiometry was then evaluated from the plot of absorbance against different concentrations of $S_2O_6^{2-}$.

c) Kinectic 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 $[S_2O_6^{2-}]$ in large excess over $[TB^+]$. The pseudo-first order plots of $\log(A_t - A_\infty)$ versus time were made, where$A_t$and$A_\infty$are the absorbance attime (t)and at theend 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 fromk_o as k_o / [$S_2O_6^{2-}$]. 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) x 10^{-2} mol dm^{-3} while [TB^+] and [$S_2O_6^{2-}$] were kept constant at T = 31 ± 1°C , λ max = 600 nm and I = 0.5 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) moldm^{-3}(NaCl) while the concentration of other reactants were kept constant at 31± 1°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 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)x 10^{-3}mol dm^{-3} where X = 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 testwas carriedout by comparing the electronic spectra of the reaction mixture and that of TB^+ alone within 400 – 700 nm.Michealis – Mentens plot of 1/k_o 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 ± 1°C, [H^+] = 1x10^{-2}mol dm^{-3} and I = 0.5mol 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:

$TB^+ + S_2O_6^{2-}$ Products…1

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) Kinectics

The pseudo-first order plot of log (A_t - A_∞) 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_o(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_o / [$S_2O_6^{2-}$] and the reading were found to be fairly constant, the results are presented in Table 1. Thus the overall order of the reaction is 5/2at constant [H^+] and the rate equation for the reaction is:

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

wherek_2 = 1.19 x 10^{-1} $dm^3mol^{-1}s^{-1}$

Similar fractional order has been reported for redox reaction of TB^+ with dithionite ion, stannous ion andphenylhydrazine (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 ofk_2 versus [H^+] was linear with an intercept on k_2 axis. The acid dependence rate constant is therefore given as:

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

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

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

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

From equation 4it 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 √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 enhancingeffects 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 throughthe origin fig. 4. This further suggests the absence of formation of intermediate complex thereby supporting the outer – sphere mechanism for this reactionBabatunde [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 excessdilute HCl indicating the presence of SO_4^{2-} ions.

a) Reaction mechanism

The mechanism proposed below accommodates all the experimental findingsfor the reaction of Toluidine blue dye with dithionate ion.

$$S_2O_6^{2-} \quad K_1 \quad \underset{\rightleftharpoons}{2{\cdot}SO_3^{-} \ldots 5}$$

$$S_2O_6^{2-} + H^+ \quad \underset{\rightleftharpoons}{K_2HS_2O_6^{-} \ldots 6}$$

$${\cdot}SO_3^{2-} + H^+ \quad \underset{\rightleftharpoons}{K_3H{\cdot}SO_3^{-} \ldots 7}$$

$$HS_2O_6^{-} + TB^+ \overset{K_4}{\rightleftharpoons} [\ TB^+ \ // \ HS_2O_6^{-}\ ] \ldots 8$$

$$H{\cdot}SO_3^{-} + TB^+ \overset{K_5}{\rightleftharpoons} [\ TB^+ // H{\cdot}SO_3^{-}\ ] \ldots 9$$

$$[\ TB^+ // HS_2O_6^{-}\ ] \text{ slow} \xrightarrow{k_6} \text{Products} \ldots 10$$

$$[\ TB^+ // H{\cdot}SO_3^{-}\ ] \text{ slow} \xrightarrow{k_7} \text{Products} \ldots 11$$

Equations10 and 11 are the rate determining steps.

$$\text{Rate} = k_6 [\ TB^+ // HS_2O_6^{-}\ ] + k_7 [\ TB^+ // H{\cdot}SO_3\ ] \ldots 12$$

From equation 8

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

And from equation 6

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

From equation 9

$$[\ TB^+ // H{\cdot}SO_3\ ] = K_5 [\ H{\cdot}SO_3\ ] [\ TB^+\ ] \ldots 15$$

From equation 7

$$[\ H{\cdot}SO_3\ ] = K_3 [\ {\cdot}SO_3^{2-}\ ][\ H^+\ ] \ldots 16$$

From equation 5

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

$$\text{Rate} = K_2K_4\ k_6 [\ S_2O_6^{2-}\ ][\ TB^+\ ] [\ H^+\ ] + K_1^{1/2}K_3K_5k_7[S_2O_6^{2-}\ ][\ TB^+\ ] [\ H^+\ ] \ldots 18$$

Rearrange equation

$$(K_2K_4\ k_6 + K_1^{1/2}K_3K_5k_7)[\ H^+\ ][\ TB^+][\ S_2O_6^{2-}\ ]^{3/2} \ldots 1$$

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

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

V. CONCLUSION

Redox reaction of toluidine blue dye with Dithionate 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].

Table1 : Pseudo-first order and second order rate constants for the reduction of TB^+ by dithionate ions in aqueous acidic medium at $[TB^+] = 1 \times 10^{-3}$ mol dm^{-3} , λ max = 600 nm , T = 31 ± 1^{O}C.

$[S_2O_6^{2-}]$ x10^{-3}	$[H^+]$	I(NaCl)	k_o k_2	
x 10^{-2}		x 10^{-3}	x 10^{-1}	
mol dm^{-3}	mol dm^{-3} mol dm^{-3}			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	

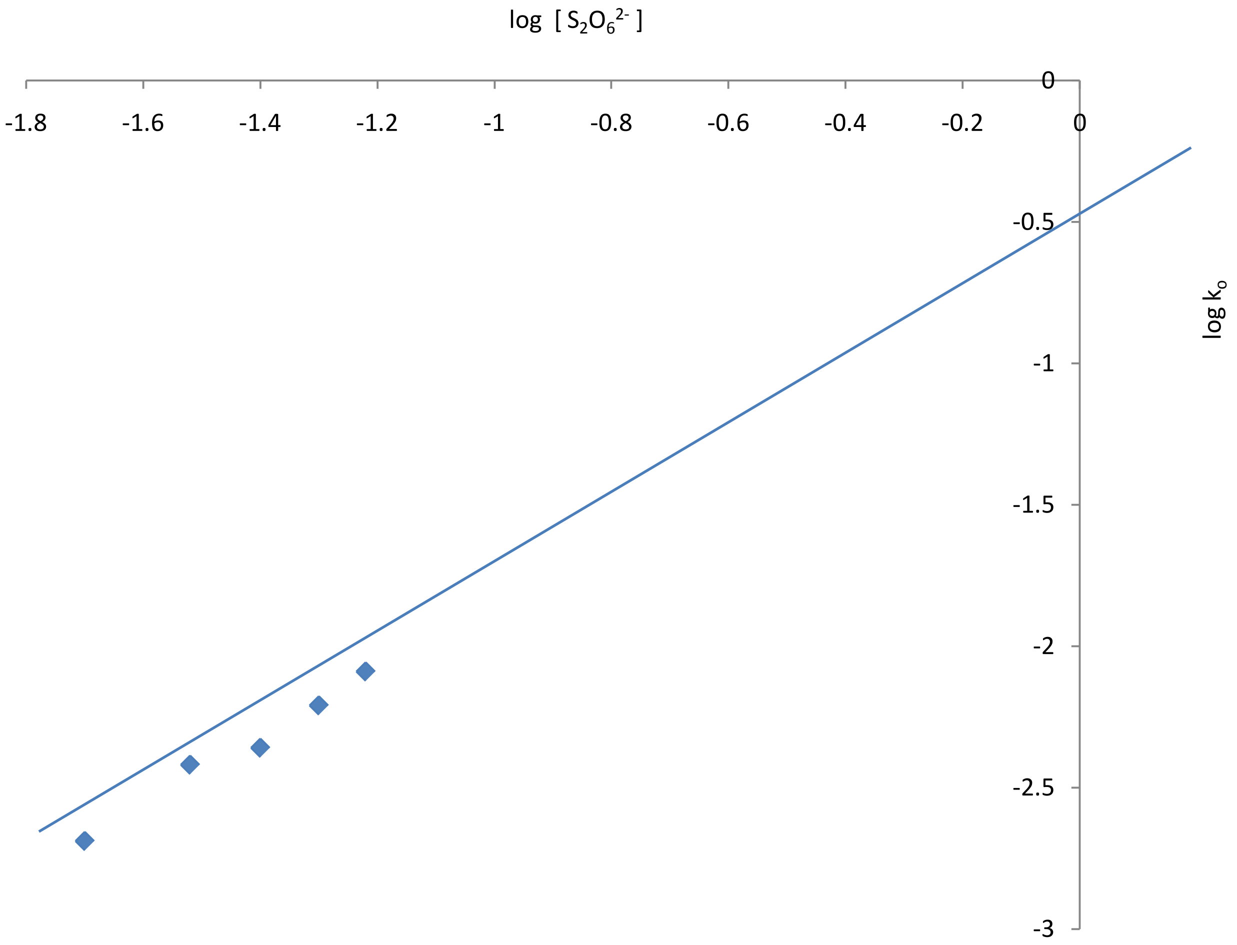

Fig.1 : Pseudo – first order plot oflog k_o versus log [$S_2O_6^{2-}$] for reduction of TB^+ by $S_2O_6^{2-}$ at [TB^+] = 1 x 10^{-3}mol dm^{-3} , [H^+] = 1 x 10^{-2} mol dm^{-3} , I = 0.5 mol dm^{-3} ,λ_{max} = 600 nm , T = 31± 1°C.

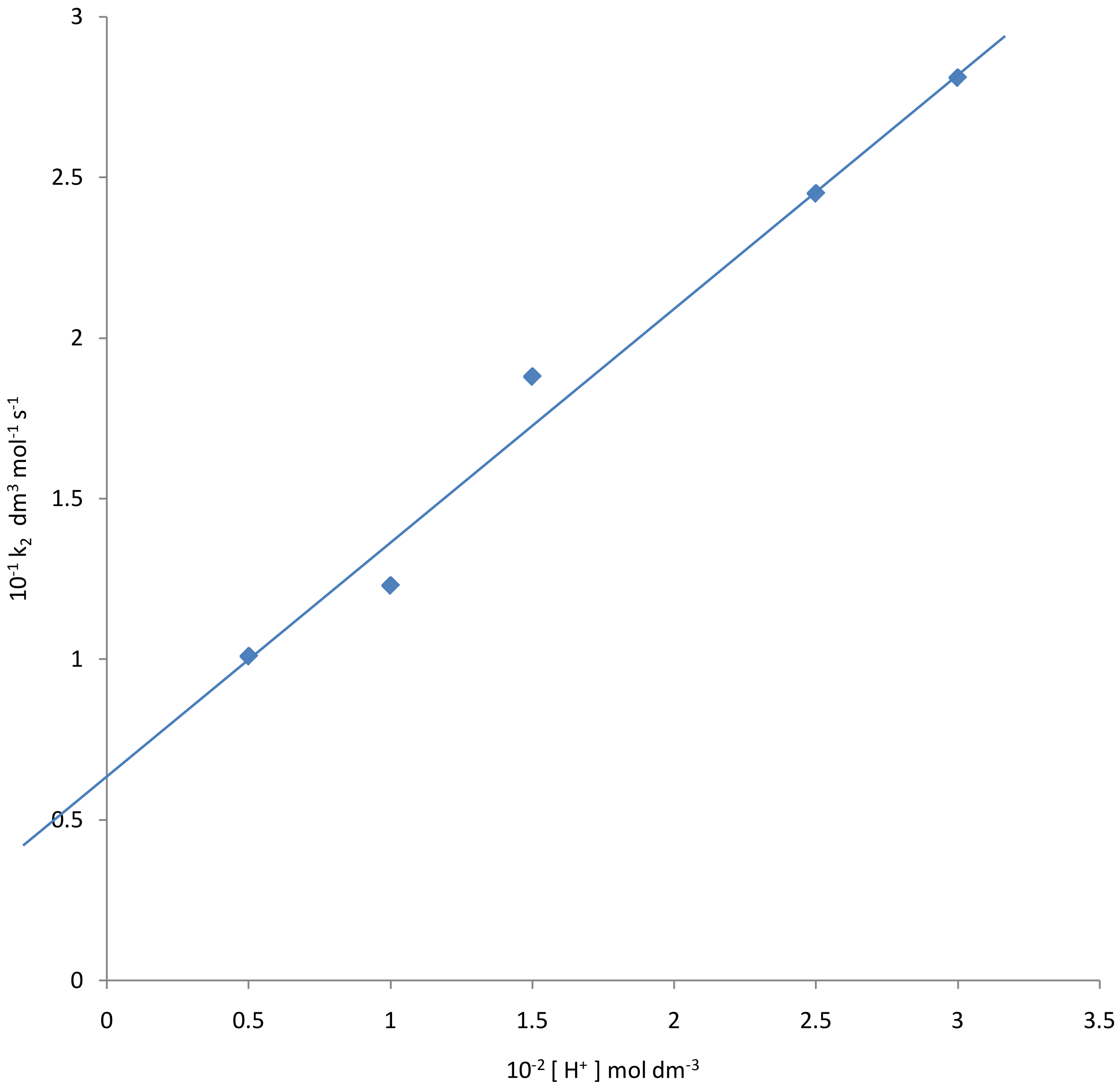

Fig. 2 : Pseudo – first order plot of k_2 versus [H^+] for the reduction of dithionate ion at [$S_2O_6^{2-}$] = 30 x 10^{-3} mol dm^{-3}, [TB^+] = 1 x 10^{-3} mol dm^{-3} , I = 0.5 mol dm^{-3} ,λ_{max} = 600 nm , T = 31 ± 1°C.

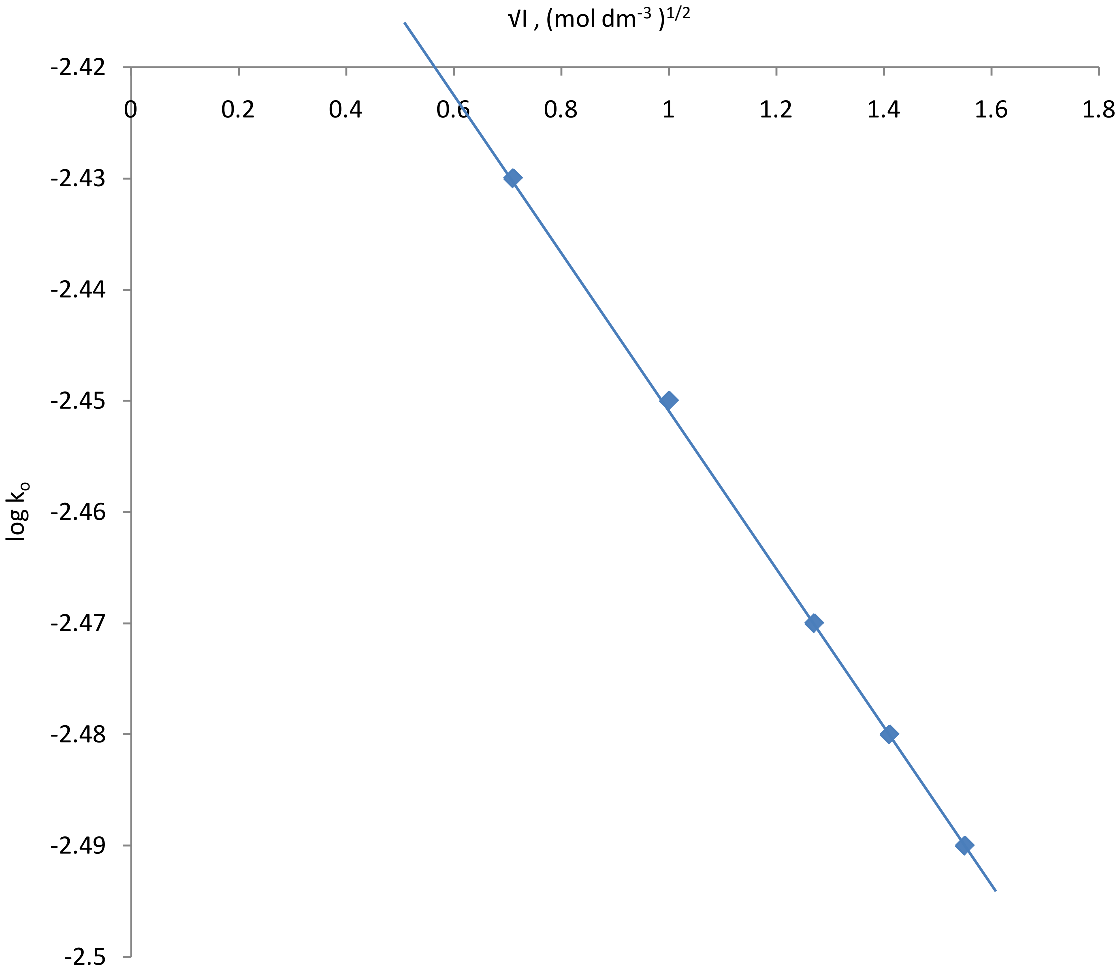

Fig.3 : Plot of logk$_o$ versus √I for the reduction of TB$^+$ by dithionate ion.

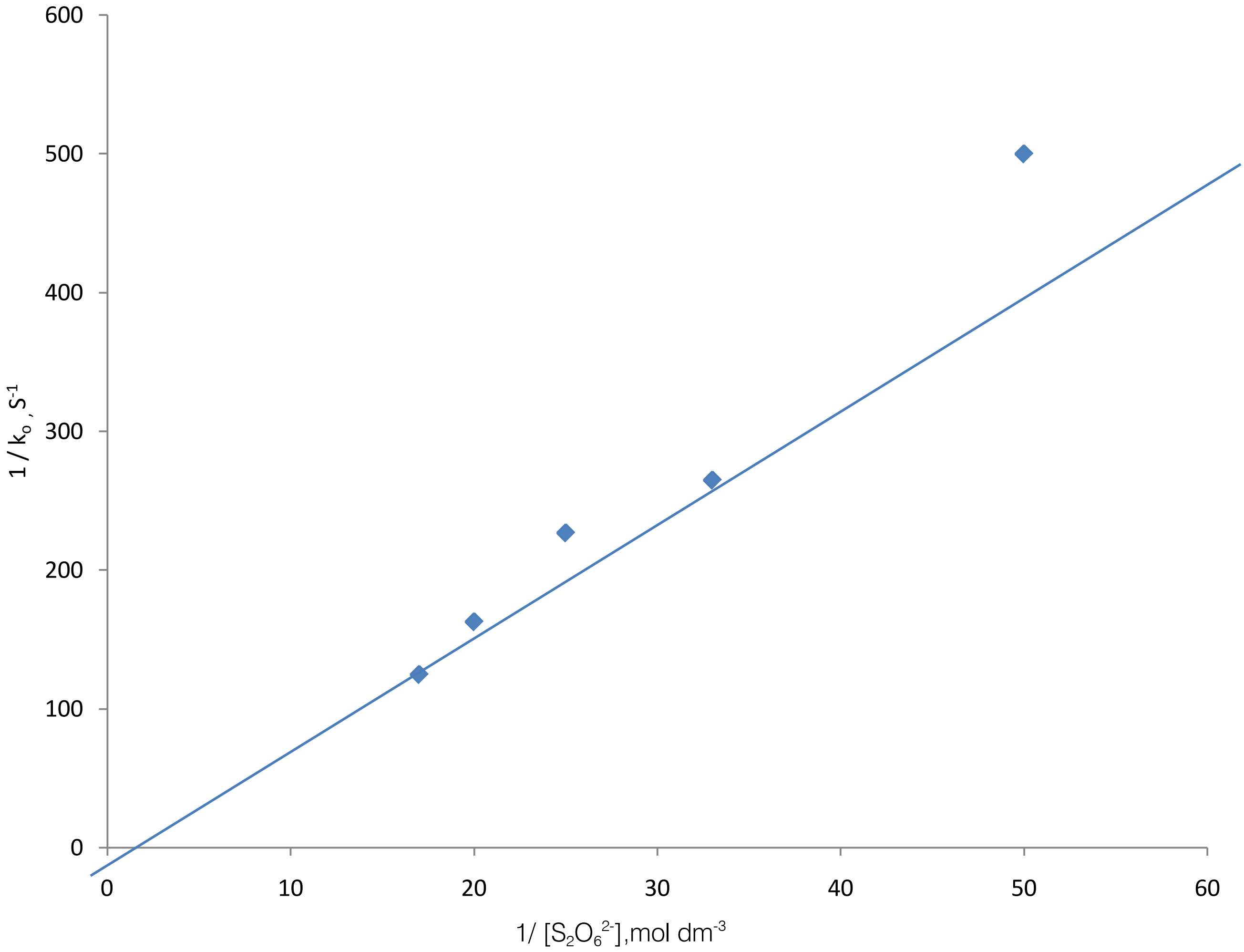

Fig. 4 : Michealis – Menten's plot for the reduction of TB^+ with $S_2O_6^{2-}$ ion at [TB^+] = 1 x 10^{-3}mol dm^{-3}, [$S_2O_6^{2-}$] = 30 x 10^{-3}mol dm^{-3}, [H^+] = 1 x 10^{-2}mol dm^{-3}, I = 0.5 mol dm^{-3}(NaCl) , λmax = 600 nm, T = 31± 1°C.

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 x10^{-3} mol dm^{-3}, [H^+] = 1 x10^{-2} mol dm^{-3}, [$S_2O_6^{2-}$] = 30 x 10^{-3}mol dm^{-3}, I = 0.5 mol dm^{-3} (NaCl) , λmax = 600 nm , T = 31± 1°C.

D s^{-1} dm^3 mol^{-1} s^{-1}	k_o x 10^{-2}	k_2 x 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 $[TB^+] = 1 \times 10^{-3}$ mol dm^{-3} , $[S_2O_6^{2-}] = 30 \times 10^{-3}$ mol dm^{-3} , $[H^+] = 1 \times 10^{-2}$ mol dm^{-3} , I = 0.5 mol dm^{-3}(NaCl) , λmax = 600 nm, T = 31± 1^{0}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

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