

Reduction Kinetics of 3,7-bis (dimethylamino)- 4-nitro-phenothiazine-5-ium Chloride (Methylene Green) with Potassium Persulfate in Presence of Halides

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Authors' contributions

This work was carried out in collaboration between all authors. Author RS designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors FU, MA, MI and ZK managed the analyses, literature searches of the study and helps in the preparation of final draft of the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

The effect of ionic strength and temperature on the kinetics of reaction between 3, 7 bis (dimethyl amino) - 4- nitro-phenothiazine-5-ium chloride (methylene green) and persulfate ions in presence of potassium iodide and potassium bromide was studied by spectrophotometric method. The overall reaction follows pseudo second order kinetics. First order with respect to persulfate and halide ions respectively and zero order kinetics with respect to Methylene green were observed. The reaction was studied at different ionic strengths and temperatures ranging from 25°C to 50°C. The kinetic data was evaluated in terms of Debye-Huckel-Bronsted (DHB) and Kilpatrick relations. It was observed that with the increase in ionic strength and temperature, the rate increases following DHB theory. The value of $z_A z_B$ was also calculated from DHB plots and

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Kilpatrick plots. The effect of ionic strength on the activation parameters was also studied.

Keywords: Methylene green; kinetics; reduction; ionic strength.

1. INTRODUCTION

The kinetics of various ionic reactions has been studied extensively and the variation of the rate of the reaction between any two ionic species as a function of ionic strength of the medium was studied by several researchers [1-10]. Kappana et al. [9] studied the reaction between bromoacetate and thiosulfate ions and concluded that the size and charge of either the cation or anion of the added electrolyte has a large effect on the rate constant which is also influenced by the concentration of reagent and temperature. Ghaziuddin et al. [7] studied the influence of ionic strength on the specific rate constant of the reaction between persulfate and iodide ions and observed that the reaction proceeded more rapidly as the ionic strength was increased.

Kinetic studies using dyes were carried out by a number of workers emphasized the rate of decolorization [11-25]. The color of the dye was due to the electronic transition between the orbitals which in turn determined the change in color in the visible range of the electromagnetic spectrum and the precise shade or hue of the dye. Dyes include a broad spectrum of different chemical structures, primarily based on substituted aromatic and heterocyclic groups. The suitability of a dye for recycling is determined by its physical and chemical properties and the mechanism by which it reacts [14-15]. Osunlaja [17] studied the influence of ionic strength, dielectric constant, temperature and concentration on the reduction kinetics of methylene blue with thiourea [16]. Saeed et al investigated the oxidation kinetics of methylene green using ascorbic acid. The kinetic data was evaluated to propose the mechanism of the reactions.

The Debye-Huckel-Bronsted relation shows the influence of ionic strength on the specific rate constant of an ionic reaction [6]:

$$\log k = \log k_o + 1.02z_A z_B \sqrt{\mu} \quad (1)$$

where k is the specific rate constant, k_o is the specific rate constant at zero ionic strength and z_A and z_B are the charges of ions A and B respectively. The equation (1) is valid for dilute and similar charges of ions. Kilpatrick [15] pointed out that ion pair formation takes place between oppositely charged ions due to the interaction between ionic reactants and cations of the electrolyte. These ion-pairs react faster than free ions due to decrease in electrostatic repulsion, therefore the rate constant increases with salt concentration in accordance with equation 2.

$$\log k = \log k_o + 1.02z_A z_B \sqrt{\mu} / (1 + \sqrt{\mu}) \quad (2)$$

2. MATERIALS AND METHODS

A spectrophotometric method was used to study the kinetics of reaction between methylene green (MG) and persulfate ions in the presence of potassium iodide and potassium bromide at different ionic strengths and temperatures.

All the glassware used was of Pyrex A grade. All the chemicals, potassium persulfate ($K_2S_2O_8$), potassium iodide (KI), potassium bromide (KBr) were supplied by Merck and 3, 7 bis (dimethyl amino) - 4- nitro-phenothiazine-5-ium chloride (methylene green) (formula weight $364.84 \text{ gm.mol}^{-1}$) of Analar grade manufactured by Fluka were used without further purification. Thermostatic water bath model Haake type 13 (Germany) was used to maintain the temperature constant throughout the course of the experiment. A spectronic 21 (Bausch and Lomb) spectrophotometer with temperature control device connected to thermostatic water bath was used to measure absorbance at constant temperature.

The spectrum of methylene green was recorded on Shimadzu UV-VIS spectrophotometer UV-160A (a microcomputer-controlled double-beam recording spectrophotometer) as shown in Fig. 1. An absorbance maximum was observed at 657 nm with molar absorptivity (ϵ) $32,111 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Stock solutions were prepared in double distilled water having conductivity of 0.06 mS.cm^{-1} . Reaction mixtures of ionic strength $0.2000 \text{ mol.dm}^{-3}$ to $0.8485 \text{ mol.dm}^{-3}$ were prepared by taking specific volumes of methylene green, persulfate and salts (KI, KBr). The absorbance was recorded as a function of time at 657 nm at fixed temperature. The temperature of the reaction mixture was kept constant by the circulation of water in outer jacket of reaction cell with the help of thermostatic water bath. The reaction was performed at different temperatures ranging from 25 to 50°C respectively. The reaction was studied for about 30 minutes at fixed temperature.

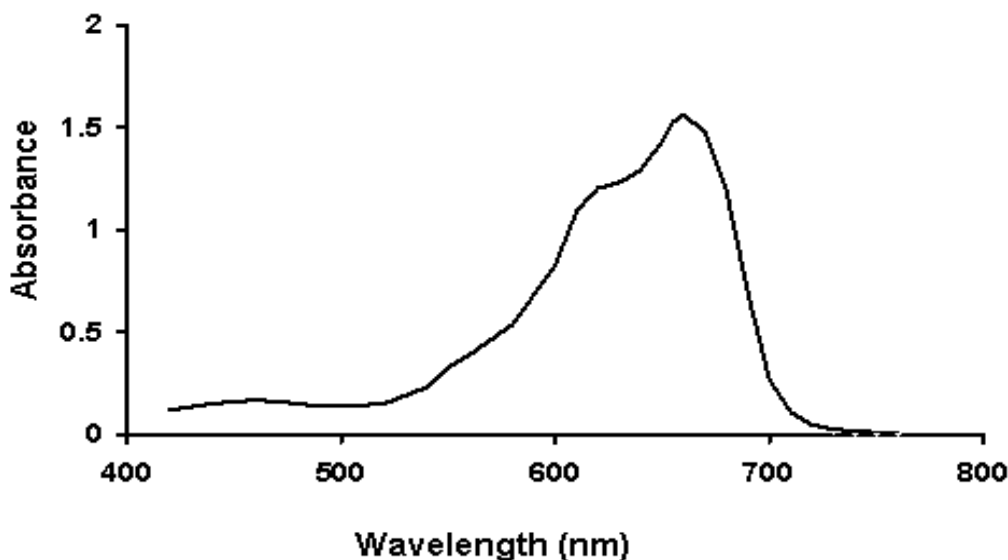


Fig. 1. Absorption spectrum of $4.9 \times 10^{-5} \text{ mol.dm}^{-3}$ methylene green in aqueous medium

3. RESULTS AND DISCUSSION

The values of rate and rate constants at different ionic strengths and temperatures at a fixed concentration of methylene green are tabulated in Tables 1 and 2 respectively. The values of specific rate constants at zero ionic strength obtained as intercept of the Debye-Huckel-Bronsted and Kilpatrick plots are tabulated in Table 3. The values of rate constants determined at different concentrations of potassium persulfate and salts (KBr, KI), while the concentration of methylene green was kept constant shows that at a particular temperature there is a gradual decrease in the rate constant with the increase in ionic strength from 0.2000 mol.dm⁻³ to 0.7899 mol.dm⁻³, followed by a gradual increase in the value of rate constant for ionic strengths at 0.8000 to 0.8485 mol.dm⁻³ range.

Table 1. Rate of reduction of 2.75×10^{-5} mol.dm⁻³ methylene green at different ionic strengths and temperatures

μ (mol.dm ⁻³)	Rate $\times 10^4$ (mol.dm ⁻³ .s ⁻¹) at different temperatures (°C)					
	25	30	35	40	45	50
	KBr					
0.2000	0.9	1.0	2.0	4.0	5.0	6.0
0.3200	1.5	2.0	3.0	5.0	7.0	7.5
0.4000	2.5	3.0	4.0	6.0	8.0	9.0
0.5200	3.0	4.0	6.0	7.0	9.0	10.0
0.6000	4.0	5.0	6.3	7.2	10.0	11.0
0.7899	4.2	5.4	6.7	7.8	10.8	12.0
0.8000	4.5	5.8	7.0	8.0	11.2	13.0
0.8246	5.0	6.2	7.2	8.5	11.5	14.0
0.8485	5.3	6.5	7.5	9.0	11.9	15.0
	KI					
0.2000	0.5	1.0	2.0	3.0	4.0	6.0
0.3200	1.0	2.0	3.0	4.0	6.0	7.0
0.4000	2.0	3.0	4.0	6.0	8.0	9.0
0.5200	3.0	4.0	5.0	7.0	9.0	12.0
0.6000	4.0	5.0	6.0	8.0	11.0	15.0
0.7899	5.0	6.0	8.0	9.0	15.0	20.0
0.8000	15.0	16.0	18.0	23.0	28.0	32.0
0.8246	22.0	23.0	27.0	29.0	32.0	35.0
0.8485	35.0	37.0	41.0	45.0	47.0	49.0

Table 2. Rate constants for the reduction of $2.75 \times 10^{-5} \text{ mol.dm}^{-3}$ methylene green at different ionic strengths and temperatures

$\mu \text{ (mol.dm}^{-3}\text{)}$	Rate constant (k) $\times 10 \text{ (dm}^3\text{.mol}^{-1}\text{.s}^{-1}\text{)}$ at different temperatures ($^{\circ}\text{C}$)					
	25	30	35	40	45	50
	KBr					
0.2000	0.36	0.40	0.80	1.60	2.00	2.40
0.3200	0.23	0.31	0.47	0.78	1.09	1.17
0.4000	0.25	0.30	0.40	0.60	0.80	0.90
0.5200	0.18	0.24	0.36	0.41	0.53	0.59
0.6000	0.18	0.22	0.28	0.32	0.44	0.49
0.7899	0.11	0.14	0.17	0.20	0.28	0.31
0.8000	0.11	0.15	0.18	0.20	0.28	0.33
0.8246	0.11	0.15	0.17	0.20	0.27	0.33
0.8485	0.12	0.14	0.17	0.20	0.26	0.33
	KI					
0.2000	0.20	0.40	0.80	1.20	1.60	2.40
0.3200	0.16	0.31	0.47	0.62	0.94	1.09
0.4000	0.20	0.30	0.40	0.60	0.80	0.90
0.5200	0.18	0.24	0.30	0.41	0.53	0.71
0.6000	0.18	0.22	0.27	0.36	0.49	0.67
0.7899	0.13	0.15	0.20	0.23	0.32	0.38
0.8000	0.38	0.40	0.45	0.58	0.70	0.80
0.8246	0.52	0.54	0.64	0.68	0.75	0.82
0.8485	0.78	0.82	0.91	1.00	1.04	1.09

Table 3. Specific rate constant (k_0) at zero ionic strength

Temperature ($^{\circ}\text{C}$)	25	30	35	40	45	50
	KBr					
$k_0 \text{ (mol}^{-1}\text{.dm}^3\text{.s}^{-1}\text{)}$	0.1048	0.1198	0.3295	0.9799	1.2139	1.2957
	KI					
$k_0 \text{ (mol}^{-1}\text{.dm}^3\text{.s}^{-1}\text{)}$	0.0029	0.0210	0.0900	0.2376	0.1316	0.2693

Kilpatrick [17] pointed out that ion-pair formation takes place between oppositely charged ions, due to interaction between ionic reactant and cation of electrolyte. These ion-pairs react faster than free ions due to decrease in electrostatic repulsion. The representative plots of Debye-Huckel-Bronsted and Kilpatrick equations expressed as $\log k$ vs. $\sqrt{\mu}$ and $\log k$ vs. $\sqrt{\mu}/(\sqrt{\mu}+1)$ at 25 to 50 $^{\circ}\text{C}$ for KBr and KI are shown in Figs. 2, 3 and 4, 5 respectively. The values of $Z_A Z_B$ calculated from the slopes of Debye-Huckel-Bronsted and Kilpatrick plots are 1.07 and 2.34 for KBr respectively, and 0.84 and 2.23 for KI respectively. It shows that Kilpatrick theory is the better representation of the values of $Z_A Z_B$ than Debye-Huckel-Bronsted theory.

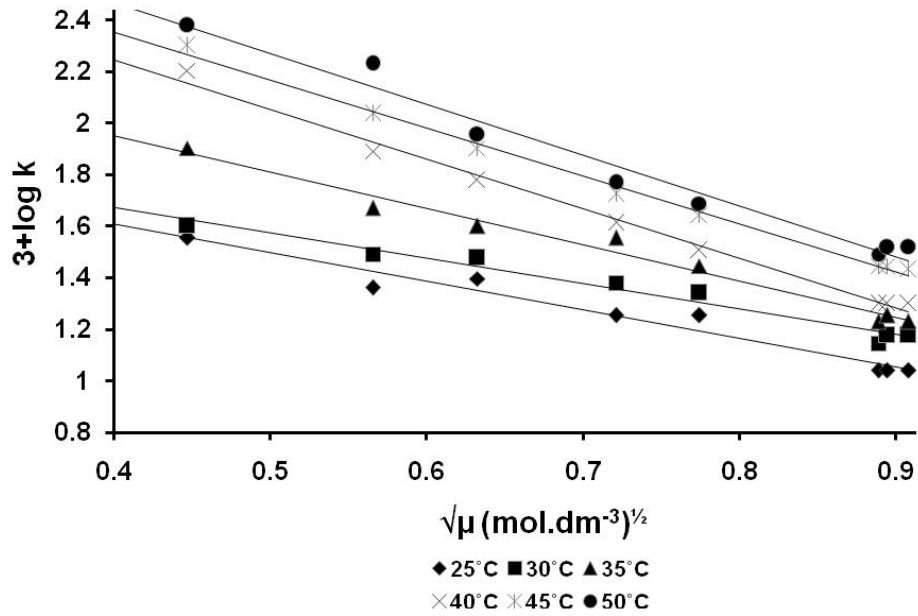


Fig. 2. Plot of $\log k$ vs. $\sqrt{\mu}$ of $4.9 \times 10^{-5} \text{ mol.dm}^{-3}$ methylene green at different temperatures in presence of KBr

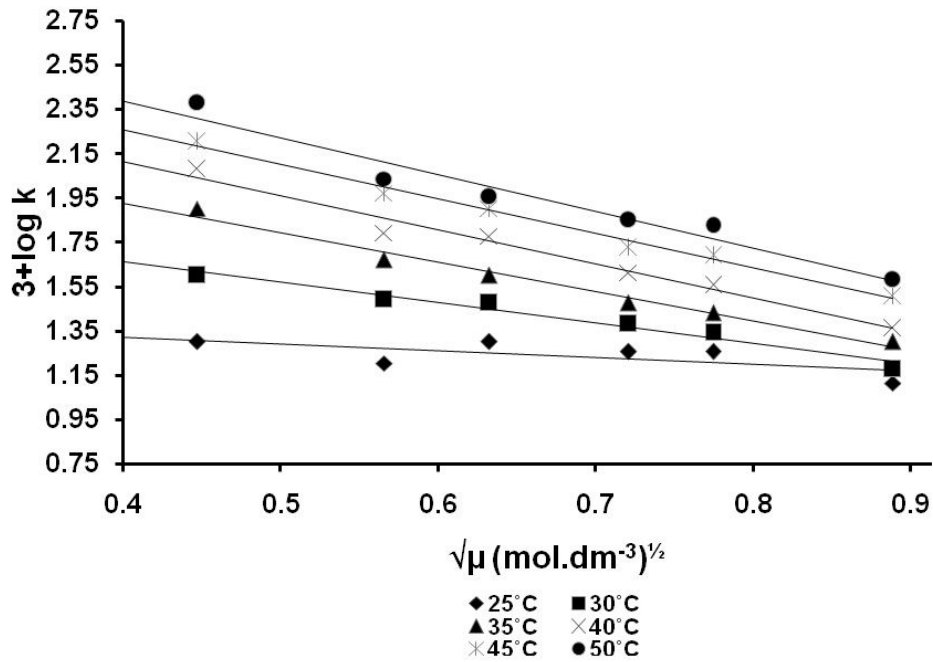


Fig. 3. Plot of $\log k$ vs. $\sqrt{\mu}$ of $4.9 \times 10^{-5} \text{ mol.dm}^{-3}$ methylene green at different temperatures in presence of KI

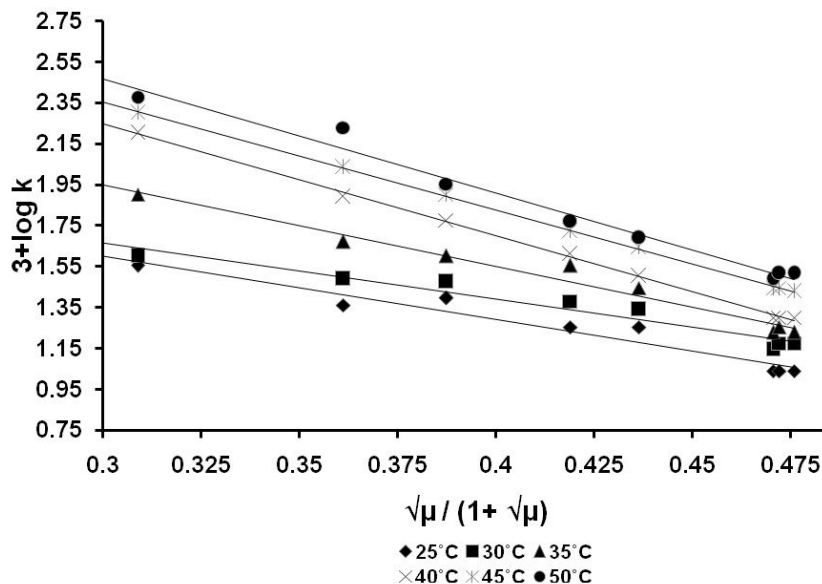


Fig. 4. Plot of $\log k$ vs. $\sqrt{\mu} / (1 + \sqrt{\mu})$ of $4.9 \times 10^{-5} \text{ mol.dm}^{-3}$ methylene green at different temperatures in presence of KBr

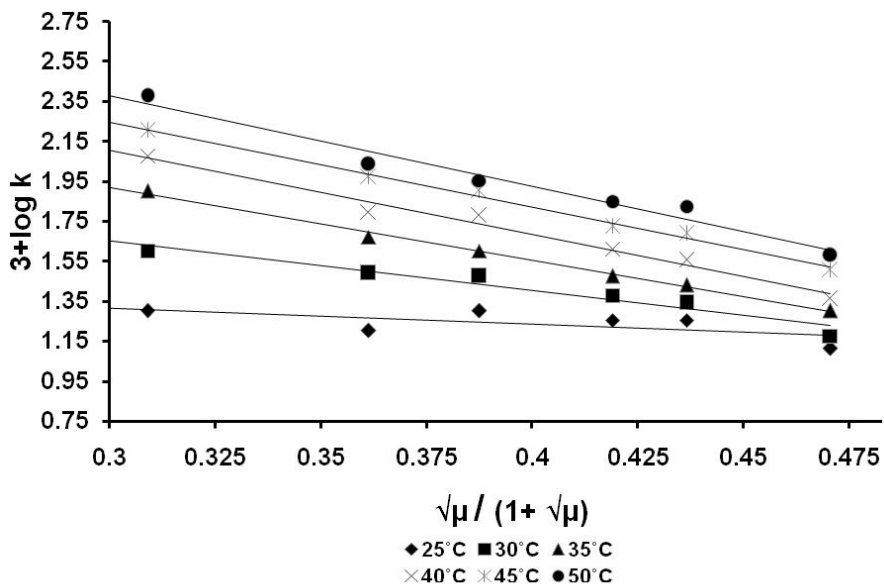


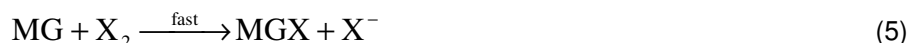
Fig. 5. Plot of $\log k$ vs. $\sqrt{\mu} / (1 + \sqrt{\mu})$ of $4.9 \times 10^{-5} \text{ mol.dm}^{-3}$ methylene green at different temperatures in presence of KI

It was observed that the reaction follows zero order kinetics with respect to methylene green as there is no change observed in the rate at different methylene green concentrations. It was also observed that the value of the rate constant in case of I^- is greater than Br^- due to the ability of I^- to supply an electron faster than Br^- at constant K^+ concentration. On the basis

of the above results for the study of the kinetics of the reaction between methylene green and persulfate ions in presence of salt of halide (X^-), it was found that the reaction follows pseudo second order and the rate can be expressed as:

$$-\frac{d[MG]}{dt} = k [S_2O_8^{2-}] [X^-] \quad (3)$$

The kinetics data shows that the reaction involves following steps:



It was observed that the formation of XSO_4^- is a slow step and hence the rate determining step. The effect of temperature on the rate constant was evaluated by Arrhenius relationship shown in equation 6 [11]. The temperature dependence indicates an exponential increase of the rate constant with temperature.

$$k = Ae^{\frac{E_a^\ddagger}{RT}} \quad (6)$$

where A is the frequency factor, E_a^\ddagger is the activation energy, R is the gas constant and T is the absolute temperature. The values of activation energy (E_a^\ddagger) were calculated from the slopes of the Arrhenius plot between $\log k$ versus $1/T$. Results for the activation energy (E_a^\ddagger) are tabulated in Table 4 and the representative plot of $\log k$ versus $1/T$ for KBr and KI are shown in Figs. 6 and 7 respectively.

Table 4. Activation parameters of the reduction of Methylene Green at different ionic strengths at 45°C.

μ (mol.dm ⁻³)	E_a^\ddagger (kJ.mol ⁻¹)	ΔH^\ddagger (kJ.mol ⁻¹)	ΔG^\ddagger (kJ.mol ⁻¹)	$-\Delta S^\ddagger$ (J.mol ⁻¹ .K ⁻¹)
KBr				
0.2000	68.75	66.11	79.84	43.18
0.3200	56.89	54.24	81.65	86.18
0.4000	44.61	41.97	82.27	126.73
0.5200	38.74	36.10	47.18	148.26
0.6000	36.16	33.51	83.84	158.27
0.7899	34.25	31.60	85.07	168.13
0.8000	33.89	31.24	53.80	169.09
0.8246	32.72	30.07	55.01	172.90
0.8485	30.53	27.88	85.16	180.12
KI				
0.2000	77.97	75.33	80.09	14.98
0.3200	61.13	58.49	81.85	75.16
0.4000	49.83	47.18	82.39	110.70
0.5200	44.34	41.69	83.17	132.59
0.6000	42.25	39.60	83.44	137.85
0.7899	35.22	32.58	84.74	164.04
0.8000	26.05	23.41	82.52	185.88
0.8246	15.47	12.83	82.28	218.41
0.8485	11.43	8.78	81.42	228.42

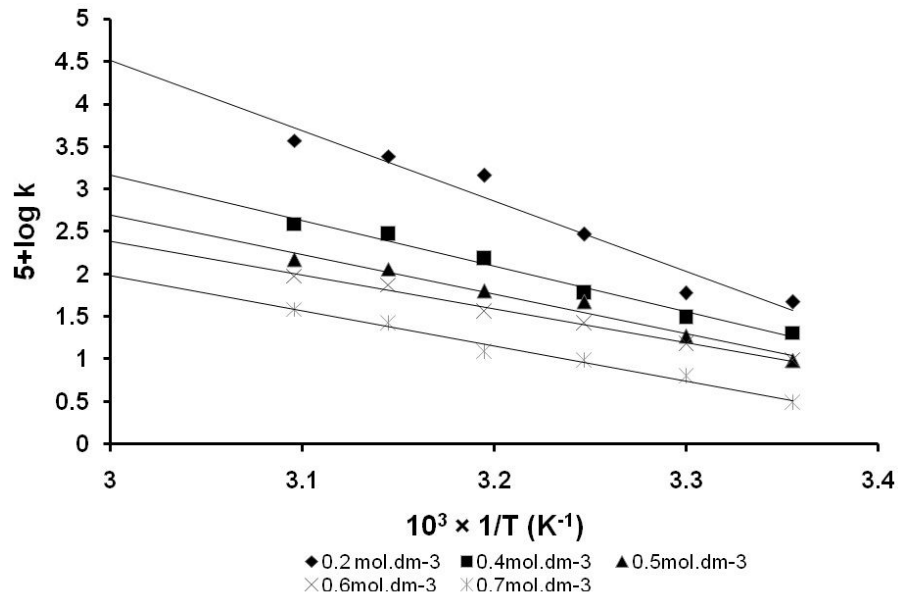


Fig. 6. Plot of $\ln k$ vs. $1/T$ of $4.9 \times 10^{-5} \text{ mol.dm}^{-3}$ methylene green at different ionic strengths in presence of KBr

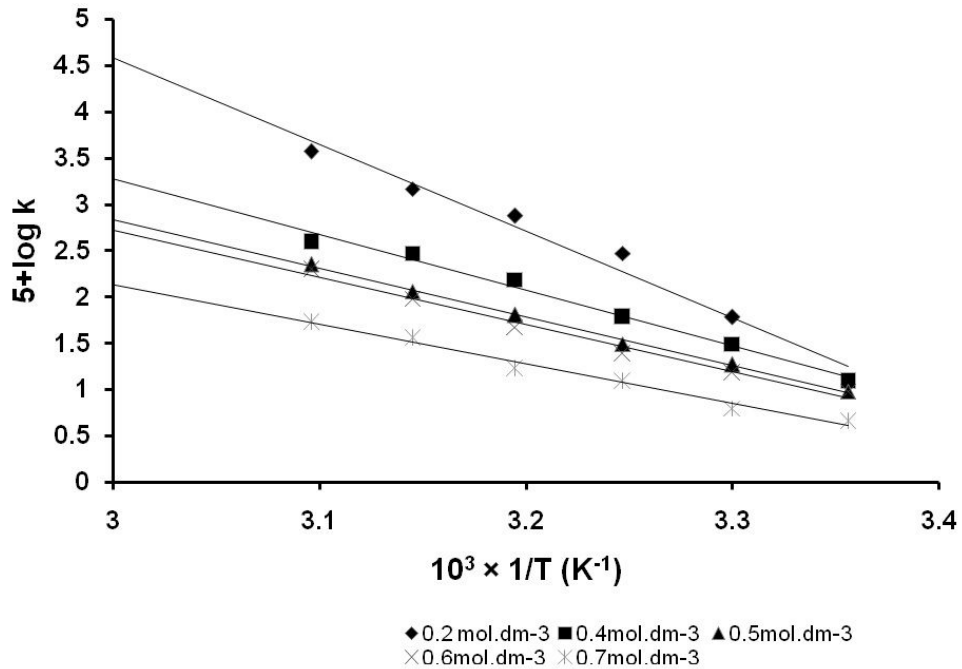


Fig. 7. Plot of $\ln k$ vs. $1/T$ of $4.9 \times 10^{-5} \text{ mol.dm}^{-3}$ methylene green at different ionic strengths in presence of KI

The relationship between energy of activation and ionic strength is given by the following equation 7 [7]:

$$E_a^\# = \frac{d \log k}{d(1/T)} = \frac{d \log k_o}{d(1/T)} - \frac{3e^3 (8\pi N/1000)^{1/2}}{2(\epsilon k)^{3/2}} \times \frac{z_A z_B \sqrt{\mu}}{2.303} \quad (7)$$

It was observed that increase in ionic strength leads to decrease in the activation energy ($E_a^\#$). This is due to the fact that as the ionic strength changes the configuration of the activated complex or the transition state changes and results in a decrease in activation energy. The representative plot of energy of activation against $\sqrt{\mu}$ shown in Fig. 8 is linear with a negative slope showing the decrease in $E_a^\#$ with increasing $\sqrt{\mu}$. The values of activation parameters such as change in enthalpy of activation ($\Delta H^\#$), change in free energy of activation ($\Delta G^\#$) and change in entropy of activation ($\Delta S^\#$) at different ionic strengths and temperatures in the presence of KBr and KI are tabulated in Table 4. The plot of $\Delta H^\#$ against $\sqrt{\mu}$, shown in Fig. 9, is linear and displays the inverse relation of $\sqrt{\mu}$ and $\Delta H^\#$. The values of change in enthalpy of activation ($\Delta H^\#$) were obtained using equation 8:

$$E_a^\# = \Delta H^\# + RT \quad (8)$$

Apparent change in entropy of activation ($\Delta S^\#$) was calculated by equation 9:

$$\Delta S^\# = R \ln(Ah/kT) \quad (9)$$

The negative values of change in entropy of activation ($\Delta S^\#$) indicate a loss of entropy due to the increased charge on activated complex with respect to the charges of separated ions.

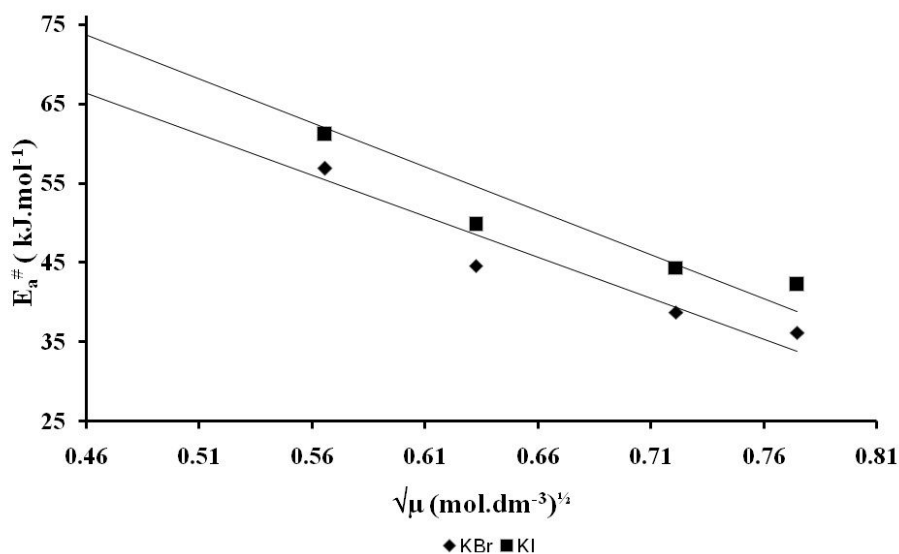


Fig. 8. Plot of $E_a^\#$ vs. $\sqrt{\mu}$ of 4.9×10^{-5} mol.dm⁻³ methylene green in presence of KBr and KI

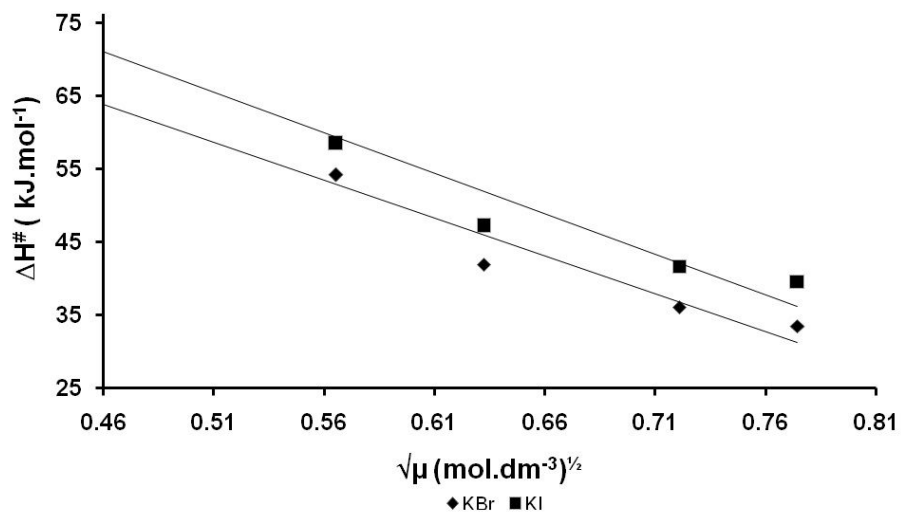


Fig. 9. Plot of ΔH^\ddagger vs. $\sqrt{\mu}$ of $4.9 \times 10^{-5} \text{ mol.dm}^{-3}$ methylene green in presence of KBr and KI

The values of change in free energy of activation (ΔG^\ddagger) were obtained by the relation:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (10)$$

The results show that the values of change in free energy of activation (ΔG^\ddagger) decrease with an increase in ionic strength. The positive values of change in free energy of activation (ΔG^\ddagger) indicate the non-spontaneous formation of activated complex.

4. CONCLUSION

It was concluded that the rate of the reaction between methylene green and persulfate ions in presence of halide ions increased with the increase in ionic strength and temperature. The rate of reaction increased with increase in ionic strength and the value of $z_A z_B$ was calculated from Debye-Huckel-Bronsted and Kilpatrick plots. It was concluded that Kilpatrick theory is a better estimate of the values of $z_A z_B$ as compared to Debye-Huckel-Bronsted theory as for Kilpatrick theory values of $z_A z_B$ found to be 2.34 for KBr and 2.23 for KI.

The energy of activation, change in enthalpy of activation (ΔH^\ddagger) and change in free energy of activation (ΔG^\ddagger) decreased with increase in ionic strength while the change in entropy of activation (ΔS^\ddagger) increased with increase in ionic strength.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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