

Effect of Solvent on Kinetics of Reduction of Methyl Violet with Potassium Iodide at Different Temperatures

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UV-visible absorption spectroscopy was used to study the effect of solvent on the kinetics of reduction of methyl violet with potassium iodide at various temperatures in water and mixed water alcohol system. The solvatochromism of methyl violet was studied at pH 4 and 6 by varying polarity of medium. Bathochromic shift was observed with decrease in polarity of solvent. The spectra showed that on decreasing polarity of medium *i.e.*, from water to butanol the intensity of band increases. The E_T values of the methyl violet in aqueous alcohol solvent showed that the position of the solvatochromic absorption band is dependent on the medium polarity. As the polarity increases λ_{max} shifts to shorter wavelength causing hypsochromic shift. The rate of reaction of methyl violet with iodide at various pH slows down by the decrease of polarity as the formation of activated state takes longer time *i.e.* energy of activation increases. The other thermodynamic factors such as ΔS^\ddagger , ΔG^\ddagger and ΔH^\ddagger were also evaluated and their changes as a function of variation of the polarity of the medium were observed.

Key Words: Kinetics, Solvatochromism, Spectroscopy, Methyl violet.

INTRODUCTION

The kinetics of reduction of methyl violet with potassium iodide in aqueous and aqueous alcohol system was investigated at various temperatures. The solvatochromic effect on the reduction process was also studied at pH 4 and 6.

Solvatochromic compounds are those compounds that induce change in the colour of the solution with the change in the solvent polarity. Typically, solvatochromic compounds can be described by the extreme resonance contributing structures: one form is quinoid, non-polarized and formally non-aromatic. The other is zwitter-ionic, polarized and fully aromatic. The change in the absorption band with the solvent arises from variation in the contribution of these canonical forms to the overall resonance hybrid. The phenomenon of solvatochromism arises when a solute dissolved in various solvents of varying polarity produced a pronounced change in position, intensity and shape of an absorption band. A shift towards longer wavelength (red) is bathochromic and towards shorter wavelength (blue) is hypsochromic with increasing solvent polarity. They are termed as positive and negative solvatochromism, respectively¹. A theoretical study of UV-visible absorption and emission solvato-

chromic property of solvent sensitive dyes were made by many researchers²⁻⁶. The influence of solvent on the λ_{\max} allows us to distinguish the kind of electronic transition. As, polarity of solvent decreases, the λ_{\max} shifts towards longer wavelength (low energy) and hyperchromic effect (increase of intensity of absorption), the transition is $n-\pi^*$ ⁷. The E_T polarity values of Brooker's merocyanine dye were calculated in binary mixture comprising of protic and non-protic solvents. The data was used for investigation of preferential solvation, solute-solute and solvent-solvent interaction of dye⁸. The solute-solvent and solvent-solvent interactions were studied in fifteen pure solvents and seven binary mixtures by monitoring the solubility of a dye in the solvents⁹. By using Vertical Self Consistent Reaction Field (VSCRF) solvation model, incorporated with the conductor like screening mode (COSMO) and Self Consistent Reaction Field (SCRF) methods, the study of solvatochromic shift of both absorption and emission bands of dyes in different solvents (water, methanol and ethanol) was made¹⁰. A theoretical model was proposed to describe the effect of concentration of polar solvent and temperature of a solution on the electronic spectra of polar solute in a binary mixture¹¹. The absorption and steady state emission spectra of two fluorescent red laser dyes (DCM and Nile Red) are measured in series of aprotic solvents with similar refractive index and different polarity¹². The various forms of spectroscopy allow us to observe the transitions. Thus the electronic transitions give rise to UV-visible absorption spectra and fluorescence spectra. Because of solute-solvent interactions, the electronic energy levels of a solute are influenced by the solvent in which it is dissolved. Therefore, the absorption and fluorescence spectra contain information about the solute-solvent interactions. A change in electronic absorption spectrum caused by a change in the solvent is called solvatochromism¹³.

Di- and triarylmethine dyes are characterized by the presence of very intense and sharp bands in their electronic spectra. This is even the case for those carbocations without electron donors in the aryl groups¹⁴. A change in solvent from a polar solvent to a non-polar solvent has been suggested to increase or decrease reaction rates depending on the type of reactions. It has generally been reported that reactions with anionic nucleophiles cause significant rate acceleration, while the ones between neutral molecules passing through a partially charged transition state structure exhibit rate retardation upon solvent change from H₂O to DMSO¹⁵. Solvent effect plays an important role in photo-physical behavior of ionic dyes, *i.e.*, the intensity, shape and maximum absorption wavelengths of the absorption bands of the ionic dyes in solution depend strongly on the solvent-solute interactions and solvent nature¹⁶⁻¹⁸. Many authors have reviewed solvent effects on reaction rates. Fahimuddin *et al.*¹⁹ studied the reaction between peroxydisulfate-iodine ions in ethanol-water and methanol-water mixtures, respectively and found that the activated complex is single sphere for both the media, *i.e.*, ethanol-water and methanol-water mixtures. Present study involves the kinetics of solvatochromism of methyl violet in aqueous alcohol system. The rate constant was observed to study the rate of chemical reaction.

EXPERIMENTAL

All the glass wares used were of Pyrex A grade quality. Apparatus were washed and dried in oven (W.T.C binder, 7200, Tuttligh/Germanny, Type28 and No. 89248). The absorbance was recorded on Shimadzu (UV-160, UV-visible spectrophotometer, using quartz cells of path length 1 cm with capacity of 3 mL). pH measurement was carried out on HI-1332 and digital pH meter (Orion, 1990 Orion research Inc. Boston, MA02129 USA). A thermometer bath (circulator, model, YCW01, made in Taiwan, Republic of China) was used for maintaining temperature of reaction constant through out the experiment.

Methyl violet of C.I. No. 42535 of Riedel-De Haen AG Seelze-Hannover of 75 % purity was used. Potassium iodide, sodium hydroxide, hydrochloric acid, sulphuric acid and sodium acetate of E. Merck were used. Methanol, ethanol, isopropanol and butanol of E. Merck were used without any purification. Freshly prepared double distilled water having conductance ($0.06 \mu\text{Scm}^{-1}$) was used for preparation of different aqueous methanol, ethanol, isopropanol and butanol as solvents.

Procedure: Stock solutions of methyl violet of concentration $2.0 \times 10^{-3} \text{ mol dm}^{-3}$, potassium iodide, hydrochloric acid, sodium hydroxide and sodium acetate were prepared in 10 % aqueous methanol, aqueous ethanol, aqueous isopropanol and 4 % aqueous butanol solvents.

The pH of the solution was maintained by Hammelt acidity function (H_0) using optical method:

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

where d_0 , d_1 and d_2 are the absorbance of indication in intermediate extreme acidic, basic and acidity solutions respectively. pK value for acidic acridine solution was taken as 5.41 ± 0.05 . The acidic range of acidity was selected 4.0 and 6.0.

A known volume of reactants at particular pH was placed in reaction cell and the absorbances were recorded at 581 nm with time interval of 50 s as a function of concentration of reductant (KI), dye, pH and temperature. The temperature of reaction mixture was maintained constant throughout the course of experiment. The values of dielectric constants for different aqueous propanol mixtures were taken from literature²⁰.

RESULTS AND DISCUSSION

The kinetics of solvatochromism of methyl violet in aqueous and 10 % aqueous alcoholic system was studied by spectrophotometry. The reaction of methyl violet with iodide was studied at $\lambda_{\text{max}} = 581 \text{ nm}$. From the λ_{max} transition energy is calculated using relation²¹:

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

where h = Planck's constant, c = speed of light and N_A = Avogadro's number. Fig. 1 (a and b) shows spectra of methyl violet in aqueous and aqueous alcohols as 10 % methanol, ethanol, iso propanol and 1 % n-butanol. Results for the transition energy (E_T) and maximum wavelength (λ_{max}) are tabulated in Table-1. The increased of transition energy (E_T) with the increase of solvent polarity shows the ground state is more polar than the excited state. An increase in the solvent polarity stabilizes the ground state in comparison to the excited state. The energy difference between ground state and excited state becomes greater corresponding to hypsochromic effect of the spectrum with increasing polarity of the solvent.

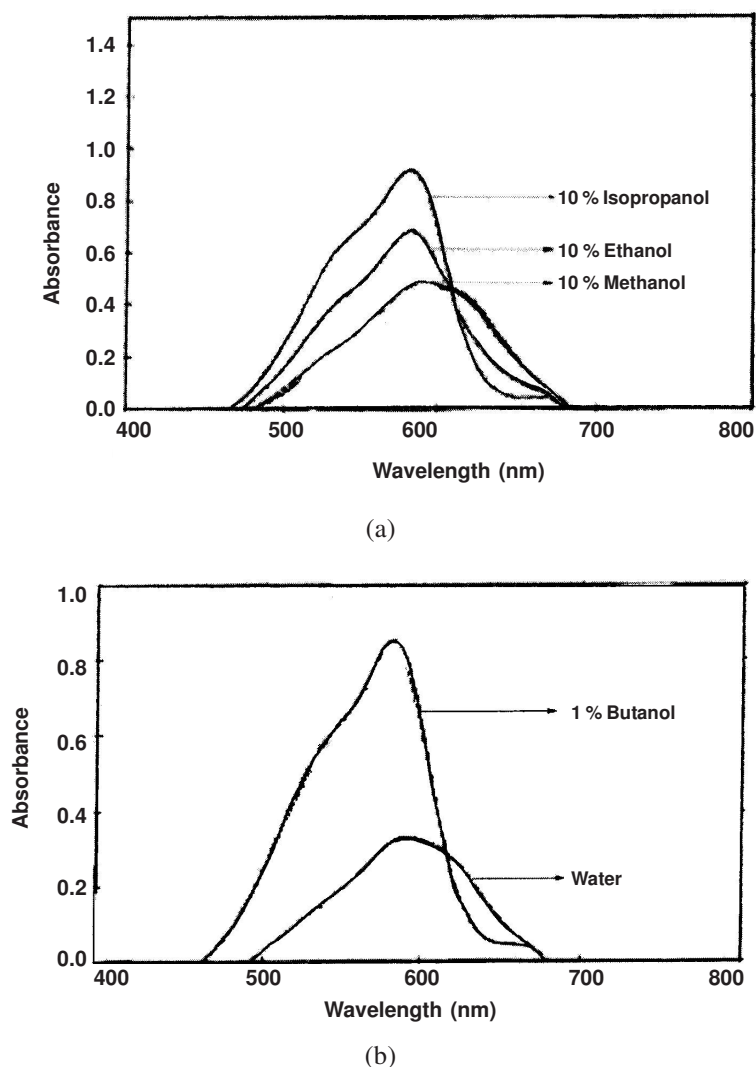
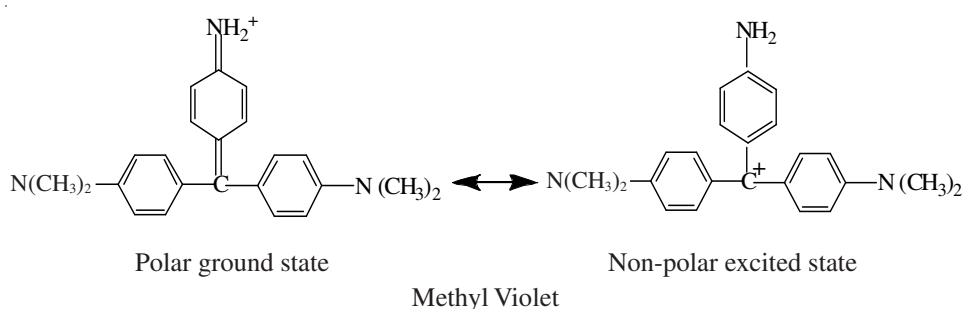


Fig.1. Spectra of 7×10^{-5} mol dm^{-3} methyl violet in various Aqueous alcohols at pH 4

TABLE-1
 λ_{\max} , ABSORBANCE, TRANSITION ENERGY (E_T) AND MOLAR ABSORPTIVITY (ϵ)

Solvent	λ_{\max} (nm)	A	ϵ ($\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$)	E_T (Kcal/mol)
Water	580.5	0.433	6186.71	49.25
10 % Methanol	581.0	0.482	5823.57	49.21
10 % Ethanol	581.0	0.725	4843.85	49.21
10 % Propanol	581.0	0.918	3071.43	49.21
1 % Butanol	581.0	0.823	7971.42	49.21

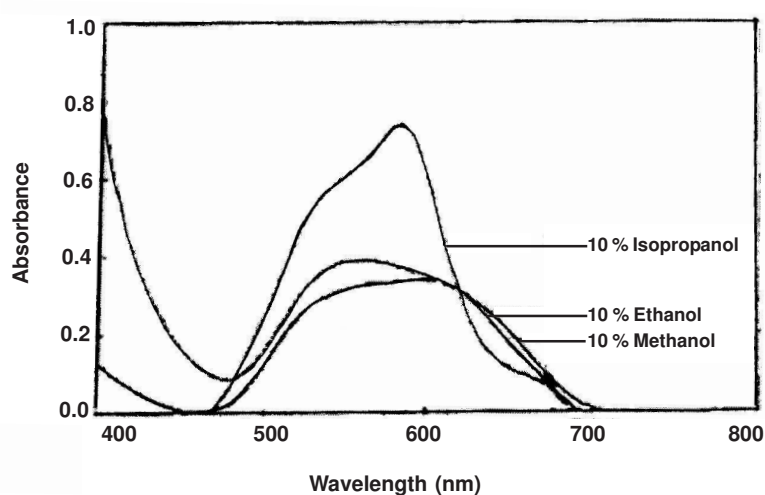


The analysis of the behaviour of solutes in mixed solvent systems is more complex than in pure solvents due to the possibility for preferential solvation (PS). It occurs when the solute has the environment of one solvent excess than the other, in comparison to the bulk composition. A comprehension of phenomena related to preferential solvation (PS) may help in the elucidation of spectral analysis, kinetics and equilibrium data for mixed solvents. An important aspect in the studies performed on mixed solvents is the role of solvent-solvent interactions in competition to the solvation of solutes. With lengthening of alkyl chain of the alcohol, the extent of preferential solvation of the dye cation increased in the water-rich region. Water makes strong hydrogen bond nets in the water-rich region, which are not easily disrupted by the cosolvent. This can explain the strong preferential solvation by the alcoholic component in this region since water preferentially interacts with itself rather than with the dye. Thus, it is expected that the interaction of the alcoholic component with the dye through both hydrogen bonding and a hydrophobic effect increased with the lengthening of the alkyl chain of the alcohol. The ability of the alcoholic cosolvent to solvate the dye cation in the water-rich region increases in the following order: methanol < ethanol < propan-2-ol < *n*-butanol. The increase in the basicity of the alcohol makes it able to compete efficiently with the dye for the water, hindering the interaction between the water and the dye. In the alcohol-rich region, the alcohol molecules are free to interact with the water and with the dye, since their nets formed by hydrogen bonds are weaker than in water. In this situation, the alcohol molecules can, to a greater or lesser extent, interact with water through hydrogen bonding. The extent of PS by the alcoholic component in the alcohol-rich region decreases in the order methanol > ethanol > propan-1-ol > propan-2-ol >

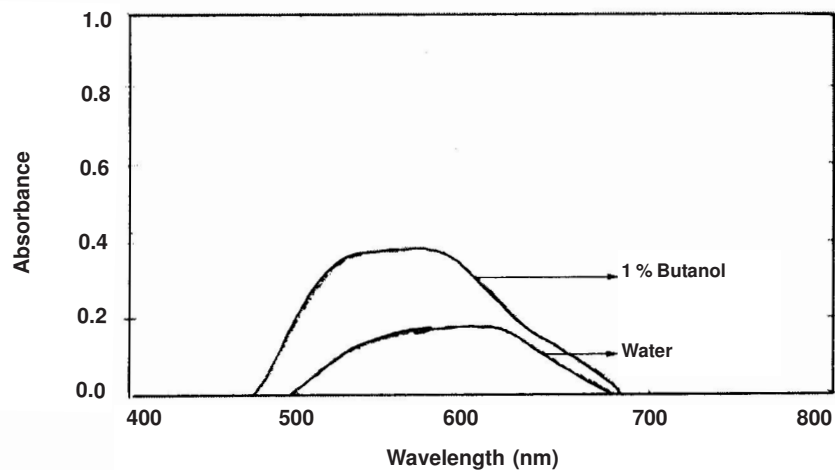
n-butanol. This is also the decreasing order of the solvent's hydrogen-bond donation capability, suggesting that the increase in the facility of the alcohol for hydrogen-bond donation makes its interaction with the dimethylamino group in the dye cation stronger and consequently, the PS by the alcohol in the alcohol-rich region increases. This order is also the increasing order of the solvent's hydrogen-bond acceptance, indicating that the change in the alcoholic component in the mixture from methanol to propan-2-ol increases the capacity of the alcohol to form hydrogen-bonded complexes with water responsible for the solvation of the dye cation in the alcohol rich region²². The preferential solvation of methyl violet in alcohol was observed. With the increase of alkyl chain of alcohol, dye cation is more solvated resulting decrease in molar absorptivity coefficient (ϵ) reported in Table-1 and decreased intensity of absorption spectra in Fig. 1.

The rate of reaction of methyl violet in aqueous alcoholic media was studied by monitoring the absorbance with the passage of time. As there was no considerable effect of dye on rate, the reaction was studied under the influence of potassium iodide. Spectra showing the behaviour of dyes in aqueous alcoholic system under the influence of potassium iodide are shown in Fig. 2. The absorbance intensity of methyl violet in aqueous alcoholic system at 581 nm decreased with the addition of potassium iodide. The kinetics of reaction of methyl violet in various alcohols media in presence of potassium iodide was studied by observing absorbance *versus* time as shown in Fig. 3. The plot shows the absorbance decreased with the passage of time, indicating fading of dye.

Table-2 shows rate constant of methyl violet with iodide in various aqueous alcohols. It was observed that rate constant decreases with decrease in polarity of medium. This could be explain by the fact that with the lengthening of alkyl chain of alcohol, the alcohol stabilize the positive charge on the peripheral nitrogen atom



(a)



(b)

Fig. 2. Spectra of $7 \times 10^{-5} \text{ mol dm}^{-3}$ methyl violet at 0.5 M KI in various aqueous alcohols at pH 4

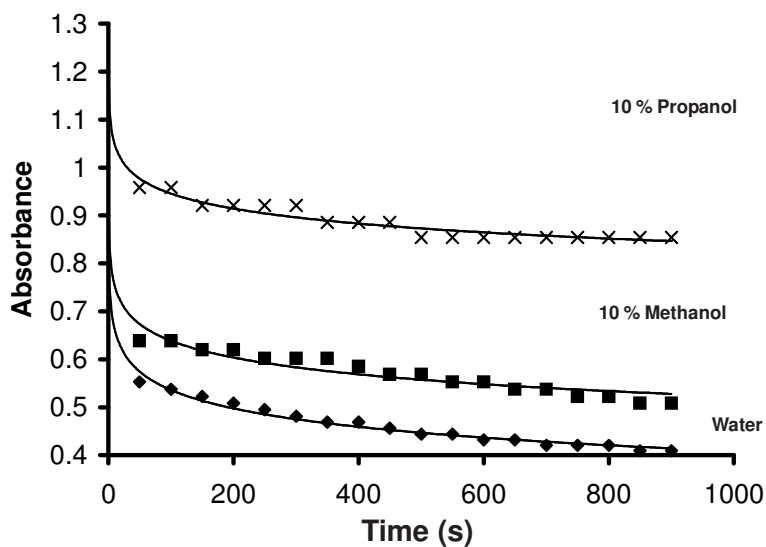


Fig. 3. Plot of absorbance vs. time of $7 \times 10^{-5} \text{ mol dm}^{-3}$ methyl violet

by its increasing hydrogen bond acceptor ability, which interact with the H^+ present with the peripheral nitrogen atom, thus hindering the formation of activated state or carbinol base. Thus attack of iodide on the activated state is inhibited as alkyl chain of alcohol increases. This leads to decrease in values of rate constant. Fig. 4 shows the kinetics of methyl violet in aqueous alcohol follows first order in excess of iodide.

TABLE-2
RATE CONSTANT (k) OF METHYL VIOLET AT
VARIOUS COMPOSITIONS OF ALCOHOLS

KI (mol dm ⁻³)	T = 313 K				pH = 4
	Water	10 % Methanol	10 % Ethanol	10 % Isopropanol	
0.1	3.370	2.730	0.439	0.841	–
0.2	1.455	1.328	0.179	0.611	0.260
0.3	1.043	1.090	0.136	0.478	0.251
0.4	0.639	0.894	0.128	0.444	0.268
0.5	0.559	0.809	0.157	0.429	0.239
pH = 6					
0.1	2.990	2.330	0.0923	0.932	–
0.2	1.934	1.393	0.1538	0.485	0.260
0.3	0.573	1.008	0.1310	0.329	0.243
0.4	0.521	0.909	0.9330	0.332	0.238
0.5	0.479	0.754	0.0923	0.431	0.312

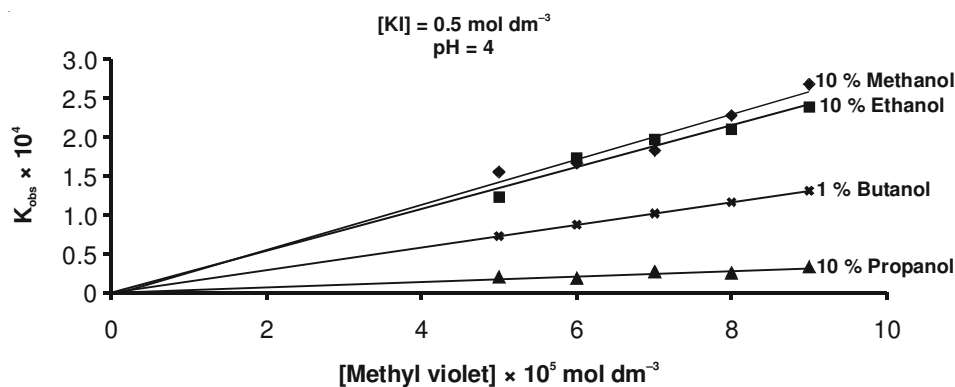


Fig. 4. Plot of k_{obs} vs. [methyl violet] at 318 K

The suggested scheme of reaction is expressed as follows:



$$\text{Rate} = k[\text{MVH}^+][\text{I}^-] \quad (\text{iii})$$

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

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

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

$$[\text{MV}]_{\text{T}} = \frac{[\text{MVH}^+]}{K[\text{H}^+]} + [\text{MVH}^+] \quad (\text{vi})$$

substituting values of $[\text{MV}]$ from eqn. (v) in eqn. (vi)

$$[\text{MV}]_{\text{T}} = \frac{[\text{MVH}^+]}{K[\text{H}^+]} + [\text{MVH}^+] \quad (\text{vii})$$

$$[\text{MV}]_{\text{T}} = \frac{[\text{MVH}^+] + K[\text{MVH}^+][\text{H}^+]}{K[\text{H}^+]} \quad (\text{viii})$$

$$[\text{MV}]_{\text{T}} = [\text{MVH}^+] \left(\frac{1 + K[\text{H}^+]}{K[\text{H}^+]} \right) \quad (\text{ix})$$

$$[\text{MVH}^+] = \frac{K[\text{MV}]_{\text{T}}[\text{H}^+]}{1 + K[\text{H}^+]} \quad (\text{x})$$

substituting values of $[\text{MVH}^+]$ from eqn. (x) in eqn. (iii)

$$\text{Rate} = \frac{Kk[\text{MV}]_{\text{T}}[\text{H}^+][\text{I}^-]}{1 + K[\text{H}^+]} \quad (\text{xi})$$

at fixed concentration of methyl violet

$$k' = \frac{Kk[\text{H}^+][\text{MV}]_{\text{T}}}{1 + K[\text{H}^+]} \quad (\text{xii})$$

$$\text{Rate} = k'[\text{I}^-] \quad (\text{xiii})$$

where $[\text{MV}^+]$ = methyl violet, $[\text{MVH}^+]$ = protonated dye, $[\text{MVI}]$ = stands for the colourless product of the reaction and $[\text{MV}^+]_{\text{T}}$ = sum of protonated and unreacted dye concentration.

To study the effect of pH on rate of reaction, kinetic runs were carried out in acidic medium. It was observed that rate constant reported in Table-2 decreased with increase of pH from 4 to 6 showing faster fading of dye in high acidic solution.

The rate of methyl violet with iodide was observed with difference of temperatures. The effect of temperature on the kinetics of reaction was studied by Arrhenius relation:

$$\ln k = \ln A - \frac{E_{\text{a}}^{\#}}{RT} \quad (3)$$

where $E_a^\#$ is energy of activation, R is gas constant and A is Arrhenius factor. Fig. 5 represents Arrhenius plot, *i.e.*, $\log k$ vs. $1/T$ for different dielectric constant. The values of energy of activation ($E_a^\#$) were obtained from the Arrhenius slopes and are reported in Table-3. The activation energies are found to be affected both by solvent composition and ionic strength of the medium. The activation energy increased by increasing the proportion of organic component in the solvent mixtures, *i.e.*, with decrease in dielectric constant of the medium. Reaction between two heavily charged opposite ions could produce a neutral, possibly charged separated activated complex that was only slightly solvated, leading to an increase in activation energy.

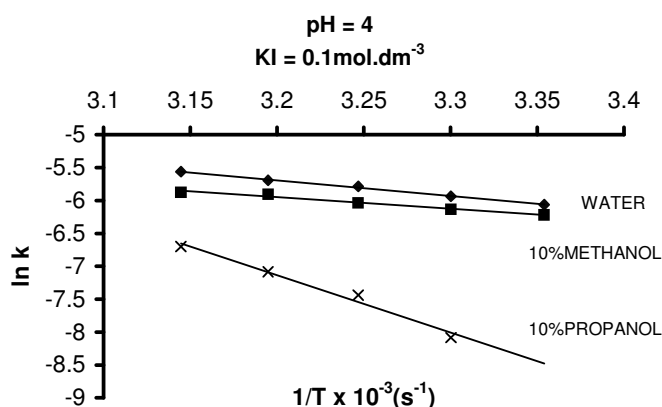


Fig. 5. Plot of $\ln k$ vs. $1/T$ of $7 \times 10^{-5} \text{ mol dm}^{-3}$ methyl violet

TABLE-3
THERMODYNAMIC PARAMETERS OF AQUEOUS
METHYL VIOLET IN ACIDIC AQUEOUS

Alcohol (v/v)	[MV] = $7 \times 10^{-5} \text{ mol dm}^{-3}$ T = 308 K [KI] = 0.3 mol dm^{-3} pH = 4			
	Energy of activation $E_a^\#$ (kJ/mol)	Enthalpy change of activation $\Delta H^\#$ (kJ/mol)	Entropy change of activation $\Delta S^\#$ (J/mol K)	Free energy change of activation $\Delta G^\#$ (kJ/mol)
Aqueous system	24.2918	21.7153	-233.227	93.5492
10 % Aqueous methanol	13.5691	10.8448	-267.341	96.6517
10 % Aqueous ethanol	10.2062	10.2029	-287.033	101.0272
10 % Aqueous propanol	46.7679	47.4130	-157.712	97.9509
4 % Aqueous butanol	58.8082	58.8074	-126.147	99.3277
	pH=6			
Aqueous system	35.4309	32.8544	-202.2740	95.1548
10 % Aqueous methanol	16.4018	13.8253	-258.4215	96.7856
10 % Aqueous ethanol	11.0169	8.40870	-292.7280	102.5065
10 % Aqueous propanol	76.4921	74.9133	-31.76860	97.4599
4 % Aqueous butanol	94.4221	93.1085	-16.68700	98.6650

The thermodynamic factors such as entropy of activation (ΔS^\ddagger), Gibb's free energy of activation (ΔG^\ddagger) and enthalpy of activation (ΔH^\ddagger) were also evaluated by using relations and were tabulated in Table-3. The represented plot is shown in Fig. 6.

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

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (5)$$

where k is rate constant, k_B is Boltzman constant, T is absolute temperature, h is Planck's constant, ΔS^\ddagger is entropy change of activation and ΔH^\ddagger is enthalpy change of activation. The value of enthalpy change of activation (ΔH^\ddagger) and entropy change of activation (ΔS^\ddagger) increased with the decrease in dielectric constant. The reaction is between ions of unlike charges, the activated complex has a total net charge less than the reactants and so the total degree of orientation of the solvent around the activated complex is less than before activation. This tends to release solvent molecules giving an increase in disorder of solvent, leading an increase in entropy in forming the activated complex. Positive values of free energy change of activation (ΔG^\ddagger) indicated that the formation of activated complex is a non-spontaneous complex and the transition state is slightly affected by the addition of organic solvent.

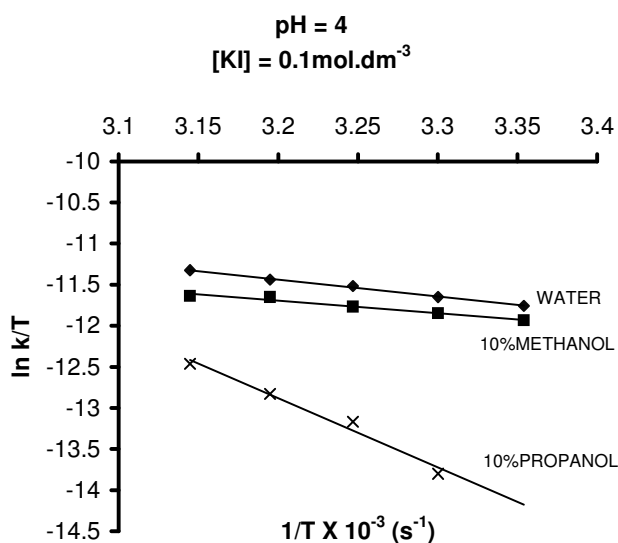


Fig.6. Plot of $\ln k$ vs. $1/T$ of $7 \times 10^{-5} \text{ mol dm}^{-3}$ methyl violet

Conclusion

Hypsochromic shift of absorption band of methyl violet was observed with increasing polarity of solvent. On increasing the polarity of solvent the absorption bands shifted towards shorter wavelength, also observed by an increase in transition

energy. This showed that the polar ground state was more solvated by polar solvent than excited state. The effect of solvent on kinetics of methyl violet in presence of potassium iodide showed the reaction follows first order kinetics with respect to methyl violet in excess of potassium iodide and overall it was pseudo first order reaction. The rate of reaction decreased with the decrease in dielectric constant of the medium.

Thermodynamics of solvatochromism also confirms the kinetics results showing high values of activation energy in aqueous solvent as compared to aqueous alcoholic solutions.

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