

Kinetics of Malachite Green Fading in Water-ethanol-1-propanol Ternary Mixtures

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The rate constant of malachite green (MG^+) alkaline fading was measured in water-ethanol-1-propanol ternary mixtures. This reaction was studied under pseudo-first-order conditions at 283–303 K. It was observed that the reaction rate constant increases in the presence of different weight percentages of ethanol and 1-propanol. The fundamental rate constants of MG^+ fading in these solutions were obtained by SESMORTAC model. In each series of experiments, concentration of one alcohol was kept constant and the concentration of the second one was changed. It was observed that at constant concentration of one alcohol and variable concentrations of the second one, with increase in temperature, k_1 values increase and this indicates that presence of ethanol (or 1-propanol) increases dissolution of 1-propanol (or ethanol) in the activated complex formed in these solutions. Also, in each zone, fundamental rate constants of reaction at each certain temperature change as $k_2 \gg k_1 \gg k_{-1}$.

Keywords: SESMORTAC model; Ethanol; 1-Propanol; Malachite green; Kinetics.

INTRODUCTION

Solvent effects on reactivity may be very large. Alcohols, as cosolvents, can change the rate of organic, inorganic and enzymatic reactions.^{1–9} Malachite green (MG^+) is a triphenylmethane dye. These dyes represent a class of dyes of commercial and analytical importance.^{10,11} Malachite green is used to dye materials like silk, leather, cotton and paper and can be used as a saturable absorber in dye lasers, as a pH indicator or as a bacteriological stain.¹² It is also used as a topical antiseptic or treat parasites and bacterial infections in fish and fish eggs.¹³ In this work, we have studied the MG^+ alkaline fading in ternary mixtures of water with different weight percentages of ethanol, and 1-propanol at 283–303 K. The MG^+ fading is a one-step reaction^{14,15} and as reported, kinetics of these kinds of reactions in binary mixtures can be studied using SESMORTAC model.^{16,17} SESMORTAC is an abbreviation for “*study of effect of solvent mixture on the one-step reaction rates using the transition state theory and cage effect*”.

EXPERIMENTAL

Materials

Malachite green oxalate, ethanol ($\geq 99.9\%$), 1-pro-

panol ($\geq 99\%$), and NaOH were purchased from Merck.

Experimental procedure

The fading of MG^+ was followed at its absorption maximum wavelength (λ_{max}) values in a thermostated cell compartment of a Shimadzu UV–160 spectrophotometer. The experiments were conducted at 283, 293 and 303 K within ± 0.1 K in a stoppered cell. All the kinetic runs were carried out at least in triplicate. To perform each kinetic run, a 100 μL aliquot of 1.38×10^{-4} M MG^+ solution was added by a microsyringe into 2.9 mL of a solution containing 5.4×10^{-4} M sodium hydroxide and a certain concentration of the used alcohols. The reaction between MG^+ and hydroxide ion has been found to be bimolecular, first order with respect to each reactant, but pseudo-first-order conditions (excess alkali) were used in all cases, Scheme I. We used the second-order reaction rate constants in our calculations.

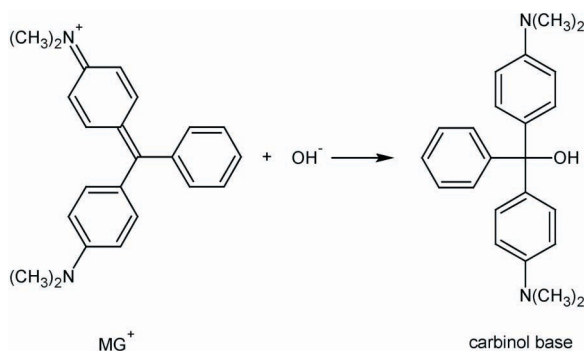
RESULTS AND DISCUSSION

The reaction of MG^+ with hydroxide ion brings about fading the color of MG^+ and results in the formation of colorless carbinol base, Scheme I and Fig. 1. In this work, we studied the influence of various concentrations of alcohol-water ternary mixtures on the rate of this reaction. We

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investigated the simultaneous effect of various concentrations of ethanol and 1-propanol on the kinetics of MG^+ fading.

Scheme I MG^+ fading reaction



Effect of 1-Propanol on MG^+ Fading in Constant Concentrations of Ethanol

These experiments were carried out in solutions involving 5, 10, 15, 20 and 25 weight percentages of ethanol and variable concentrations of 1-propanol. As seen in Fig. 2, with increase in weight percentage of the 1-propanol, the λ_{max} value of MG^+ shifts to red. The red shift has been previously reported for other compounds upon going from polar to apolar solvents, as a result of hydrophobic interaction.¹⁸ Reaction of MG^+ fading is an electrophile-nucleophile combination reaction. The rate constants for these reactions are correlated by Ritchie equation.^{19,20}

$$\log k = \log k_0 + N_+ \quad (1)$$

where k is the rate constant for reaction of a given cation

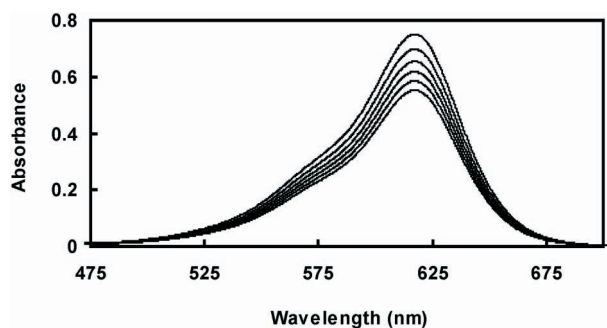


Fig. 1. Typical absorption spectra of MG^+ during its alkaline fading reaction in 2-minute intervals that show decrease in MG^+ absorption.

with a given nucleophilic system (i.e. given nucleophile in a given solvent). k_0 is the rate constant for the same cation with water in water and, N_+ is a parameter which is characteristic of the nucleophilic system and independent of cation. This equation is applied to the reactions between nucleophiles and certain large and relatively stable organic cations in various solvents. k_0 values for MG^+ are 1.46×10^{-8} and $9.93 \times 10^{-8} \text{ M}^{-1} \text{ min}^{-1}$ at 283 and 303 K, respectively.¹⁵ N_+ values obtained for hydroxide ion in the MG^+ fading reaction increase with increase in alcohol weight percentage and decrease with increase in temperature, as given in footnotes of Tables S1-S5 (shown in Supplementary Data). As shown in Tables S1-S5 and Fig. 3, with increase in the content of 1-propanol the rate constant of reaction increases. Alcohols have a lower dielectric constant than water and according to Hughes-Ingold rules for solvent effects in nucleophilic substitution reactions,²¹⁻²³ formation of the neutral carbinol base from two oppositely

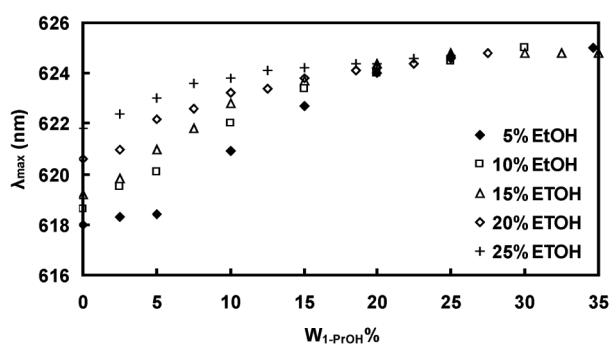


Fig. 2. λ_{max} values of MG^+ vs. weight percentages of 1-propanol in ternary mixtures of water-ethanol-1-propanol under alkaline conditions at room temperature.

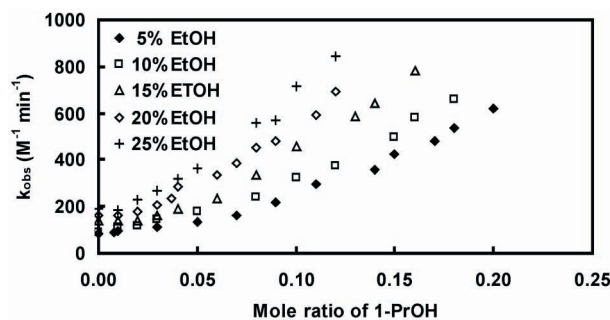


Fig. 3. k_{obs} values of MG^+ fading reaction vs. mole ratios of 1-propanol in ternary mixtures of water-ethanol-1-propanol under alkaline conditions at 293 K.

charged reactants (MG^+ and OH^-) is more favorable in higher weight percentages of alcohols in binary mixtures²⁴⁻²⁶ and similar results are observed in this work.

Data of Tables S1-S5 were analyzed by SESMORTAC model. In SESMORTAC model,¹⁶ a range of solvent composition in which the equation of logarithm of reaction rate constant, $\log k$, versus reciprocal of dielectric constant of the solution, D^{-1} , is linear,²⁷⁻³⁴ is called a “zone” and a solvent composition in which a zone finishes and another zone starts, is called “mechanism change point” (or abbreviated as *mc* point). Consideration a mechanism on the basis of point charge on a dielectric continuum suggests that the plots of $\log k$ against D^{-1} , should be linear. The failure of the simple electrostatic interpretation shows the importance of hydrogen bonding and other nonelectrostatic medium effects in controlling the reactivity of the substrates.^{33,35} In such cases, the differential solvation of the initial and transition states is the controlling factor for changes in the rate constant with the solvent composition. In SESMORTAC model, variation in mechanism is followed through the study of changes in microenvironment (or solvent cage) of the activated complex. Dielectric constants of the aqueous ethanol and 1-propanol binary solutions are obtained from the work of Åkerlof.³⁶ It is shown that in throughout weight percentage of ethanol-water or 1-propanol-water, D^{-1} values of solutions are proportional to second power of weight percentages ($\text{w}\%^2$) of the used alcohols.³⁶ Thus, in this work, we can determine the zone boundaries of the used ternary mixtures using the linear relation between $\log k$ and $\text{w}\%^2$ values of alcohol with variable concentration (shown in Supplementary Data).

It is found that in the used concentration range of 1-propanol, mixtures of water-ethanol-1-propanol were two-zone in 5, 10, 15, 20 and 25 weight percentages of ethanol, Tables S1-S5.

ΔS^\ddagger and ΔH^\ddagger values of the fading reaction are negative and positive respectively, Figs. 4 and 5. These may be due to the dissolution of 1-propanol molecules in the solvent cage and hydrogen bonding (as previously reported for interaction of dyes with protic solvents)³⁷ and nonelectrostatic, especially hydrophobic interactions³⁸ between MG^+ and alcohol molecules when ACSM forms. As shown experimentally, dissolution of hydrocarbons in water is exothermic and results in more ordered structure of water

around the dissolved hydrocarbon molecules.³⁹ Due to hydrophobic interaction between hydrocarbon molecules fewer water molecules are in direct contact with them. Thus, the ordering influence of the hydrophobic molecules will be decreased and the entropy decreases and thermal energy is required for the destructuring of the hydration shells around hydrocarbon molecules.³¹ Also, dissolution of 1-propanol in water is exothermic and increases entropy of reaction. Therefore, with increase in 1-propanol concentration ΔS^\ddagger and ΔH^\ddagger values become less negative and more positive, respectively and with more increase in 1-propanol concentration ΔS^\ddagger and ΔH^\ddagger values become more negative and less positive, respectively.

ACSM is an abbreviation for “activated complex formed in the second mechanism” and will be explained later.

Solvent cage is microenvironment of $\text{MG}^{\delta+} \cdots \text{OH}^{\delta-}$

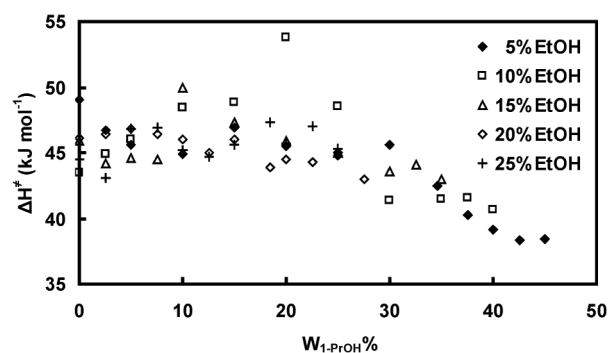


Fig. 4. ΔH^\ddagger values of MG^+ fading reaction vs. weight percentages of 1-propanol in ternary mixtures of water-ethanol-1-propanol under alkaline conditions at 293 K.

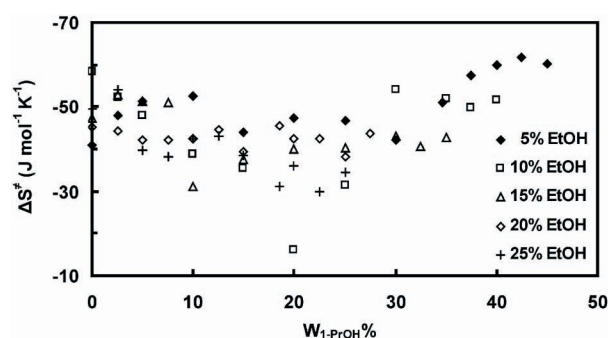
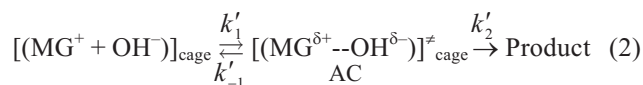


Fig. 5. ΔS^\ddagger values of MG^+ fading reaction vs. weight percentages of 1-propanol in ternary mixtures of water-ethanol-1-propanol under alkaline conditions at 293 K.

contact pair and, in spite of the first solvation shell, includes many water and alcohol molecules. Thus, in each region, n molecules of water can be replaced by n molecules of alcohol. Here, two processes occur simultaneously, chemical reaction between MG^+ and OH^- (first-order in contact ion) and replacement of n water molecules of ACSM microenvironment by n alcohol molecules of its surrounding (n order in solvent molecules).

As written in the theory of SESMORTAC model (and as seen in Table 1), the values of n are different from each zone to the next one and it causes a break in a plot of $\log k$ vs. D^{-1} at each mc point.

In this reaction, solvent is not a reactant. Thus, due to SESMORTAC model, this reaction is of type I.¹⁶ If in the presence of organic solvent the reaction rate increases, the proposed mechanism for reaction in these solutions involves two kinds of mechanism. The first mechanism occurs in pure solvent (for example water). This mechanism in the first point of the first zone can be written as follows:



where AC is an abbreviation for activated complex and k'_1 , k'_{-1} and k'_2 are the fundamental rate constants of MG^+ fading reaction and we can not determine them. But, in these series of experiments in this point there is a ethanol-water binary mixture and is considered as a mc point and the related rate equation, v_1 , is written as follows:

$$v_1 = k_{bm} [\text{MG}^+][\text{OH}^-] \quad (3)$$

where k_{bm} is the observed rate constant in ethanol-water solution. Thus, in this point rather than AC an ACSM forms. This ACSM is called ACSM_{bm} which is an abbreviation for "ACSM formed in binary mixture", Fig. 6.

Adding an organic solvent to a solvent (for example ethanol to water) or a binary mixture (for example 1-propanol to an aqueous ethanol) involving reactants results in

Table 1. n , k_1 , k_{-1} , k_2 and $E_a(k_1)$ values of different zones for the MG^+ fading reaction in various water-ethanol-1-propanol ternary mixtures in constant concentrations of ethanol obtained from SESMORTAC model at 283-303 K

T (K)	n		k_1 ($\text{M}^{-(n+1)} \text{min}^{-1}$)		k_{-1} ($\text{M}^{-n} \text{min}^{-1}$)		k_2 (min^{-1})		$E_a(k_1)$ (kJ mol^{-1})	
	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
water-ethanol(5%)-1-propanol										
283	0.986	2.222	10.33	8.71	2.30E5	6.35E-5	1.18E7	1.28E7		
293	1.304	2.003	18.77	21.40	2.04E5	7.48E-5	8.79E6	8.16E6	26.5	61.5
303	1.329	1.813	21.61	48.96	4.54E4	1.01E-4	7.97E6	4.44E6		
water-ethanol(10%)-1-propanol										
283	0.877	2.169	9.32	13.40	1.79E-2	8.30E-5	1.24E7	1.05E7		
293	0.754	1.742	39.34	41.90	4.81E-3	2.28E-4	2.37E6	4.46E6	65.5	59.9
303	0.915	1.790	57.83	71.47	1.94E-3	6.67E-5	2.42E6	1.01E7		
water-ethanol(15%)-1-propanol										
283	RC	1.921	–	19.99	–	6.87E-5	–	8.56E6		
293	RC	1.792	–	46.26	–	1.03E-4	–	4.23E6	–	56.6
303	RC	1.696	–	97.74	–	2.32E-5	–	7.65E5		
water-ethanol(20%)-1-propanol										
283	RC	1.847	–	24.65	–	2.98E-4	–	7.43E6		
293	RC	1.724	–	55.78	–	5.63E-2	–	1.05E9	–	48.2
303	RC	1.781	–	95.05	–	2.45E-6	–	8.54E4		
water-ethanol(25%)-1-propanol										
283	RC	1.663	–	41.78	–	2.53E-4	–	3.77E6		
293	RC	1.579	–	97.88	–	1.41E-5	–	1.81E5	–	54.2
303	RC	1.539	–	191.09	–	7.67E-5	–	1.46E6		

RC is an abbreviation for the statement: rate constant is approximately constant. $E_a(k_1)$ values are activation energy of k_1 values.

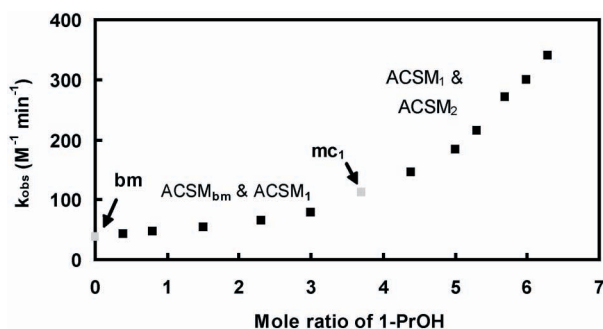
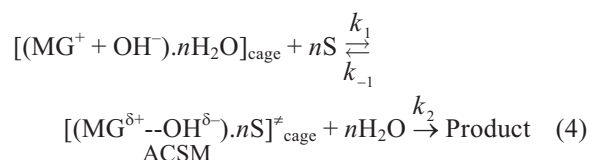


Fig. 6. Schematic representation of SEEMORTAC model for two-zone ethanol-1-propanol-water ternary mixtures involving constant weight percentage of ethanol.

formation of ACSM and increases the reaction rate. Mechanism of reaction in these mixed solvents is written as follows:



where ethanol molecules in water-ethanol solvents or 1-propanol molecules in water-ethanol-1-propanol ternary mixtures are shown by S and k_1 , k_{-1} and k_2 are the fundamental rate constants of MG^+ fading reaction in these solvents. In each ternary mixture, structure of ACSM depends on the structure of solvent cage. Dielectric constant values of alcohols are less than that of water and when ACSM forms in each zone, n molecules of water existing in the solvent cage are replaced by n molecules of 1-propanol from its surrounding that decreases dielectric constant value of microenvironment of $(MG^{\delta+} \cdots OH^{\delta-})$ in ACSM and formation of neutral product, MGOH, becomes more favorable and results in an increase in the rate of fading reaction. In the first zone, increase in 1-propanol weight percentage increases concentration ACSM formed in this zone (shown as $ACSM_1$) and decreases concentration of $ACSM_{bm}$ and finally in mc_1 point only $ACSM_1$ forms. Similar situation occurs in the second zone and with increase in 1-propanol weight percentage, concentration of $ACSM_1$ decreases and concentration of $ACSM_2$ (ACSM formed in the second zone) increases, Fig. 6. In the first zone, assuming that a steady-state concentration of $ACSM_1$ is reached in the used

ternary mixtures, we have:

$$[ACSM_1] = \frac{k_1^1 [MG^+] [OH^-] [S]^n}{k_{-1}^1 ([H_2O]_{bm} - [H_2O])^n + k_2^1} \quad (5)$$

where $[H_2O]_{bm}$ is the concentration of water in the used ethanol-water binary solution and k_1^1 , k_{-1}^1 and k_2^1 are the fundamental rate constants of MG^+ fading reaction in the first zone.

The effect of 1-propanol molecules to the reaction rate equation in the first zone, v_2 , is as follows:

$$v_2 = k_2^1 [ACSM_1] = \frac{k_1^1 k_2^1 [MG^+] [OH^-] [S]^n}{k_{-1}^1 ([H_2O]_{bm} - [H_2O])^n + k_2^1} \quad (6)$$

and the equation of reaction rate in ternary mixtures, v , is:

$$v = v_1 + v_2 = \left(k_{bm} + \frac{k_1^1 k_2^1 [S]^n}{k_{-1}^1 ([H_2O]_{bm} - [H_2O])^n + k_2^1} \right) [MG^+] [OH^-] = k_{obs} [MG^+] [OH^-] \quad (7)$$

where

$$k_{obs} = k_{bm} + \frac{k_1^1 k_2^1 [S]^n}{k_{-1}^1 ([H_2O]_{bm} - [H_2O])^n + k_2^1} \quad (8)$$

In the second zone $v_1 = k_{mc1} [MG^+] [OH^-]$ and Eq. (6) is replaced by:

$$v_2 = k_2^2 [ACSM_2] = \frac{k_1^2 k_2^2 [MG^+] [OH^-] ([S] - [S]_{mc1})^n}{k_{-1}^2 ([H_2O]_{mc1} - [H_2O])^n + k_2^2} \quad (9)$$

and Eq. (8) is replaced by:

$$k_{obs} = k_{mc1} + \frac{k_1^2 k_2^2 ([S] - [S]_{mc1})^n}{k_{-1}^2 ([H_2O]_{mc1} - [H_2O])^n + k_2^2} \quad (10)$$

where

$$k_{mc1} = k_{bm} + \frac{k_1^1 k_2^1 [S]_{mc1}^n}{k_{-1}^1 ([H_2O]_{bm} - [H_2O]_{mc1})^n + k_2^1} \quad (11)$$

where $[S]_{mc1}$ and $[H_2O]_{mc1}$ are the concentrations of 1-propanol and water in mc_1 point, respectively, k_{mc1} is the rate constant in mc_1 point and k_1^2 , k_{-1}^2 and k_2^2 are the fundamental rate constants of MG^+ fading reaction in the second zone.

Also, it has been shown that k_1 values in each zone obey the Arrhenius equation¹⁶ and the related activation en-

ergy, $E_a(k_1)$, values are given in Table 1. Rate constants in the first and second zone were fitted suitably in Eqs. (8) and (10) respectively and the results are given in Table 1. As shown in Tables S1-S5 and,¹⁷ in each certain temperature, the rate constant values of reaction in ternary mixtures are greater than those of binary aqueous mixtures involving similar 1-propanol concentrations. At each certain temperature and zone, as given in Table 1:

(a) Increase in weight percentage of ethanol in ternary solutions, increases ethanol content of ACSM₁ in the first zone and ACSM₂ in the second zone and these result in n values of 1-propanol are approximately constant or decrease and k_1 values increase. (b) Fundamental rate constants of reaction at each certain temperature change as $k_2 \gg k_1 \gg k_{-1}$. Also, comparison of the results for ternary mixtures, Table 1, to data of aqueous 1-propanol binary solutions shows:¹⁷

(a) At each certain temperature and zone, n values of

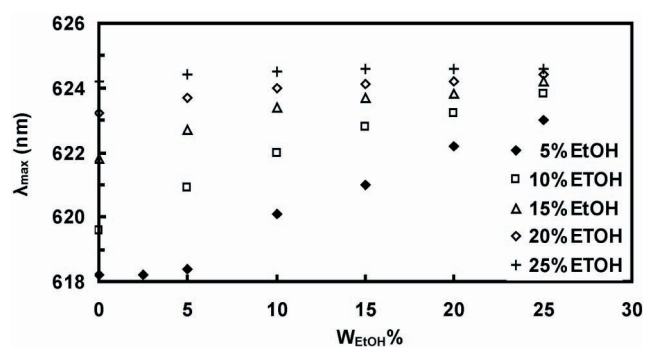


Fig. 7. λ_{\max} values of MG^+ vs. weight percentages of ethanol in ternary mixtures of water-ethanol-1-propanol under alkaline conditions at room temperature.

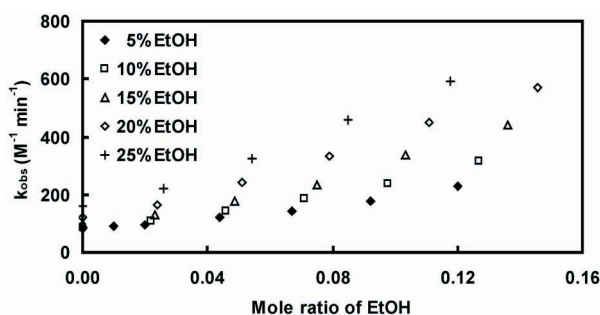


Fig. 8. k_{obs} values of MG^+ fading reaction vs. mole ratios of ethanol in ternary mixtures of water-ethanol-1-propanol under alkaline conditions at 293 K.

1-propanol in the used ternary mixtures are less than those of 1-propanol-water binary mixtures.

(b) At each certain temperature and zone, with increase in weight percentage of ethanol in ternary solutions, k_1 and k_2 values become greater than those of 1-propanol-water binary system.

Effect of Ethanol on MG^+ Fading in Constant Concentrations of 1-Propanol

These experiments were carried out in solutions involving 5, 10, 15, 20 and 25 weight percentages of 1-propanol and variable concentrations of ethanol. With increase in weight percentage of the ethanol, the λ_{\max} value of MG^+ shifts to red and rate constant of the MG^+ fading reaction increases, Figs. 7 and 8. Data of Tables S6-S10 (shown in Supplementary Data) were analyzed by SESMORTAC model and in Eqs. (3)-(11), 1-propanol and ethanol are re-

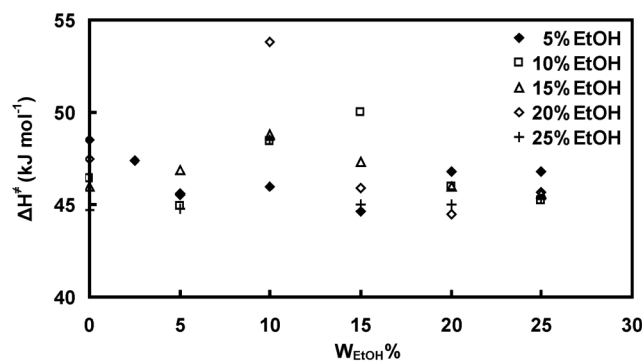


Fig. 9. ΔH^\ddagger values of MG^+ fading reaction vs. weight percentages of ethanol in ternary mixtures of water-ethanol-1-propanol under alkaline conditions at 293 K.

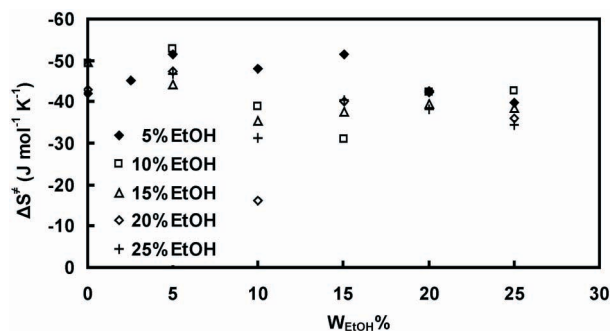


Fig. 10. ΔS^\ddagger values of MG^+ fading reaction vs. weight percentages of ethanol in ternary mixtures of water-ethanol-1-propanol under alkaline conditions at 293 K.

Table 2. n , k_1 , k_{-1} , k_2 and $E_a(k_1)$ values of MG^+ fading reaction in various water-ethanol-1-propanol ternary mixtures in constant concentrations of 1-propanol obtained from SESMORTAC model at 283-303 K

T (K)	n	k_1	k_{-1}	k_2	$E_a(k_1)$
water-ethanol-1-propanol(5%)					
283	1.502	8.30	2.31E-3	1.29E7	45.1
293	1.600	15.07	1.43E-3	9.85E6	
303	1.610	29.41	7.43E-4	6.96E6	
water-ethanol-1-propanol(10%)					
283	1.982	4.92	4.00E-4	1.62E7	64.5
293	1.674	15.42	5.03E-4	9.75E6	
303	1.679	29.89	2.82E-4	6.91E6	
water-ethanol-1-propanol(15%)					
283	1.796	9.65	1.81E-4	1.21E7	57.2
293	1.722	21.93	1.85E-4	8.10E6	
303	1.627	48.07	1.98E-4	5.04E6	
water-ethanol-1-propanol(20%)					
283	1.853	12.94	5.64E3	1.06E7	58.1
293	1.527	39.46	2.58E-5	5.61E6	
303	1.607	65.66	4.96E-6	1.01E5	
water-ethanol-1-propanol(25%)					
283	1.731	20.52	2.62E-4	8.50E6	52.4
293	1.680	45.59	2.82E-4	4.46E6	
303	1.646	89.07	4.49E-5	7.35E5	

MG^+ fading reaction in water-ethanol-1-propanol(5%) is two-zone which in the first zone, reaction rate is constant and parameters of the second region are given in Table 2. $E_a(k_1)$ values are activation energy of k_1 values. Dimensions of k_1 and k_{-1} , k_2 and $E_a(k_1)$ are $\text{M}^{-(n+1)} \text{min}^{-1}$, $\text{M}^{-n} \text{min}^{-1}$, min^{-1} and kJ mol^{-1} , respectively.

placed by each other.

It is found that in the used concentration range of ethanol, mixtures of water-ethanol-1-propanol were one-zone in 5 weight percentage of 1-propanol and two-zone in 10, 15, 20 and 25 weight percentages of 1-propanol, Tables S6-S10. As shown in Figs. 9 and 10, ΔS^\ddagger and ΔH^\ddagger values become less negative and more positive, respectively and with more increase in ethanol concentration ΔS^\ddagger and ΔH^\ddagger values become more negative and less positive, respectively which has been explained before in the case of adding 1-propanol to water-ethanol mixtures.

In each certain temperature, the observed rate constant values of reaction in ternary mixtures are greater than those of binary aqueous mixtures involving similar ethanol concentrations, and n and k_1 values of these ternary mixtures, Tables S6-S10, are less than and greater than those of

ethanol-water binary mixtures¹⁷ respectively.

As given in Table 2, in these ternary solutions: (a) At each temperature, with increase in weight percentage of 1-propanol, k_1 values increase. (b) In each weight percentage of 1-propanol, k_2 values decrease with increase in temperature which is according to the trend of hydroxide ion nucleophilic parameter, N_+ , values. (c) Fundamental rate constants of reaction at each certain temperature change as $k_2 \gg k_1 \gg k_{-1}$.

CONCLUSIONS

The rate constant of MG^+ fading reaction increases in ternary mixtures of water-ethanol-1-propanol. The results show that in each certain temperature, rate constant of reaction in ternary mixtures are greater than that of binary aqueous mixtures involving similar alcohol concentrations. The fundamental rate constants of MG^+ fading reaction in the used ternary solvent systems are obtained by SESMORTAC model. It was observed that at constant concentration of one alcohol and variable concentrations of the second one, with increase in temperature, k_1 values increase and this indicates that presence of ethanol (or 1-propanol) may increase dissolution of 1-propanol (or ethanol) in ACSM. At each temperature, due to increase in alcohol content of ACSM, n values of the used ternary mixtures are less than those of the related alcohol-water binary mixtures. Also, in each certain zone and temperature, fundamental rate constants of reaction change as $k_2 \gg k_1 \gg k_{-1}$.

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