



Chiang Mai J. Sci. 2015; 42(4) : 963-971

<http://epg.science.cmu.ac.th/ejournal/>

Contributed Paper

Kinetic Study of Reduction of N-[4-[Bis[4-dimethylamino)-phenyl]-methylene]-2,5-cyclohexadiene-1-ylidene]-methanaminium Chloride with Iodide in Aqueous Ethanol System

Maria Ashfaq*[a], Rehana Saeed [a], Summyia Masood [a] and Sameera Razi Khan [b]

[a] Department of Chemistry, University of Karachi, Karachi-75270, Pakistan.

[b] Department of Chemistry, Federal Urdu University of Arts, Science and Technology, Karachi-75300, Pakistan.

*Author for correspondence; e-mail: maria_chemku@yahoo.com; ashfaqmaria01@gmail.com and rehana_saeed01@hotmail.com

Received: 25 April 2014

Accepted: 14 December 2014

ABSTRACT

The kinetics of reduction of N-[4-[Bis[4-dimethylamino)-phenyl]-methylene]-2,5-cyclohexadiene-1-ylidene]-methanaminium chloride (methyl violet) with potassium iodide was studied in ethanol-water solvent spectrophotometrically at 579 nm. The reduction of methyl violet was studied at different concentrations of potassium iodide ranging from 0.1-0.5 mol. dm⁻³ in 10-30% ethanol-water system at pH 4.99 and 6.0. The rate of the reaction was studied at various temperature ranges from 298-318 K. The rate of the reaction was also influenced by medium and found to be faster as the polarity of the medium was lowered. The kinetic analysis show reduction of methyl violet with iodide is pseudo first order as first order with respect to potassium iodide and found independent of methyl violet concentration. Effect of temperature on the rate constant were analysed by Arrhenius relation used to calculate activation energy (E_a^*) from reduction reaction. The activation parameters such as enthalpy change of activation (ΔH^*), entropy change of activation (ΔS^*) and Gibbs free energy change of activation (ΔG^*) were also evaluated.

Keywords: methyl violet, reduction, kinetics, activation parameters

1. INTRODUCTION

N-[4-[Bis[4-dimethylamino)-phenyl]-methylene]-2,5-cyclohexadiene-1-ylidene]-methanaminium chloride (methyl violet), is a triphenylmethane dye. Triphenylmethane dyes are aromatic xenobiotic compounds possess outstanding intensity of color and their brilliant shades of red, blue and green. They are used

extensively in many industrial processes, such as textile (wool, silk and nylon), dyeing, paper printing, and food, cosmetic manufacture, leather, pharmaceutical industries, medical and related biological processes. They exhibit antibacterial properties and are used for the disinfection of post – operative wounds. Also

dyes of this class are frequently used to assay proteins and others are utilised in cytology and histology to stain tissue [1-11].

The kinetics of fading of dyes has been investigated as a function of various parameters such as pH, salt effect, dielectric constant, surfactants and light [12-26]. The rate of reaction of alkaline hydrolysis of crystal violet in aqueous medium was inhibited in the presence of surfactants, sodiumdodecylbenzene sulfonate (SDBS) and sodiumdodecyl sulfate (SDS) [12]. The electrical charge on the surfactant also affect the fading of crystal violet. The rate constant of crystal violet in presence of non ionic and cationic surfactant increases while decrease in presence of anionic surfactant [13]. The basic hydrolysis of malachite green displayed a negative salt effect. The reaction rate was found to decrease with increase in anionic concentration and increase solvent polarity [14,15]. The rate of redox reaction of malachite green with permanganate in acidic medium decreased with ionic strength and increase with decrease in dielectric constant of the medium [16].

Methyl violet act as a cationic dye having intense violet color due to the extended conjugated system of alternate single and double bonds. Iodide behaves as a nucleophile and attacks the conjugated system of methyl violet converting into a colorless product. Present study reveals the spectrophotometric study of the kinetics of the reduction of methyl violet in aqueous ethanol system in the presence of salt (KI) as function of pH, concentration of dye, concentration of potassium iodide and temperature. The transition energies of excited states (E_T), activation energy, free energy change, enthalpy change and entropy change for reduction have been studied.

2. MATERIALS AND METHODS

All the glasswares of Pyrex A grade quality were used. Apparatus were washed, rinsed and

dried in oven (W.T.C binder, 7200, Tuttlingsh/Germany, Type28, No.89248).

The absorbance of reaction mixture was recorded using a spectrophotometer (Shimadzu (UV-160) meanwhile pH measurement was carried out on HI-1332 and digital pH meter (Orion, 1990 Orion research Inc. Boston, MA02129 USA). A constant temperature of reaction mixture was maintained throughout the whole experiment by using a bath (circulator model, YCW01).

2.1 Material

N-[4-[Bis[4-dimethylamino)-phenyl]-methylene]-2,5-cyclohexadiene-1-ylidene]-methanaminium chloride commonly known as methyl violet (C.I Nr.42535) of Riedel-De Haen AG Seelze-Hannover of 75% purity was used without further purification. potassium iodide, sodium hydroxide, hydrochloric acid, sulphuric acid, and sodium acetate of E. Merck were used. Ethanol of E. Merck having density (0.79 kg/L) was used without any purification. Freshly prepared double distilled water having conductivity (0.06mScm^{-1}) was used for preparation of solutions.

2.2 Methods

The stock solutions of methyl violet, potassium iodide, hydrochloric acid, sodium hydroxide, sodium acetate and sulphuric acid were prepared in aqueous ethanol solvents as 10, 20 and 30% (v/v) respectively. The pH of solution was maintained by Hammelt acidity function (H_0) using optical method: [20-21]

$$H_0 = pK + \log \frac{d_1 - d_0}{d_0 - d_2} \quad (1)$$

where d_0 , d_1 and d_2 are the absorbance of intermediate, extreme acidic, basic acidity solutions respectively. pK value for acidic acridine solution was taken as 5.41 ± 0.05 . The acidic range of acidity was selected 4.99 and 6.0.

The maximum wavelength of methyl violet was found 579 nm recorded on UV-Visible double beam spectrophotometer (Shimadzu (UV-160)). The kinetics study of reduction of methyl violet with potassium iodide was carried out in water and ethanol-water solvent on double beam spectrophotometer at 579 nm within temperature range 298-318 K. Different aliquots of reactants were placed in a reaction cell of capacity 3 ml. The pH of the reaction was maintained at 4.99 and 6.0 using sodium acetate buffer. The concentration of methyl violet was fixed at $7 \times 10^{-5} \text{ mol.dm}^{-3}$, while concentration of potassium iodide was varied from 0.1 - 0.5 mol.dm^{-3} . The absorbance change was recorded at λ_{max} 579 nm at regular intervals of time.

3. RESULTS AND DISCUSSION

The reduction kinetics of methyl violet with potassium iodide in aqueous and aqueous ethanol mixtures was studied spectrophotometrically. The absorption spectrum of methyl violet in aqueous and aqueous ethanol mixture was recorded at λ_{max} 579 nm. The spectrum showed shifting of band toward shorter wavelength as the polarity of the medium is increased, causing hypsochromic shift. The molar absorptivity coefficient (ϵ) of methyl violet in aqueous and aqueous ethanol was found to be 3.457×10^3 and $10.3571 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$. The values of λ_{max} and molar absorptivity coefficient (ϵ) (Table 1) increased with the decrease in polarity of the medium [17,18]. The shifting of band is due to differential stabilization of the ground

and excited state, which causes changes in the energy between these electronic states. Non-polar excited state is stabilized more in non-polar solvent, decreasing the energy gap between the two states resulting in increase of wavelength. As the energy gap between the two states decrease in non polar solvent, the probability of transition increases which in turn increase the molar absorptivity coefficient, which is also shown by the values of transition energy decrease as reported in Table 1, calculated by relation: [22]

$$E_T = \frac{hcN_A}{\lambda_{\text{max}}} \quad (2)$$

Where h is the Planck's constant, c is the speed of light, λ_{max} is the wavelength of maximum absorption and N_A is the Avogadro's number. The reaction rate of methyl violet with iodide was studied with varying concentration of potassium iodide (0.1-0.5 mol.dm^{-3}) at temperature range 298-318K with a difference of 5 K in acidic medium. The solvent composition was varied from 10 - 30% aqueous ethanol mixture at pH 4.99 and 6.0. The repeated spectral scan of reduction of methyl violet with iodide is shown in Figure 2.

The decrease in the absorbance was recorded for the reduction of methyl violet with potassium iodide as decolorisation was observed with time. The change in absorbance of methyl violet was found to decrease by increasing the concentration of potassium iodide from 0.1 - 0.5 mol.dm^{-3} in aqueous and aqueous ethanol system. The increase in

Table 1. Wavelength, absorbance, transition energy (E_T) and molar absorptivity (ϵ) of methyl violet in aqueous and aqueous ethanol system.

Solvent	λ_{max} (nm)	Absorbance	ϵ ($\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$)	E_T (kJ.mol^{-1})
Water	579	0.242	3457.14	206.69
10% ethanol	581	0.725	10357.1	205.89

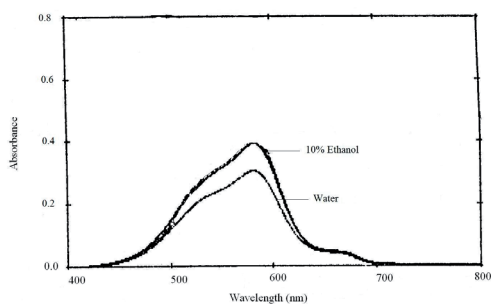


Figure 1. Absorption spectrum of methyl violet in aqueous and aqueous ethanol.

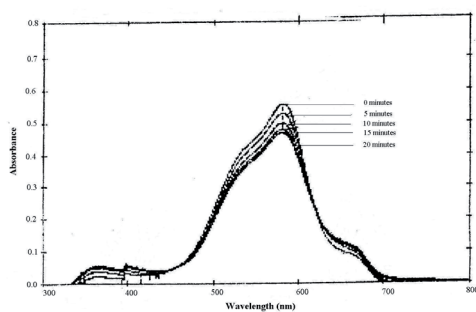


Figure 2. Repeated spectral scan of reduction of methyl violet in acidic 10% aqueous ethanol at $KI = 0.4 \text{ mol.dm}^{-3}$.

concentration of potassium iodide increase the effective collisions between reactant's molecules resulting immediate formation of activated state. The iodide as a nucleophile attacks the central carbon of methyl violet cation, disrupting the conjugation of methyl violet. The decrease in conjugation of molecule leads to the decrease in absorbance, and increase in rate of reaction. The plot of absorbance versus time is shown in Figure 3. The values for rate constants (k) were determined by the linear plot of $\ln(A_t - A_\infty)$ versus time and results are reported in Table 2 and Table 3. The representative plot of $\ln(A_t - A_\infty)$ versus time in 10% aqueous ethanol system is shown in Figure 4.

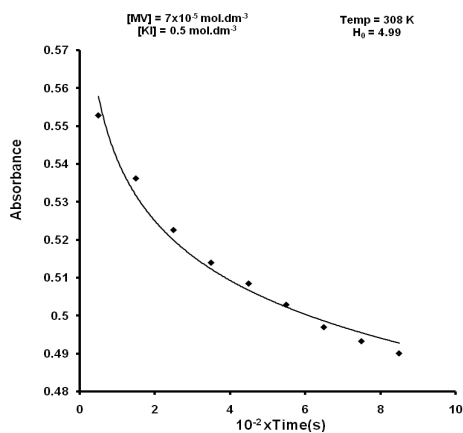


Figure 3. Plot of absorbance of methyl violet against time in 10% ethanol.

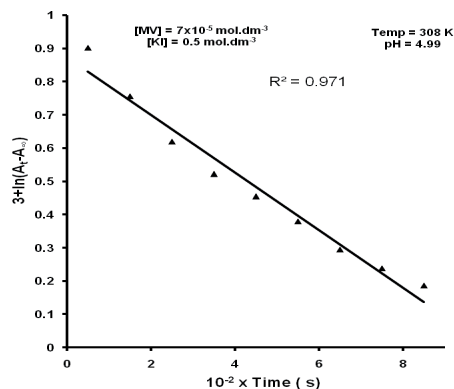


Figure 4. Plot of $\ln(A_t - A_\infty)$ of methyl violet against time in 10% ethanol.

The influence of methyl violet concentration on the reaction of methyl violet with iodide was examined over a range of 1×10^{-5} - $9 \times 10^{-5} \text{ mol.dm}^{-3}$. The reaction was studied at temperature range 298 - 318 K in 10-30% aqueous ethanol. The rate was found to be independent of methyl violet concentration. The rate of reaction was also studied as the function of pH, and the rate was found to be slightly effected by the variation in pH.

The influence of medium on rate constant in aqueous and aqueous ethanol system at various temperatures was studied using Laidler Eyring equation [23,25]:

Table 2. Rate constants of methyl violet in aqueous ethanol at $H_0 = 4.99$ at various temperatures.

$$[MV] = 7 \times 10^{-5} \text{ mol.dm}^{-3}$$

$10^3 k \text{ (s}^{-1}) \text{ in Aqueous Ethanol}$			
T (K)	10%	20%	30%
$[KI] = 0.1 \text{ mol.dm}^{-3}$			
298	1.343	1.963	
303	1.471	2.375	2.493
308	1.562	2.421	2.568
313	1.827	2.475	2.683
318	1.830	2.679	2.962
$[KI] = 0.2 \text{ mol.dm}^{-3}$			
298	2.100	2.428	-
303	2.190	2.498	2.585
308	2.400	2.170	2.612
313	2.450	2.858	2.844
318	2.680	2.910	2.971
$[KI] = 0.3 \text{ mol.dm}^{-3}$			
298	2.210	2.509	2.685
303	2.500	2.708	2.809
308	2.540	2.743	2.897
313	2.690	2.886	3.028
318	2.700	2.977	3.139
$[KI] = 0.4 \text{ mol.dm}^{-3}$			
298	2.711	-	2.833
303	3.017	2.763	3.000
308	3.137	2.893	3.015
313	3.150	2.999	3.179
318	3.262	3.082	3.250
$[KI] = 0.5 \text{ mol.dm}^{-3}$			
298	2.891	3.170	3.19
303	3.048	3.185	3.423
308	3.182	3.356	3.506
313	3.239	3.403	3.643
318	3.389	3.531	3.754

ESD = ± 0.007 **Table 3.** Rate constants of methyl violet in aqueous ethanol at $H_0 = 6$ at various temperatures.

$$[MV] = 7 \times 10^{-5} \text{ mol.dm}^{-3}$$

$10^3 k \text{ (s}^{-1}) \text{ in Aqueous Ethanol}$			
T (K)	10%	20%	30%
$[KI] = 0.1 \text{ mol.dm}^{-3}$			
298	2.200	2.221	2.432
303	2.248	2.361	2.559
308	2.415	2.501	2.731
313	2.574	2.718	2.886
318	2.720	2.800	2.997
$[KI] = 0.2 \text{ mol.dm}^{-3}$			
298	2.100	2.434	2.628
303	2.200	2.463	2.810
308	2.475	2.683	2.824
313	2.709	2.800	3.020
318	2.740	2.930	3.185
$[KI] = 0.3 \text{ mol.dm}^{-3}$			
298	2.230	2.642	2.739
303	2.610	2.741	2.814
308	2.840	2.901	2.949
313	2.939	2.978	3.076
318	3.110	3.098	3.170
$[KI] = 0.4 \text{ mol.dm}^{-3}$			
298	2.500	2.961	-
303	2.720	3.070	3.049
308	3.150	3.186	3.194
313	3.216	3.313	3.358
318	3.403	3.397	3.349
$[KI] = 0.5 \text{ mol.dm}^{-3}$			
298	3.000	3.180	3.000
303	3.235	3.254	3.556
308	3.374	3.373	3.743
313	3.490	3.500	3.795
318	3.585	3.596	3.926

ESD = ± 0.009

$$\ln k_0 = \ln k_\infty - \frac{Z_A Z_B e^2}{\epsilon d_{AB} k_B T} \quad (3)$$

where k_∞ is the rate constant at zero ionic strength. $Z_A = (+1)$ is the charge of methyl violet and $Z_B = (-1)$ is the charge of iodide. r_{AB} is the distance between the centers of methyl violet and iodide in activated complex, e is the electric charge, k_B is the Boltzmann constant and ϵ is the dielectric constant of the medium.

The rate of reduction reaction between methyl violet and the iodide increased in the percentage of ethanol due to decrease in the dielectric constant of medium from water to 30% aqueous ethanol (i.e 72.82 to 61.06 at 298 K). The decreasing trend of the dielectric constant for the medium enhances the electrostatic attraction between opposite charge ions. This led to the conclusion that there is an increase in the electrostatic interaction between the methyl violet cation and iodide at lower dielectric constant in order

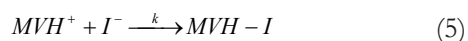
30% ethanol > 20% ethanol > 10% ethanol,

As the ethanolic content increases, the polarity of the medium decreases, as well as dielectric constant decreases. As the activated state is less polar than charged reactants,

therefore activated state is more solvated in aqueous ethanol than in aqueous medium.

The reduction of methyl violet with potassium iodide is relatively higher in 30% ethanol than in 20% and 10% ethanol shown in Figure 5.

On the basis of experimental data the mechanism of the above reaction was evaluated as under:



$$Rate = k[MVH^+][I^-] \quad (6)$$

$$K = \frac{[MVH^+]}{[MV][H^+]} \quad (7)$$

$$[MV] = \frac{[MVH^+]}{K[H^+]} \quad (8)$$

At equilibrium the total MV is the sum of protonated and unreacted methyl violet concentration

$$[MV]_r = [MV] + [MVH^+] \quad (9)$$

substituting values of $[MV]$ from eq.(8) in eq.(9)

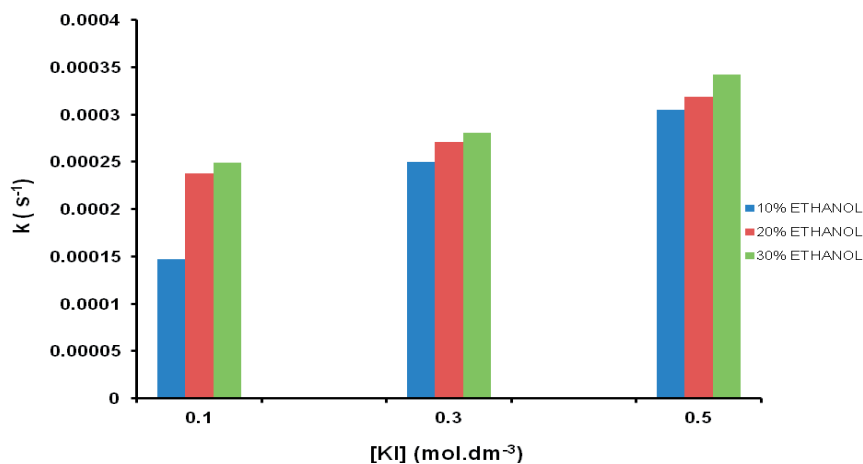


Figure 5. Plot of rate constant (k) against $[KI]$ in various composition of aqueous ethanol at 303 K.

$$[MV]_r = \frac{[MVH^+]}{K[H^+]} + [MVH^+] \quad (10)$$

$$[MV]_r = \frac{[MVH^+] + K[MVH^+][H^+]}{K[H^+]} \quad (11)$$

$$[MV]_r = [MVH^+] \left(\frac{1 + K[H^+]}{K[H^+]} \right) \quad (12)$$

$$[MVH^+] = \frac{K[MV]_r[H^+]}{1 + K[H^+]} \quad (13)$$

substituting values of $[MVH^+]$ from eq.(13) in eq.(6)

$$Rate = \frac{Kk[MV]_r[H^+][I^-]}{1 + K[H^+]} \quad (14)$$

at fixed concentration of methyl violet, the $\frac{Kk[H^+][MV]_r}{1 + K[H^+]}$ is replaced by k' i.e.

$$Rate = k'[I^-] \quad (15)$$

Where $[MV]$ = Methyl violet, $[MVH^+]$ = Protonated Dye, $[MVH-I]$ = Stands for the colorless product of the reaction and $[MV]_r$

= Sum of protonated and unreacted dye concentration.

The effect of temperature on the kinetics of reaction was studied by Arrhenius relation:

$$\ln k = \ln A - \frac{E_a^*}{2.303RT} \quad (16)$$

where E_a^* is energy of activation, R is gas constant and A is Arrhenius factor. The energy of activation (E_a^*) was calculated from the slope of the plot $\ln k$ vs $1/T$. Representative plot is shown in Figure 6 and the values of activation energy are tabulated in Table 4. It was observed that energy of activation decreased with increase in the ethanol content show that the reactant is less solvated than the activated complex and there is more electrostatic attraction between ions.

The activation parameters [26] such as enthalpy of activation (ΔH^*), free energy of activation (ΔG^*) entropy of activation (ΔS^*) were calculated by using equation:

$$k = \frac{k_B T}{h} \exp \frac{\Delta S^*}{R} \exp - \frac{\Delta H^*}{RT} \quad (17)$$

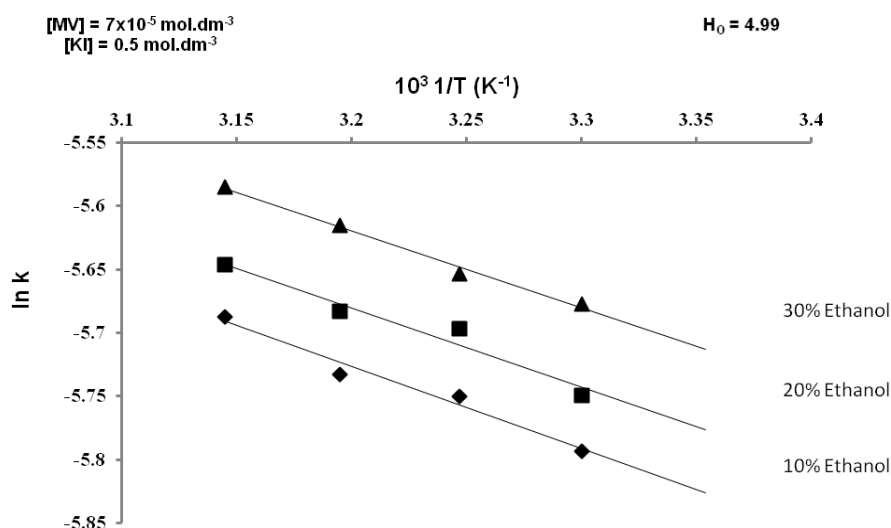


Figure 6. Plot of $\ln k$ versus $1/T$ for reduction of methyl violet with potassium iodide in aqueous ethanol.

where k is rate constant, k_B is Boltzman constant, T is temperature, h is Planks constant, ΔS^* is entropy of activation, ΔH^* is enthalpy of activation and R is gas constant. The values of activation parameters are tabulated in Table 4.

The values of enthalpy of activation (ΔH^*) increased with the increase in dielectric constant. The entropy of activation also increased with the increase of dielectric constant of the medium. The low value of entropy of activation (ΔS^*) was due to more solvation of activated complex by ethanol. The results show that free energy of activation (ΔG^*) decreased with the decrease in dielectric constant indicating the spontaneity of the reaction at low dielectric constant. i.e. the spontaneity of reaction follows the trend:

30% ethanol > 20% ethanol > 10% ethanol

4. CONCLUSION

The kinetics of reduction of methyl violet in aqueous and aqueous ethanol mixture was studied spectrophotometrically, and observed hypsochromic shift (shorter wavelength) of the spectrum with increasing polarity of the solvent. The influence of the solvent on the λ_{max} showed π - π^* transition. The kinetic study of reduction of methyl violet with iodide led to the conclusion that reaction is first order

with respect to iodide and zero order with respect to methyl violet in acidic medium. The linear plot of $\ln k$ vs $1/\epsilon$ with positive slope indicate that the rate constant increased with decrease in dielectric constant. The change in enthalpy of activation (ΔH^*), Entropy of activation (ΔS^*) and Gibbs free energy of activation (ΔG^*) at pH 4 and 6 was in a range of 2.4 to 2.9 $\text{kJ}\cdot\text{mol}^{-1}$, -281 to -284 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ and 89 to 90 $\text{kJ}\cdot\text{mol}^{-1}$ respectively. The activation parameters evaluated also supports the kinetic data.

REFERENCES

- [1] Duxbuy D.F., *Chem. Rev.*, 1993; **93**: 381-433.
- [2] Culp S. G. and Beland F. A., *J. Am. Coll. Toxicol.*, 1996; **15**: 219-238.
- [3] Babatunde O.A., *World J. Chem.*, 2009; **4** (1): 39-44.
- [4] Adetoro J., Iyun F. and Idris S. O., *Res. J. Appl. Sci. Eng. Technol.*, 2011, **3**(10): 1159-1163.
- [5] Adetoro J., Iyun F. and Idris S. O., *Arch. Appl. Sci. Res.*, 2010; **2** (6): 177-184.
- [7] Sires I., Guivarch E., Oturan N. and Oturan M. A., *Chemosphere*, 2008; **72**: 592-600.

Table 4. Activation parameters of methyl violet in acidic aqueous ethanol.

$[\text{MV}] = 7 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$, $[\text{KI}] = 0.5 \text{ mol}\cdot\text{dm}^{-3}$

$H_0 = 4.99$				
Ethanol % (v/v)	E_a^* ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔH^* ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔS^* ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)	ΔG^* ($\text{kJ}\cdot\text{mol}^{-1}$)
10	6.0127	3.4362	-281.837	90.2419
20	5.1929	2.6114	-284.090	90.1111
30	5.0490	2.4684	-284.040	89.9527
$H_0 = 6$				
10	5.4881	2.9065	-283.009	90.7334
20	5.0597	2.4834	-284.340	90.0601
30	4.9885	2.4069	-283.849	89.8324

- [7] Mittal A., Gajbe V. and Mittal J., *J. Hazard. Mater.*, 2008; **150**(2): 364-375.
- [8] Hameed B. H., *J. Hazard. Mater.*, 2008; **154**: 204-212.
- [9] Hamza M., Abdelhedi R., Brillas E. and Sires I., *J. Electroanal. Chem.*, 2009; **627**: 41-50.
- [10] Bekci Z., Özveri C., Seki Y. and Yurdakoc K., *J. Hazard. Mater.*, 2008; **154**: 254-261.
- [11] Crini G., Peindy H. N., Gimbert F. and Robert C., *Sep. Purif. Technol.*, 2007; **53**: 97-110.
- [12] Kabir A. M. R. and Susan Md. A. B. H., *J. Saudi Chem. Soc.*, 2008; **12**(4): 543-554.
- [13] Samiey B. and Ashoori F., *Acta Chim. Slov.*, 2011; **58**: 223-232.
- [14] Tanimu A., Idris S. O. and Iyun J. F., *Int. J. Sci. Technol.*, 2012; **2**(3) : 112-115.
- [15] Samiey B. and Zafari M., *J. Chin. Chem. Soc.*, 2012; **59**: 32-39.
- [16] Mohammad Y., Iyun J. F. and Idris S.O., *Afr. J. Pure Appl. Chem.*, 2009; **3**(12): 269-274.
- [17] Saeed R., Ashfaq M. and Uddin F., *Chinese J. Chem.*, 2012; **28**(6): 891-895.
- [18] Saeed R., Ashfaq M. and Khan S. R., *Asian J. Chem.*, 2010; **22**(3): 1787-1798.
- [19] Saeed R., Khan S. R. and Ashfaq M., *Asian J. Chem.*, 2012; **24**(8): 3745-3750.
- [20] Saeed R., Uddin F. and Khalid Z., *Turk. J. Chem.*, 2004; **28**:s 351-367.
- [21] Saeed R. and Uddin F., *Int. J. Pure App Chem.*, 2006; **1**(1): 65-74.
- [22] Machado C. and Machado V. G., *J. Chem. Educ.*, 2001; **78**(5): 649-651.
- [23] Laidler K. J. *Chemical Kinetics*, McGraw Hill, New York, **1967**.
- [24] Tapalad T., Neramittagapong A., Neramittagapong S. and Boonmee M., *Chiang Mai J. Sci.*, 2008; **35**(1), 63-68.
- [25] Abdel-Rahman L. H. A., El-Khatib R. M., Nassr L. A. E. and Abu-Dief A. M., *Russ. J. Gen. Chem.*, 2013; **83**(12), 2510-2518.
- [26] Abu-Gharib E. A., EL-Khatib R. M., Nassr, Lobna A. E. and Abu-Dief A. M., *J. Korean Chem. Soc.*, 2011; **3**, 346 -351.