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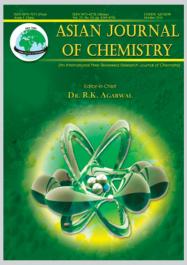

Effect of Ionic Strength on the Kinetics of Oxidation of Ascorbic Acid by Methylene Green in Aqueous Methanol System

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The effect of ionic strength and temperature on the kinetics of the reaction between methylene green and ascorbic acid was studied in presence of iodine by spectrophotometric method. The oxidation of ascorbic acid was carried out in 10, 15, 20, 25 and 30 % aqueous methanol and decrease in the values of rate of reaction was observed with decrease in dielectric constant of solvent. The absorbance data was collected at 656 nm at different ionic strength and temperature ranges from 2.7063×10^{-4} mol dm^{-3} to 8.9604×10^{-4} mol dm^{-3} and 298 to 318 K with the difference of 5 K respectively. It was observed that with the increase in ionic strength and temperature the rate of the reaction also increased. The presence of iodine enhances the rate of chemical reaction. The reaction follows first order kinetics with respect to ascorbic acid and fractional order with respect to methylene green. The overall reaction is pseudo first order. Energy of activation (E_a^*) was calculated with the help of kinetic data by using Arrhenius relationship. Thermodynamic parameters such as enthalpy change of activation (ΔH^*), Gibbs free energy change of activation (ΔG^*) and entropy change of activation (ΔS^*) were also evaluated.

Key Words: Kinetics, Oxidation, Methylene Green, Ascorbic acid, Iodine.

INTRODUCTION

The kinetics and mechanism of the oxidation of ascorbic acid by complexes has been studied by many researchers[1-3]. Vilarino *et al.*[4] studied the effect of ionic strength on the kinetics of the oxidation of ascorbic acid by hexacynoferrate(III) in acidic medium and determine the dependence of rate constant on ionic strength according to different specific interaction theories and the mean spherical approximation. Chatterjee[5] also studied the kinetics and mechanism of oxidation of ascorbic acid by cobalt(III) complexes as a function of pH, temperature, ionic strength and ascorbic acid concentration and found that the reaction was first order with respect to both the complex and ascorbic acid. Sowa *et al.*[6] perform a redox titration of ascorbic acid using standard iodine solution to determine the amount of vitamin C per citrus fruit. The redox reaction of ascorbic acid with iodine is shown as:

$$C_6H_8O_6 + I_2 \longrightarrow C_6H_6O_6 + 2H^+ + 2I^- \qquad (1)$$

Recently the use of dye to evaluate the mechanism of chemical reaction instead of formation metal complexes is of interest due to the ease of spectrophotometric analysis.

Dyes are the coloured compounds. The colour of dye is due to electronic transition between the orbitals, which determine the colour variation in the visible region of electromagnetic spectrum. Kinetics of several chemical reactions using dyes were investigated by different techniques[7-16].

Spectrophotometric method in its applications is simple, accurate and sensitive over many other methods so it was successfully used to study the kinetics of reactions having absorbing species[17-20].

Saeed *et al.*[21] studied the kinetics of photochemical reduction and proposed the mechanism of reaction. The role of phenothiazine dyes in biological system has also well documented. Most of the thiazine dyes interacts with nucleic acids, protein, lipids and induced photosensitized reactions, which can be used for sequence-specific cleavage of DNA, back bone. Such reactions damage the structure of DNA molecules[22].

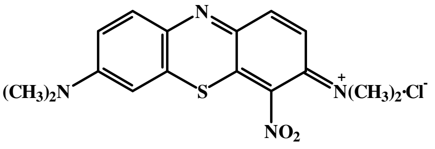
Oxidation of ascorbic acid using dyes was also investigated by Arya *et al.*[23] and Noroozifar and Khorasani-Motlagh[24] observed that ascorbic acid is easily oxidized by methylene blue (thiazine dye) and follows first order with respect to ascorbic acid in acidic media.

Present study reveals the spectrophotometric study of the kinetics of oxidation of ascorbic acid with methylene green in the presence of iodine in aqueous methanol solvent at various ionic strength and temperatures. Thermodynamic study will also be made to support the kinetic data.

EXPERIMENTAL

All the glasswares used were of Pyrex A grade quality. Apparatus were washed and dried in oven (W.T.C binder, 7200, Tuttlingh/Germany. Type 28, No 89248).

All the chemicals used were of extra pure quality. Ascorbic acid of E. Merck methylene green of AnalaR grade manufacturer by Fluka (C.I. No 52020), potassium iodide, iodine, citric acid and disodium hydrogen phosphate of (BDH) were used without further purification. Methanol of 99.9 % of E. Merck was used as solvent system. Freshly prepared double distilled water having conductivity 0.06 mS cm^{-1} was used for preparation of different aqueous methanol (% v/v) solutions. Methylene Green of AnalaR grade manufacturer by Fluka (C.I.No. 52020) was used having structural formula:



Phenothiazine-5-ium,3,7-*bis*-(dimethyl amino)-4-nitro chloride (MG)

Procedure: Different compositions of methanol ranges from10-30 % v/v were prepared in double distilled water, which were used as solvents. Stock solutions of 5 × 10^{-4} mol dm^{-3} methylene green, 0.05 mol dm^{-3} ascorbic acid and 0.05 mol dm^{-3} iodine were prepared in 10 to 30 % (v/v) aqueous methanol solvent. Iodine solution was prepared by dissolving known amount of iodine in potassium iodide solution. Buffer solution of pH 3 was prepared by mixing appropriate volume of 0.2 mol dm^{-3} disodium hydrogen phosphate and 0.1 mol dm^{-3} citric acid to maintain the pH at 3 with the help of digital pH meter (Orion, 1990 Orion research Inc. Boston MA 02129 USA.

The oxidation of ascorbic acid in the presence of iodine was studied at various ionic strength ranges from 2.7063 × 10^{-4} mol dm^{-3} to 8.9604 × 10^{-4}. The pH of reaction mixture was kept constant at 3 with temperature ranging from 298 to 318 K with a difference of 5 ± 0.1 K. The reaction was studied for 30 min and selected 15 min for study as after that time the rate of the reaction was slow.

A known volume of ascorbic acid, methylene green, iodine and buffer was taken with the help of micropipette (1 mL) in a quartz cell of capacity 3 mL. The absorbance data of the oxidation reaction was recorded at 656 nm as a function of concentration of iodine, ascorbic acid and temperatures in aqueous and aqueous methanol system using Electro Thermocouple spectrophotometer (HeλIOS.) connected with. A thermostatic bath (circulator, model, YCWOI, made in Taiwan, R.O.C) having circulation of water to maintain temperature of reaction mixture constant throughout the experiment.

RESULTS AND DISCUSSION

The kinetics of the reaction between ascorbic acid and methylene green in presence of iodine was studied spectrophotometrically using initial rate method. The absorption spectrum of methylene green in water and aqueous methanol was shown in Fig. 1. The value of λ_{max} and molar extinction coefficient of methylene green were found to be 656 nm and 2.7447 × 10^4 mol dm^{-3} cm^{-1} respectively. The reaction was studied at 656 nm in aqueous and 10 to 30 % aqueous methanol system.

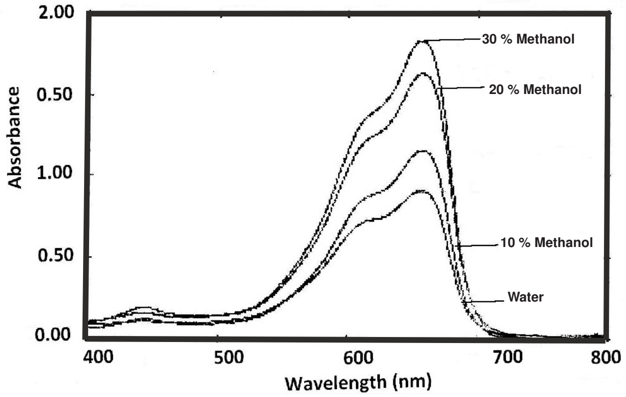


Fig. 1. Absoprtion spectrum of 3.333 × 10^{-5} mol dm^{-3} methylene green in water

The absorbance data was recorded at regular interval of time from 298 to 318 K in 10 to 30 % (v/v) compositions of aqueous methanol system in the range of ionic strength 2.7063 × 10^{-4} mol dm^{-3} to 8.9604 × 10^{-4} mol dm^{-3} at pH 3. The plot of absorbance *versus* time with respect to iodine and ascorbic acid is shown in Fig. 2. The results show that the absorbance was decreased with the increase in ionic strength and temperature. In presence of the iodine the rate of reaction also increased. The representative spectrum shown in Fig. 3 represent the decrease in absorbance with variation of iodine at fixed concentration of methylene green and ascorbic acid in 20 % aqueous methanol. The decrease in the values of absorbance indicates that with the increase in concentration of iodine the number of protons released from ascorbic acid increased. These liberated protons are responsible for reducing methylene green. Hence, increasing concentration of iodine enhances reduction of methylene green. The absorbance data recorded was used to plot graph between $\ln(A_t - A_\infty)$ and time as shown in Fig. 4. The linear plots with R value 0.99 were observed as a function of ascorbic acid concentration. The values of rate constants were evaluated from the slopes of the linear plots of $\ln(A_t - A_\infty)$ *versus* time.

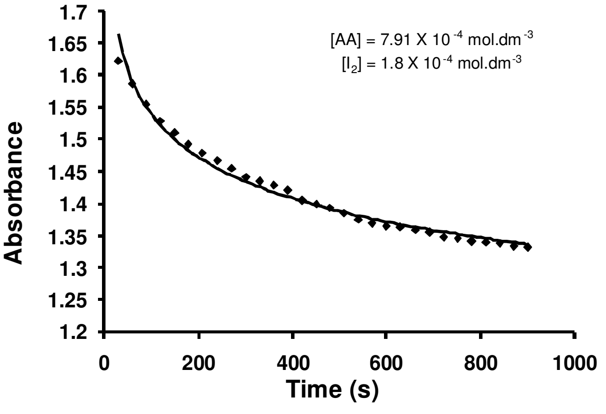


Fig. 2. Plot of Absorbance of 3.333 × 10^{-5} mol dm^{-3} methylene green *versus* time in 20 % aqueous methanol at 308 K

The effect of ionic strength on the rate constant was studied by Debye Huckel relation:

$$\ln k = \ln k_O + e^3 \frac{\left(\frac{8\pi N_A}{1000}\right)^{\frac{1}{2}}}{(Dk_BT)^{\frac{3}{2}}} . Z_A Z_B \quad (2)$$

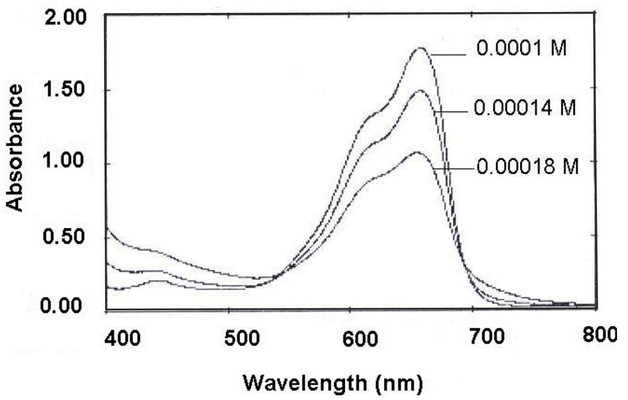


Fig. 3. Absorption spectrum of 3.333 × 10^{-5} mol dm^{-3} methylene green and 7.91 × 10^{-4} mol dm^{-3} ascorbic acid at various concentrations of iodine

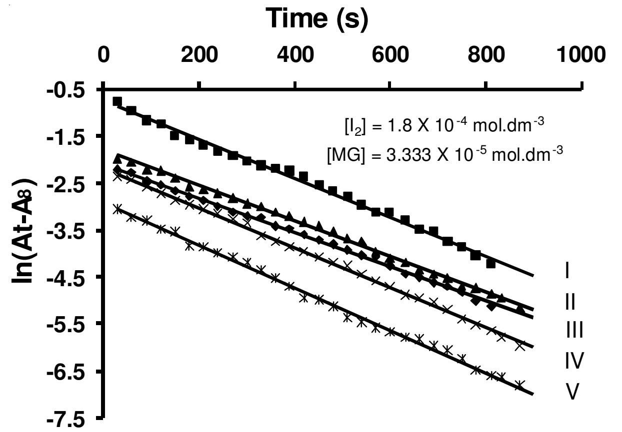


Fig. 4. Plot of ln(A_t-A_∞) *versus* time at 308 K in 20 % aqueous methanol at various ionic strength. (I: 7.0434 × 10^{-4} mol^{-1} dm^{-3}, II: 7.5204 × 10^{-4} mol^{-1} dm^{-3}, III: 8.0004 × 10^{-4} mol^{-1} dm^{-3}, IV: 8.4804 × 10^{-4} mol^{-1} dm^{-3}, V: 8.9604 × 10^{-4} mol^{-1} dm^{-3})

$$\log k = \log k_O + 1.02\, Z_A Z_B (\mu)^{\frac{1}{2}} \tag{3}$$

where k_o is rate constant at zero ionic strength, e is electrostatic charge, N_A is avogadro's number, Z_A and Z_B are the charges on ions A and B, μ is ionic strength and D is dielectric constant. The effect of presence of iodine was also studied from the rate constants obtained from the plot of ln(A_t-A_∞) *versus* time tabulated in Table-1. It was observed that the rate constant increased in the presence of iodine which show the reduction of methylene green with ascorbic acid was enhanced by the addition of iodine.

TABLE-**1**
VALUES OF RATE CONSTANTS (k) in 20 % AQUEOUS METHANOL WITHOUT ADDITION OF IODINE
[MG] = 3.33 × 10^{-5}/mol dm^{-3}

Temperature (K)	10^3 k/s^{-1} in 20 % aqueous methanol				
	10^4 [AA]/mol dm^{-3}				
	0.79	0.95	1.10	1.27	1.43
298	2.07	2.19	2.27	2.36	2.50
303	2.26	2.36	2.45	2.56	2.63
308	2.41	2.54	2.59	2.71	2.77
313	2.55	2.76	2.76	2.84	2.92
318	2.79	2.87	2.87	2.97	3.09

The results tabulated in Table-2 show that the rate constant increased as a function of ionic strength and temperature while decreased with the increase in the methanol content. The relation indicates that ionic strength is related directly to the rate constant when the reaction occurs between two similar charged ions. The increase in values of rate constant as a function of ionic strength indicated that the reaction between same charge ions are enhanced by addition of iodine and ascorbic acid which decrease the repulsion between the similar charges in denser ionic environment. Hence, resulting in the formation of activated state immediately. The representative plot of ln k *versus* square root of ionic strength in 20 % methanol at 308 K is shown in Fig. 5.

TABLE-2
EFFECT OF IONIC STRENGTH ON RATE CONSTANTS (k) FOR VARIOUS COMPOSITIONS OF METHANOL AS A FUNCTION OF ASCORBIC ACID

Temperature (K)	10^3 k/s^{-1} in aqueous methanol				
	10 %	15 %	0 %	25 %	30 %
μ = 7.0434 × 10^{-4} mol dm^{-3}					
298	4.10	3.67	3.39	2.35	1.30
303	4.26	3.85	3.53	3.48	1.38
308	4.47	4.03	3.65	3.65	1.48
313	4.60	4.19	3.88	3.76	1.58
318	4.81	4.34	4.02	2.86	1.65
μ = 7.5204 × 10^{-4} mol dm^{-3}					
298	4.52	3.93	3.42	2.53	1.36
303	4.65	4.07	3.58	2.66	1.45
308	4.87	4.24	3.77	2.78	1.53
313	5.06	4.44	3.89	2.94	1.65
318	5.24	4.60	4.07	3.06	1.72
μ = 8.0004 × 10^{-4} mol dm^{-3}					
298	5.25	4.09	3.80	2.59	1.38
303	5.45	4.29	3.95	2.70	1.45
308	5.64	4.48	4.12	2.85	1.54
313	5.87	4.62	4.30	2.95	1.65
318	6.03	4.81	4.48	3.15	1.74
μ = 8.4804 × 10^{-4} mol dm^{-3}					
298	6.08	4.42	3.92	2.65	1.44
303	6.28	4.59	4.07	2.76	1.57
308	6.49	4.76	4.27	2.91	1.64
313	6.70	4.96	4.40	3.03	1.75
318	6.91	5.15	4.62	3.20	1.82
μ = 8.9604 × 10^{-4} mol dm^{-3}					
298	6.50	4.75	4.16	2.73	1.53
303	6.68	4.94	4.31	2.86	1.63
308	6.87	5.12	4.50	3.00	1.73
313	7.13	5.33	4.66	3.16	1.83
318	7.35	5.50	4.87	3.28	1.91

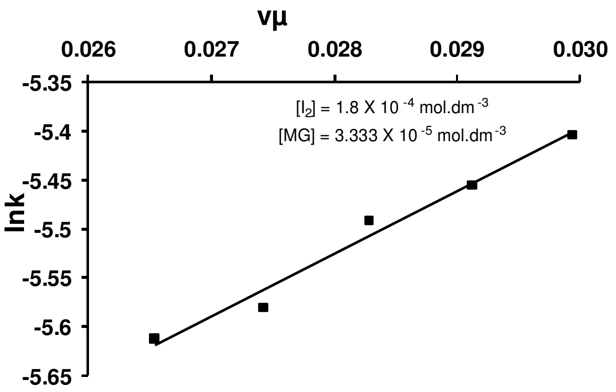


Fig. 5. Plot of ln k *versus* √μ at 308 K in 20 % aqueous methanol

Arrhenius relation was used to study the dependence of rate constant on temperature.

$$k = A.e^{-\frac{E_a^*}{RT}} \quad (4)$$

where, k is rate constant, A is frequency factor, E_a^* is energy of activation, R is gas constant and T is absolute temperature. It was observed that the rate constant increased with the rise in temperature due to increase in the collisions between the molecules present in the reaction mixture, which result in the formation of activated state leading to product formation. Linear plots of ln k *versus* 1/T obtained as shown in Fig. 6. From the slopes of the plots, the values of energy of activation (E_a^*) were calculated. The plot of energy of activation (E_a^*) against square root of ionic strength was linear as shown in Fig. 7. Results of energy of activation with and without addition of iodine are reported in Tables 3 and 4. The values of energy of activation are found to decrease with the addition of iodine, which show the enhancement of rate of reaction in presence of iodine. The values of energy of activation show gradual decrease with the increase in ionic strength at constant temperature because more molecule of reaction mixture collide with sufficient energy to break some of the chemical bonds as a result more H^+ were produced which reduced the dye molecules. It was also observed that energy of activation (E_a^*) decreased with the increase in alcoholic content from 10 to 30 % methanol.

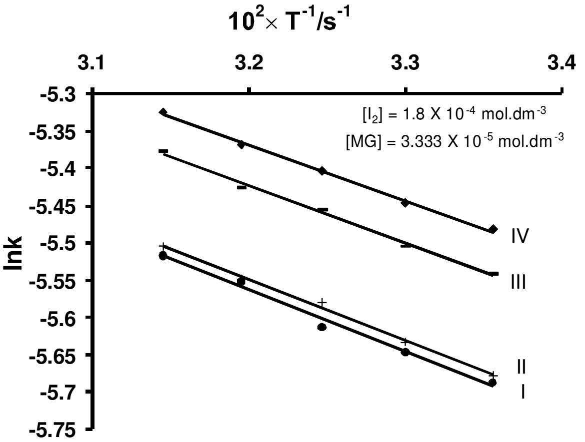


Fig. 6. Plot of l nk *versus* 1/T in 20 % aqueous methanol at different ionic strength. (I: 7.0434 × 10^{-4} mol^{-1} dm^{-3}, II: 7.5204 × 10^{-4} mol^{-1} dm^{-3}, III: 8.4804 × 10^{-4} mol^{-1} dm^{-3}, IV: 8.9604 × 10^{-4} mol^{-1} dm^{-3})

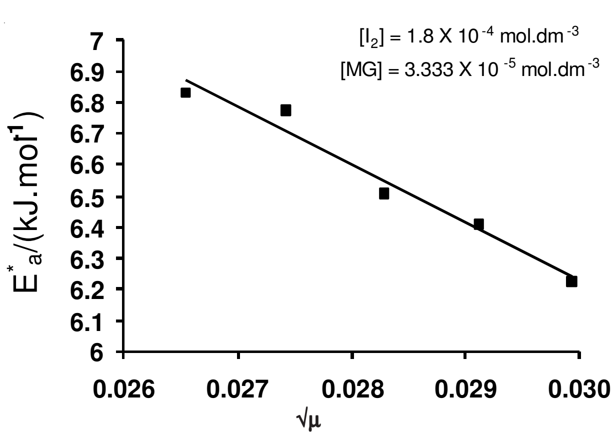


Fig. 7. Plot of E_a^* *versus* √μ at 308 K in 20 % aqueous methanol

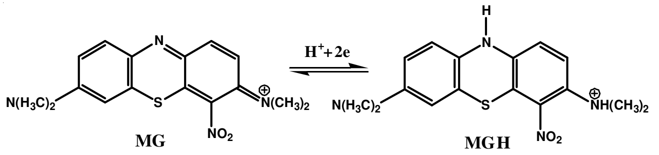
TABLE-3
THERMODYNAMIC PARAMETERS IN 20 % AQUEOUS METHANOL AS A FUNCTION OF ASCORBIC ACID WITHOUT ADDITION OF IODINE
[MG] =3.33 × 10^{-5} mol dm^{-3}

10^2 [AA] /mol dm^{-3}	Energy of Activation E_a^*/kJ mol^{-1}	Enthalpy of activation ΔH^*/kJ mol^{-1}	Change in Gibbs free energy ΔG^*/kJ mol^{-1}	Entropy of activation ΔS^*/J mol^{-1} K^{-1}
0.79	11.266	8.705	88.388	-258.710
0.95	10.468	7.908	88.271	-260.918
1.10	9.344	6.783	88.211	-264.377
1.27	8.922	6.361	88.109	-265.415
1.43	8.408	5.848	87.022	-266.798

TABLE-4
THERMODYNAMIC PARAMETERS IN AQUEOUS METHANOL AT 308 K AS A FUNCTION OF IONIC STRENGTH WITH RESPECT TO ASCORBIC ACID

10^2 √μ/mol dm^{-3}	Energy of activation E_a^*/kJ mol^{-1}	Enthalpy of activation ΔH^*/kJ mol^{-1}	Change in Gibbs free Energy ΔG^*/kJ mol^{-1}	Entropy of activation ΔS^*/J mol^{-1} K^{-1}
10 % (v/v) Methanol				
2.6539	6.24	3.679	86.818	-269.932
2.7423	5.986	3.425	86.588	-270.009
2.8285	5.547	2.986	86.206	-270.194
2.9121	5.059	2.948	85.850	-270.622
2.9934	4.836	2.275	85.691	-270.830
15 % (v/v) Methanol				
2.6539	6.609	4.048	87.080	-269.585
2.7423	6.410	3.849	86.932	-269.749
2.8285	6.277	3.716	86.814	-269.799
2.9121	6.032	3.471	86.636	-270.014
2.9934	5.817	3.256	86.454	-270.123
20 % (v/v) Methanol				
2.6539	6.833	4.272	87.295	-269.555
2.7423	6.778	4.217	87.257	-269.609
2.8285	6.505	3.944	87.008	-269.689
2.9121	6.410	3.849	86.931	-269.746
2.9934	6.222	3.661	86.789	-269.895
25 % (v/v) Methanol				
2.6539	7.924	5.363	88.177	-268.875
2.7423	7.657	5.391	88.306	-269.203
2.8285	7.572	5.011	87.962	-269.321
2.9121	7.360	4.799	87.823	-269.559
2.9934	7.342	4.781	87.901	-269.869
30 % (v/v) Methanol				
2.6539	9.557	6.996	89.640	-268.324
2.7423	9.407	6.846	89.535	-268.470
2.8285	9.350	6.789	89.519	-268.601
2.9121	8.951	6.390	89.370	-269.416
2.9934	8.785	6.224	89.245	-269.547

The following reaction mechanism has been proposed for the reaction under consideration.



$$H_2A \xleftrightarrow{K_1} HA^- + H^+ \quad \text{(i)}$$

$$HA \xleftrightarrow{K_2} A^{2-} + H^+ \quad \text{(ii)}$$

$$MG + H^+ \xleftrightarrow{K_3} MGH^+ \quad \text{(iii)}$$

$$MGH^+ + H_2A \xrightarrow[\text{slow}]{k} MGH + HA^\bullet + H^+ \quad \text{(iv)}$$

$$MGH^+ + HA^\bullet \xrightarrow[\text{fast}]{} MGH + H^+ + A \quad \text{(v)}$$

$$\text{Rate} = -\frac{d[MG]}{dt} = k[MGH^+]\,[H_2A] \quad \text{(vi)}$$

$$K_3 = \frac{[MGH^+]}{[MG]\,[H^+]} \quad \text{(vii)}$$

$$[MG] = \frac{[MGH^+]}{K_3[H^+]} \quad \text{(viii)}$$

$$[MGH^+] = K_3[MG][H^+] \quad \text{(ix)}$$

$$\text{Rate} = -\frac{d[MG]}{dt} = k[MGH^+][H_2A] \quad \text{(x)}$$

$$\text{Rate} = -\frac{d[MG]}{dt} = kK_3[MG][H^+][H_2A] \quad \text{(xi)}$$

$$k' = kK_3[H^+] \quad \text{(xii)}$$

$$-\frac{d[MG]}{dt} = k'[MG][H_2A] \quad \text{(xiii)}$$

$$-\frac{d[MG]}{dt} = k''[H_2A] \quad \text{(xiv)}$$

$$k'' = k'[MG] \quad \text{(xv)}$$

where, H_2A represents undissociated ascorbic acid, HA^- = ascorbate monoanion, A^{2-} = ascorbate dianion [MG] = total methylene green, MGH^+ = monoprotonated form of methylene green, MGH = reduced form of methylene green, K_1 and K_2 = dissociation constants of ascorbic acid, K_3 = formation constant for monoprotonated methylene green and k = rate constant for reduction of methylene green.

Results for thermodynamic parameters such as energy of activation (E_a^*), change in enthalpy of activation (ΔH^*), change in free energy of activation (ΔG^*) change in entropy of activation (ΔS^*), without iodine addition and in presence of iodine are summarized in Tables 3 and 4 respectively. The thermodynamic data also supports that reduction of methylene green with ascorbic acid is influenced by presence of iodine.

The values of change in enthalpy of activation (ΔH^*), change in free energy of activation (ΔG^*) and change in entropy of activation (ΔS^*) were calculated using following relations:

$$\Delta H^* = E_a^* - RT \quad (5)$$

where, (ΔH^*) is change in enthalpy of activation, E_a^* is energy of activation, R is gas constant and T is absolute temperature.

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (6)$$

where, ΔG^* is change in free energy of activation, ΔH^* is change in enthalpy of activation, T is absolute temperature and ΔS^* is change in entropy of activation.

$$\Delta S^* = R \ln\left(\frac{Ah}{k_B T}\right) \quad (7)$$

where, ΔS^* is change in entropy of activation, R is gas constant A is frequency factor obtained from Arrhenius plot, k_B is Boltzman constant and h is Plank's constant and T is absolute temperature.

The plots of ΔH^*, ΔG^* and ΔS^* against square root of ionic strength shown in Figs. 8-10 respectively. Results show that the change in enthalpy of activation (ΔH^*), change in free energy of activation (ΔG^*) and change in entropy of activation (ΔS^*) decreased with the increase in ionic strength.

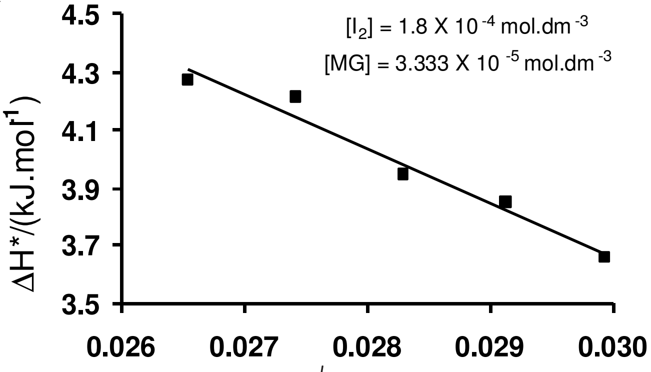


Fig. 8. Plot of ΔH^* *versus* $\sqrt{\mu}$ at 308 K in 20 % aqueous methanol

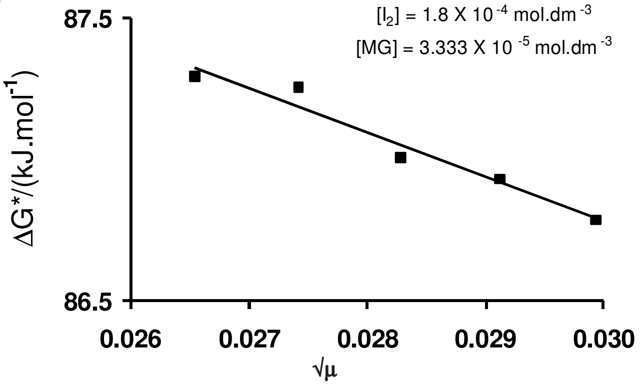


Fig. 9. Plot of ΔG^* *versus* $\sqrt{\mu}$ at 308 K in 20 % aqueous methanol

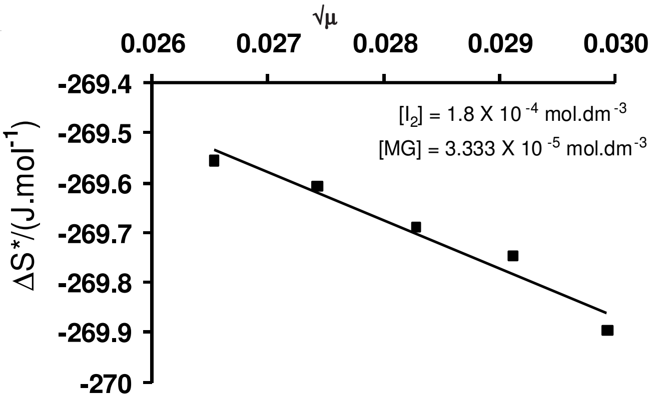


Fig. 10. Plot of ΔS^* *versus* $\sqrt{\mu}$ at 308 K in 20 % aqueous methanol

Decreasing values of change in free energy of activation with increase in ionic strength show that the formation of activated state is spontaneous process. The negative values of entropy show decrease in randomness as a result of increase in charge on activated state as compare to individual ions. The randomness occurs due to interconversion of translational and rotational degree of freedom to vibrational degree of freedom of activated state. It was also observed that change in enthalpy of activation (ΔH^*), change in free energy of activation (ΔG^*) and change in entropy of activation (ΔS^*) increased with the increase in alcoholic content from 10 to 30 % methanol.

Conclusion

The kinetic data was used to determine the effect of ionic strength and temperature on the oxidation reaction between ascorbic acid and methylene green. It was observed that by the addition of iodine the rate of reaction increased. The rate constants show a gradual increase with the increase ionic strength. The rate of reaction is found to be decreased with the increase in methanol content and increased with the increase in concentration of ascorbic acid increased the rate of reaction, which is enhanced by the addition of iodine. The reaction follows first order kinetics with respect to ascorbic acid, fractional order with respect to methylene green and overall reaction follows pseudo first order kinetics. Thermodynamic parameter were also evaluated as a function of ionic strength and the change in free energy of activation (ΔG^*) was found to be decreased with increase in ionic strength that shows the formation of product is spontaneous process.

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