

Kinetics of Methylene Green and Ascorbic Acid Reaction in Aqueous 2-propanol at Different Temperatures

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Authors' contributions

This work was carried out in collaboration between all authors. Author ZK designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors RS, FU and MA managed the analyses and the 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 kinetics of reaction of methylene green with ascorbic acid was carried out spectrophotometrically in mixed solvent system by using aqueous 2-propanol ratios as a solvent in the presence of hydrochloric acid. The pseudo-first order rate constants were proposed on the basis of the experimental kinetic data.

The reaction was carried out in 10%, 20%, 30%, 40%, 50% aqueous 2-propanol ratios at different ionic strength. The effects of these solvent compositions and ionic strength on rate of reaction were studied. The effect of concentration of ascorbic acid on the rate of reduction was also determined. The values of rate constants at all initial concentrations of methylene green revealed that reaction follows 1st order kinetics with respect to ascorbic acid and relatively higher value of the rate of the reaction was observed in the solvent of high dielectric constant. The reaction was found to be zero order dependence on the concentration of methylene green, and the variation of hydrochloric acid concentration did not bring about significant changes in the values of rate constants in various aqueous propanol mixtures.

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The influence of temperature on the rate constant as a function of ascorbic acid concentration was also studied. The Arrhenius relationship was used to determine the various activation parameters such as activation energy (E_a), change in enthalpy (ΔH^\ddagger), change of entropy (ΔS^\ddagger), and the change of free energy of activation (ΔG^\ddagger). The activation parameters determined were found to be dependent on concentration of ascorbic acid and solvent composition. The radii of the activated complex was calculated. It was found that activated complex exists as a single sphere model. The iso-kinetic temperature was also calculated.

Keywords: Kinetics; methylene green; iso-kinetic temperature; activation parameter; radii of activated complex.

1. INTRODUCTION

Dyes photochemistry has a vast contribution to the understanding of the mechanism of electron transfer reactions in photochemical devices. Numerous photoinduced redox reactions of dyes and different reducing agents have been studied in electrochemical cells for the conversion of solar energy to electrical energy by chemical means [1-7]. The role of phenothiazine dyes in biological system has well documented. Photosensitisation of photoexcited dye molecules are widely used in photodynamic therapy of tumors and other diseases [8]. Most of the thiazine dyes interact with nucleic acids, proteins, lipids and induce photosensitized reactions. It binds to deoxyribonucleic acid (DNA) molecule and induces photosensitized reaction, which can be used for sequence-specific cleavage of DNA backbone. Such reactions damage the structure of DNA molecule [9-11]. Phenothiazine dyes have been widely used in adsorption and adsorption processes heterogeneous catalysis, chromatographic analysis, dyeing in textiles and clarification of various effluents [12]. Earlier investigations of the electrochemistry, acid-base chemistry, and dimerization of dyes are readily available in the literature [13-16].

Kinetics and reaction mechanism for different reaction by using various techniques has been a topic of interest for many researchers [17-27]. The kinetics of the oxidation of organic sulfides by butyltriphenylphosphonium dichromate was studied by IR and H^1 NMR spectroscopy [23]. It was concluded that the oxidation was first order with respect to butyltriphenylphosphonium dichromate and second order with the sulfides. The mechanism for the reaction was also proposed. The kinetics of methyl violet with iodide in aqueous methanol system was studied spectrophotometrically. The reaction was found to increase with the increase in alcoholic content and increase in concentration of potassium iodide. Thermodynamic parameters were evaluated as well as the mechanism for the reaction was also proposed [25-26].

The present work reveals the study of the kinetic aspects of the reaction of methylene green with ascorbic acid in mixed solvent system by spectrophotometry. The effect of different parameters such as concentration of ascorbic acid, temperature and dielectric constant on the above reaction process will be helpful in finding out the optimum conditions for a particular dye in connection to its application in different fields as ascorbic acid also have significant importance in medicinal and biological aspects.

2. EXPERIMENTAL

All the reagents used were of analytical reagent grade. All solutions were prepared in doubly distilled water and the dielectric constant of the media was altered by using various compositions of 2- propanol. The ascorbic acid was used as a reducing agent. Spectrophotometric method was adopted to study the reaction of methylene green in mixed solvent system. The wavelength maxima (λ_{\max}) and molar absorption coefficient of methylene green were found as 657 nm and $4.3 \times 10^4 \text{ mol.dm}^{-3}$ respectively at different compositions of solvent. The kinetics was investigated at constant pH 1.2 maintained with hydrochloric acid. The quantitative dependence of rate on various factors such as a concentration of methylene green, concentration of ascorbic acid, concentration of hydrochloric acid, temperature and dielectric constant of media were determined. All stock solutions such as methylene green, ascorbic acid and hydrochloric acid were kept in the water bath (type 52 Haake Karlsruhe which maintained constant temperature within $\pm 0.1^\circ\text{C}$) for about half an hour before the experimental measurements. The calculated volumes of stock solution such as hydrochloric acid, methylene green and ascorbic acid were mixed in a cuvette having capacity of 3.0 ml volume. The absorbance was recorded at 657 nm on UV – 160A Shimadzu spectrophotometer. The reactions were carried out at temperatures ranging from $20 - 60^\circ\text{C} \pm 0.1^\circ\text{C}$ and at various composition ranges from 10% - 50% aqueous 2- propanol as a function of ascorbic acid concentration in acidic pH 1.2.

3. RESULTS AND DISCUSSION

3.1 Calculation of Rate Constant

The kinetics of reaction between methylene green [MG] and ascorbic acid [AA] was studied spectrophotometrically. It was observed that the absorbance decreased as the concentration of ascorbic acid was increased. The rate of decolorization of methylene green with ascorbic acid was found to be slower in less polar medium. The representative plot of absorbance versus time of methylene green with ascorbic acid is shown in Fig. 1. The effect of methylene green was studied by varying concentration from 1×10^{-6} to $3 \times 10^{-6} \text{ mol.dm}^{-3}$. There was no significant change in the rate of reaction was observed with change in concentration of methylene green indicates the reaction follows zero order kinetics with respect to methylene green [14,15].

The reaction kinetics was studied at various temperatures as a function of ascorbic acid concentration at constant pH 1.2. The plots of $\ln(A_t - A_\infty)$ verses time are shown in Fig. 2 and Fig. 3 as function of ascorbic acid and aqueous 2-propanol respectively. The plots shows straight line relation and the values of rate constants (k_{exp}) reported in Table 1, were calculated from slopes of plot $\ln(A_t - A_\infty)$ versus time.

The rate of reaction was found to be dependent to the concentration of ascorbic acid in various solvent compositions. The reaction order with respect to ascorbic acid was found to be 1.04, with correlation factor of 0.91 indicating first order reaction with respect to the concentration of ascorbic acid in media of different dielectric constant.

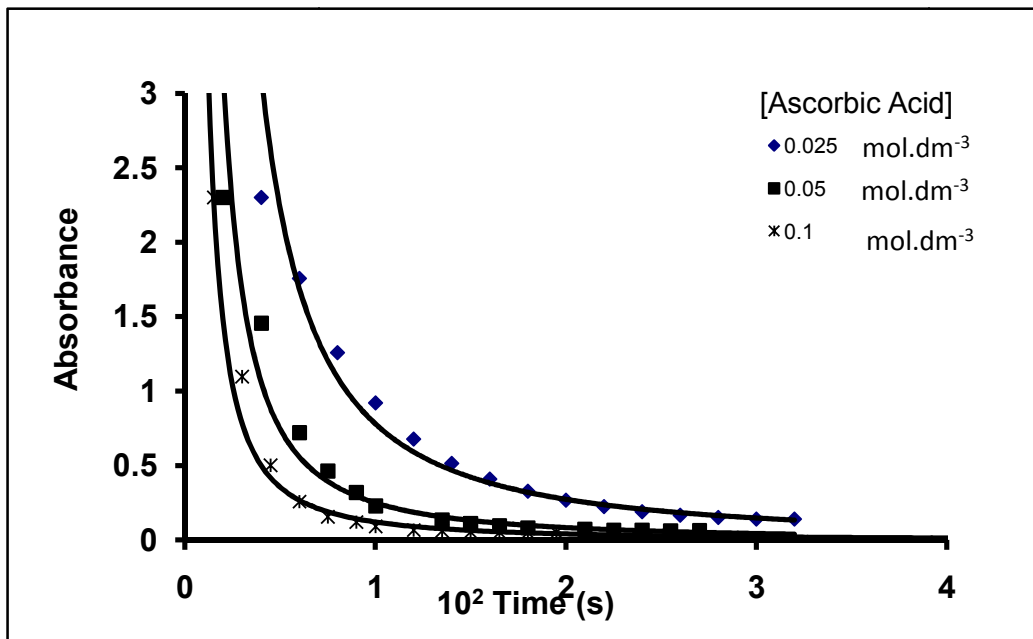


Fig. 1. Plot of absorbance versus time at 657 nm at various concentrations of ascorbic acid in 10% aqueous 2-propanol.

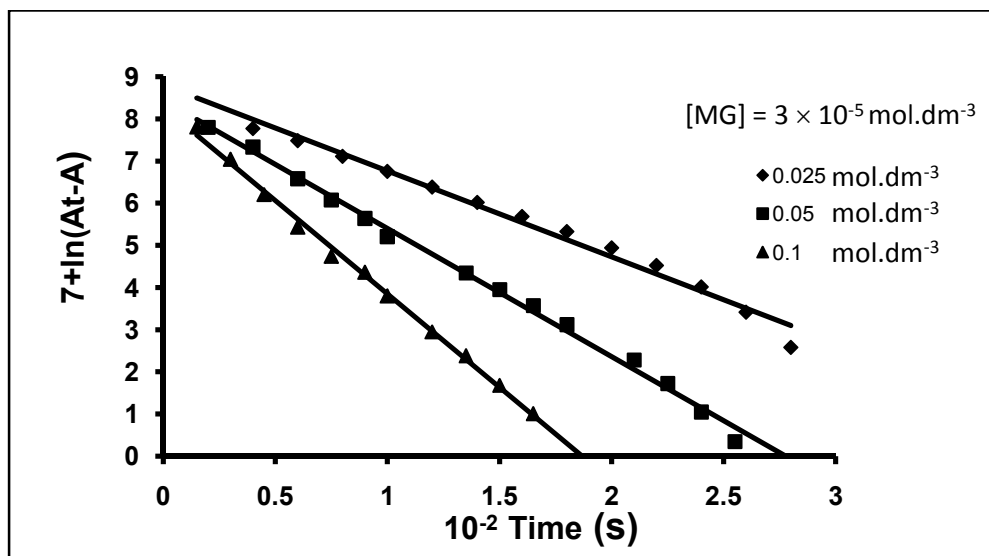


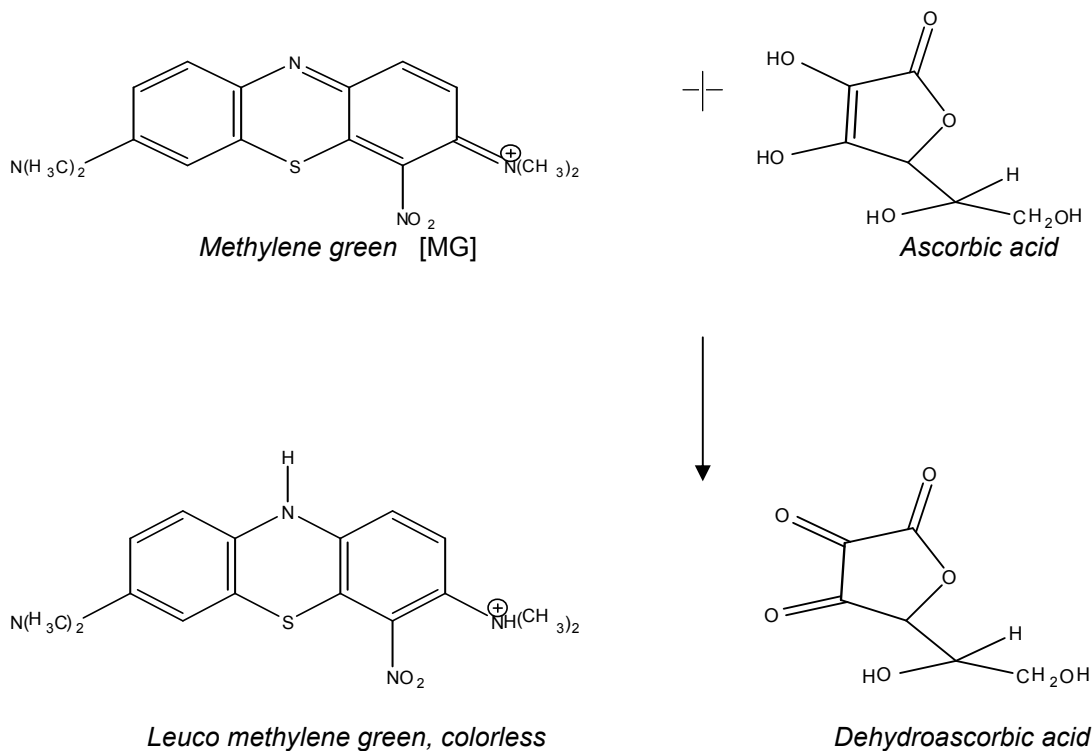
Fig. 2. Plot of $7+\ln(A_t-A_\infty)$ versus time at 293 K in 10% aqueous 2-propanol

The empirical rate law can be expressed as:

$$\text{Rate} = -\frac{d[\text{MG}]}{dt} = k_o = k_{\text{exp}} [\text{AA}] \quad (1)$$

$$k_{\text{exp}} = \frac{k_0}{[\text{AA}]} \quad (2)$$

Where [MG] and [AA] are concentration of methylene green and ascorbic acid respectively, k_0 is the zero order rate constant. The absorbance values of MG at 657 nm were plotted against time. A straight line with negative slope shows the zero order kinetics with respect to dye with slope k_0 . Since zero order kinetics was observed with respect to the dye and 1st order kinetics in ascorbic acid, the transition state should contain only the later ions.



3.2 Variation of Rate Constants with Solvent Composition

The reaction was studied at various compositions such as 10, 20, 30, 40 and 50% aqueous 2-propanol as a function of concentration of ascorbic acid and temperature. The results of rate constants conducted are tabulated in Table 1. The rate constants were obtained from slopes of the line plotted between $\ln(A_t - A_\infty)$ and time shown in Fig. 2 and Fig. 3. The rate constants were found to be influenced by the dielectric constant of the media. The results indicate that the rate of reaction is greatly influenced by the physicochemical properties and polarity of the solvents. At lower dielectric constant, the polarity of the system decreases because in aqueous alcoholic solutions the hydrogen bonding of alcohol shows interaction with water molecules. Moreover breaking of water structure due to added solvent induces the hydrophobic character of the reactants. As the association of organic solvent prevents the self-association of methylene green at lower dielectric constant, there is a decrease in the rate of reaction.

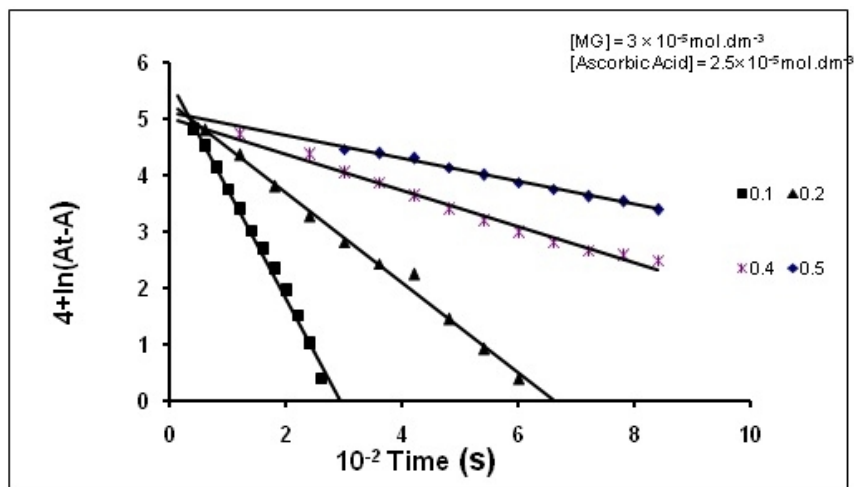


Fig. 3. Plot of $4+\ln(A_t-A_\infty)$ versus time in different aqueous 2-propanol system at 293 K

3.3 Effect of Temperature

The effect of temperature on reaction rate was studied and results are summarized in Table 1. The values of rate constant were found to decrease as the 2-propanol composition increases and increases with the rise of temperature. The effect of temperature on reaction rate is defined by Arrhenius relation:

$$k = A.e^{\frac{E_a}{RT}} \quad (3)$$

Where E_a is the apparent activation energy, R is the universal gas constant and T is the temperature in Kelvin. A plot of $\ln k$ against $1/T$ as a function of concentration of ascorbic acid in 10% aqueous 2-propanol was found to be linear over the accessible temperature range as shown in Fig. 4.

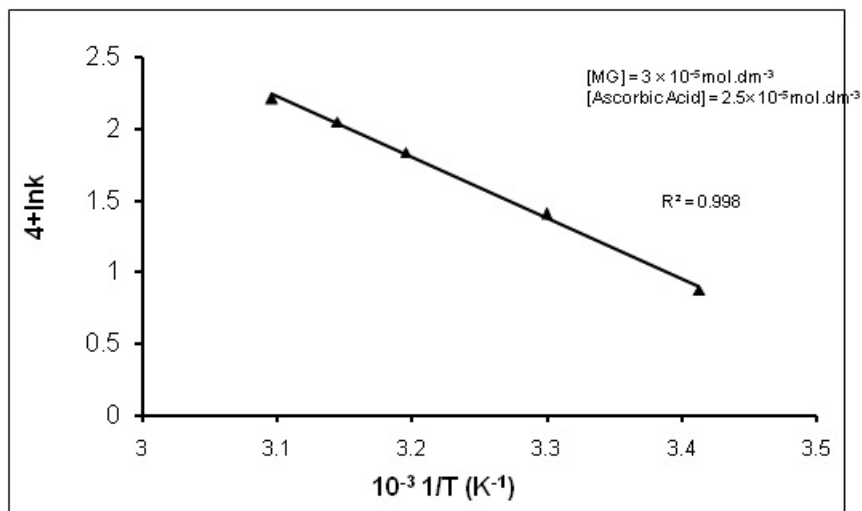


Fig. 4. Plot of $\ln k$ versus $1/T$ in 10% aqueous 2-propanol

Table 1. The values of Rate constant (k_{exp}) of reduction of methylene green with ascorbic acid in aqueous 2-propanol at different temperatures

% Aqueous 2-propanol	$10^2 k_{\text{exp.}} (\text{s}^{-1})$ at temperature (K)				
	293	303	313	318	323
[ascorbic acid] = $2.5 \times 10^{-2} \text{ mol.dm}^{-3}$					
10	1.95	2.69	4.14	6.75	8.36
20	0.86	1.61	2.35	4.45	6.64
30	0.60	1.00	1.71	2.83	4.10
40	0.33	0.66	1.09	1.67	2.97
50	0.21	0.50	0.60	1.09	2.01
[ascorbic acid] = $5.03 \times 10^{-2} \text{ mol.dm}^{-3}$					
10	3.04	5.38	6.36	10.51	13.71
20	2.04	2.75	4.47	7.67	11.17
30	0.97	2.19	3.07	5.00	7.31
40	0.94	1.30	2.09	2.83	5.1
50	0.54	0.74	1.42	2.23	3.87
[ascorbic acid] = $7.53 \times 10^{-2} \text{ mol.dm}^{-3}$					
10	4.24	5.91	10.93	12.80	15.67
20	2.13	4.14	6.60	7.88	11.69
30	1.46	2.66	3.99	6.10	9.30
40	0.97	1.90	2.85	4.92	6.49
50	0.82	0.97	1.97	3.45	4.73
[ascorbic acid] = $8.83 \times 10^{-2} \text{ mol.dm}^{-3}$					
10	4.41	7.45	11.49	14.18	16.70
20	2.75	4.32	7.31	8.53	14.09
30	1.55	3.10	4.67	7.19	10.07
40	1.078	1.99	3.01	4.94	7.14
50	0.823	1.06	2.16	3.50	4.82
[ascorbic acid] = $10.03 \times 10^{-2} \text{ mol.dm}^{-3}$					
10	5.25	9.39	11.79	15.15	18.40
20	3.07	5.31	8.19	10.38	15.54
30	1.97	3.20	4.86	7.90	10.61
40	1.33	2.20	3.24	5.86	8.208
50	0.995	1.19	2.85	3.91	5.58

$$[\text{Methylene Green}] = 3 \times 10^{-6} \text{ mol.dm}^{-3}$$

The resulting Arrhenius parameters E_a (energy of activation) and frequency factor (A) are obtained from the value of slopes and intercepts of plot $\ln k$ versus $1/T$ respectively. The energy of activation was found to increase with the decrease in dielectric constant of the medium. The rise of energy of activation shows the reaction is slower in solvent of low dielectric constant. When the reaction occurs between two similar charge ions, the activated state becomes highly charged than reactants. The polarized activated state becomes less stable in less polar solvent; therefore the formation of activated state becomes slow as the concentration of 2-propanol increases. It was also observed that the values of frequency factor (A) which depends on collision frequency and steric factor is found to be in the following order in aqueous 2-propanol:

$$10\% < 20\% < 30\% < 40\% < 50\%$$

$$9.99 < 13.12 < 13.91 < 13.98 < 14.72$$

The values show the frequency factor increased with decrease in dielectric constant of solvent. As due to the decrease in polarity of solvent by the increase in alcohol content the steric hinderance increased, that results the decrease in the collision frequency and effective number of collision, so the rate of reaction became slow in less polar solvent.

The Eyring parameters, such as the change in activation enthalpy (ΔH^\ddagger), entropy change (ΔS^\ddagger) and free energy change (ΔG^\ddagger) were calculated by using usual relations [18]

$$k = \frac{K_B T}{h} e^{\frac{\Delta H^\ddagger}{RT}} e^{\frac{\Delta S^\ddagger}{R}} \quad (4)$$

where K_B is Boltzman constant and h is Planck's constant. The results are summarized in Table 2. The positive values of enthalpy change show that the reaction is endothermic. The result show that the free energy of reaction increase very slowly with increase in the solvent composition indicate the stability of the transition state, which is very slightly affected by the addition of organic solvent. The variation of enthalpy and entropy of activation obeys the Barclay – Bulter rule [18-21] by the following relation:

$$\Delta H^\ddagger = \Delta H_0^\ddagger + \beta \Delta S^\ddagger \quad (5)$$

Where ΔH^\ddagger is change in enthalpy of activation, ΔS^\ddagger is change in entropy of activation, β is iso-kinetic temperature and ΔH_0^\ddagger is enthalpy change at zero entropy. The iso-kinetic temperature was evaluated from the slope of the plot of ΔH^\ddagger against ΔS^\ddagger . The representative plot of ΔH^\ddagger versus ΔS^\ddagger is shown in Fig. 5, the value of iso-kinetic temperature (β) is found to be 409.8916 K. The value of slope predicts strong interaction at activated state and change in solvation does not change the actual mechanism. The values of free energy change of activation (ΔG^\ddagger) were found to increase with the increase in alcoholic content indicating slow reaction.

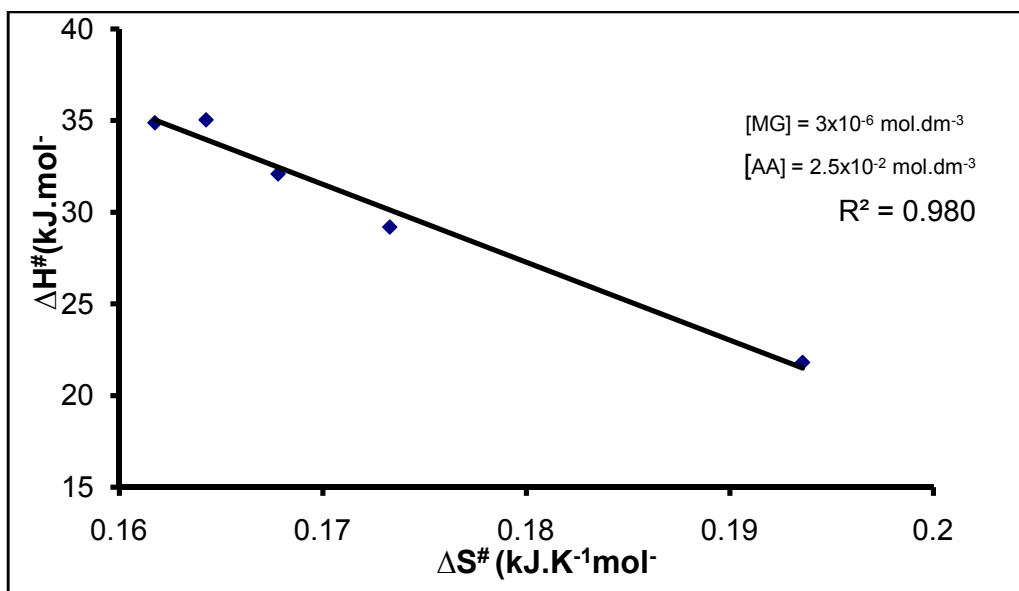


Fig. 5. Plot of ΔH^\ddagger against ΔS^\ddagger in aqueous 2-propanol

Table 2. Activation parameters for the reduction of methylene green with ascorbic acid at 313 K

10 ² Ionic Strength, (mol.dm ⁻³)	10% 2-propanol	20% 2-propanol	30% 2-propanol	40% 2-propanol	50% 2-propanol
E_a (kJ mol⁻¹)					
2.50	31.0900	40.7585	39.6644	43.2261	43.0111
5.03	29.9199	35.8184	39.6220	40.7070	41.2424
7.50	27.6399	33.0370	37.5410	38.5978	38.6451
8.80	27.0379	32.0790	37.3348	38.1222	38.3541
10.03	24.4049	31.8509	34.6843	37.4754	37.6349
ΔH[#] (kJ mol⁻¹)					
2.50	28.4962	38.8297	37.0705	40.6322	40.4160
5.03	27.3239	28.2360	37.0270	31.0328	38.4995
7.50	25.0426	30.4417	34.9470	36.0384	36.0503
8.80	24.4614	29.4781	34.7400	35.5282	35.7593
10.03	21.8101	29.1896	32.0904	34.8806	35.0416
ΔS[#]/(JK⁻¹ mol⁻¹)					
2.50	-180.542	-151.693	-160.798	-153.243	-157.328
5.03	-180.132	-164.472	-155.950	-178.246	-158.661
7.50	-185.270	-171.859	-160.368	-159.805	-162.791
8.80	-186.324	-173.835	-160.087	-160.827	-163.361
10.03	-193.574	-173.290	-167.808	-161.746	-164.266
ΔG[#] (kJ mol⁻¹)					
2.50	87.1968	86.3086	87.4003	88.5973	89.6597
5.03	83.7052	79.7157	85.8393	86.8238	88.1604
7.50	83.0321	84.2336	85.1422	86.0574	87.0039
8.80	82.7808	83.8885	84.8472	85.8671	86.8913
10.03	82.3988	83.4294	84.6143	85.5071	86.4569

$$[\text{Methylene Green}] = 3 \times 10^{-6} \text{ mol.dm}^{-3}$$

3.4 Evaluation of Ionic Radii of the Activated Complex

The values of the rate constant at zero ionic strength were evaluated by using the following relation [18]

$$\log k = \log k_o + \frac{e^3 \left(\frac{8N_A}{1000} \right)^{\frac{1}{2}} Z_A Z_B \sqrt{\mu}}{(DK_B T)^{\frac{3}{2}} 2.303} \quad (6)$$

Where k_o is the rate constant at zero ionic strength, e and N_A are charge on electron and Avogadro's number, Z_A and Z_B are the charges on methylene green (MG^+), and H^+ ion released by ascorbic acid, μ is the ionic strength, D and K_B are dielectric constant and Boltzmann constant respectively. The values of k_o are reported in Table 3.

The representative plot of $\log k_o$ against $1/D$ were drawn and shown in Fig. 6 represents straight line with negative slope. The slope indicates that the activated complex is more solvated than the reactants and there is increase in electrostatic interaction between the reacting ions at lower dielectric constant. The values of slope were used to calculate the radii

of single sphere activated complex $r^\#$ and double sphere activated complex r_{AB} [18-20] by using the equations (7) and (8) respectively

$$\ln k_o = \ln k_\infty - \frac{e^2}{2DK_B T} \left[\frac{(Z_A + Z_B)^2}{r^\#} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B} \right] \quad (7)$$

$$\ln k_o = \ln k_\infty - \left[\frac{e^2 Z_A Z_B}{D K_B T r_{AB}} \right] \quad (8)$$

Where r_A and r_B are the radii of the methylene green (MG^+) and hydrogen ion (H^+) respectively. $r^\#$ is the radius of single sphere activated complex and r_{AB} is the radius of double sphere activated complex. The values of single sphere and double sphere activated complex, calculated are 6.4586 Å and 3.2431 Å respectively.

Table 3. The Values of k_o for the reduction of methylene green in various composition of 2- propanol at different ionic strengths

10^{-2} μ (mol.dm ⁻³)	k_o at temperature (K)				
	293	303	313	318	323
10% 2-propanol					
2.50	0.2174	0.3029	0.3716	0.3766	0.4149
5.03	0.2848	0.3951	0.4943	0.4952	0.5589
7.50	0.3488	0.5307	0.5724	0.5737	0.6308
8.80	0.3643	0.5572	0.6152	0.6167	0.6673
10.03	0.4017	0.5764	0.6479	0.6496	0.7126
20% 2-propanol					
2.50	0.1573	0.2448	0.3229	0.3263	0.3889
5.03	0.2506	0.3550	0.4488	0.4555	0.5375
7.50	0.2734	0.4551	0.4872	0.4960	0.5903
8.80	0.3151	0.4868	0.5205	0.5308	0.6620
10.03	0.3392	0.5251	0.5820	0.5942	0.7104
30% 2-propanol					
2.50	0.1403	0.2226	0.2774	0.2795	0.3304
5.03	0.1925	0.3207	0.3970	0.4013	0.4475
7.50	0.2495	0.3907	0.4709	0.4771	0.5907
8.80	0.2658	0.4345	0.5255	0.5329	0.6242
10.03	0.3042	0.4564	0.5651	0.5736	0.6602
40% 2-propanol					
2.50	0.1146	0.1947	0.2347	0.2369	0.2171
5.03	0.2061	0.2962	0.3385	0.3430	0.4487
7.50	0.2314	0.3759	0.4775	0.4853	0.5559
8.80	0.2529	0.4034	0.5014	0.5103	0.6090
10.03	0.2877	0.4331	0.5616	0.5722	0.6045
50% 2-propanol					
2.50	0.1023	0.1583	0.2128	0.2155	0.2849
5.03	0.1823	0.2542	0.3456	0.3158	0.4555
7.50	0.2480	0.3261	0.4765	0.4869	0.5716
8.80	0.2480	0.3562	0.5089	0.5209	0.7737
10.03	0.2996	0.4183	0.5612	0.5753	0.6897

[Methylene Green] = 3×10^{-6} mol.dm⁻³

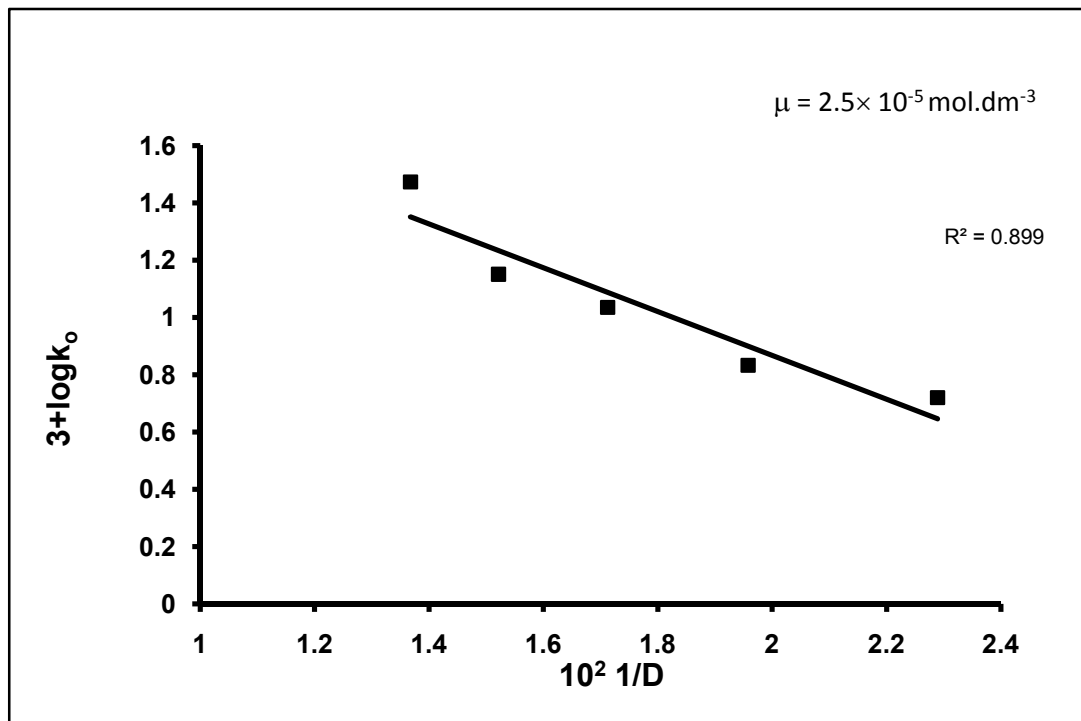


Fig. 6. Plot of $\log k_o$ versus $1/D$ in aqueous 2-propanol at 293K.

3.5 Theoretical Calculation of Radii of Activated Complex

The radii of the methylene green (MG^+) and hydrogen ion (H^+) are calculated on the assumption that the volume of the molecule of a compound, which is supposed to be spherical, is the sum of the volumes of individual ions, therefore the numerical values of radii of constituent ions were taken from literature [27]. The values of radius of MG^+ ion was calculated as [19,20]

$$\begin{aligned} \text{Volume } (MG^+) &= 16V_C^{+4} + 17V_H^+ + 4V_N^{-3} + V_S^{-2} + 2V_O^{-2} \\ \text{Since volume } (V) &= \frac{4}{3} \pi r^3 \\ r(MG^+) &= 5.6955 \text{ \AA} \end{aligned} \quad (9)$$

Radius of ascorbate ion was calculated and found to be 4.298 Å. The radius of activated complex for double sphere model r_{AB} is calculated on the assumption that the radius of activated complex is the sum of radii of the reactants:

$$\begin{aligned} r_{AB} &= r(MG^+) + r(AA^+) \\ &= 5.6955 + 4.298 \\ &= 9.9935 \text{ \AA} \end{aligned} \quad (10)$$

The radius of the activated complex for single sphere model (r^\ddagger) is calculated on the basis of assumption that the volume of single sphere complex is the sum of volumes of reactants:

$$V^\ddagger = V_A + V_B \quad (11)$$

$$r^{\#} = 6.4163 \text{ \AA}$$

The theoretical value of the radius of activated complex for double sphere model r_{AB} and the radius of the activated complex for single sphere model ($r^{\#}$) is calculated as 9.9935 Å and 6.4163 Å.

The comparison of the average experimental values of single sphere activated complex ($r^{\#}$) and double sphere activated complex (r_{AB}) was made with the theoretical values. The result showed that the Laidler-Eyring's [18] approach of single sphere model holds more closely than that of double sphere model, proposed by Amis and Scatchard [18].

4. CONCLUSION

The kinetics study show that the rate of reaction is a function of the concentration of ascorbic acid and varies with temperature. The reaction follows first order kinetics and activated state folds single sphere model. It was also shown that activation energy is found to be decreased by increasing the dielectric constant of the media. The enthalpy of activation ($\Delta H^{\#}$) and the values of free energy of activation ($\Delta G^{\#}$) decreases by increasing concentration of ascorbic acid. These values were found to be minimum at higher dielectric constant. The value of iso-kinetic temperature was found to be 409.8916 K.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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