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Study of Malachite Green Fading in Water–Ethanol–Ethylene Glycol Ternary Mixtures

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Abstract The rate constant of malachite green (MG^+) alkaline fading was measured in water–ethanol–ethylene glycol ternary mixtures. This reaction was studied under pseudo-first-order conditions at 283–303 K. In each series of experiments, the concentration of ethanol was kept constant and the concentration of ethylene glycol was changed. It was shown that due to hydrogen bonding and hydrophobic interaction between MG^+ and alcohol molecules the observed reaction rate constant, k_{obs}, increased in the water–ethanol–ethylene glycol ternary mixtures. The fundamental rate constants of MG^+ fading in these solutions (k_1, k_{-1} and k_2) were obtained by the SESMORTAC model. Analysis of k_1 and k_2 values in solutions containing constant ethanol concentrations show that in low concentrations of ethylene glycol, hydrogen bonding formed between ethanol and ethylene glycol molecules and in high concentrations of ethylene glycol, ethanol as a solvent for ethylene glycol affected the reaction rate.

Keywords SESMORTAC model · Ethylene glycol · Ethanol · Malachite green · Kinetics

List of symbols

SESMORTAC	Study of effect of solvent mixture on the one-step reaction rates using the transition state theory and cage effect
ACSM	Activated complex formed in the second mechanism
$ACSM_{bm}$	ACSM formed at the bm point
$ACSM_1$	ACSM formed in the first zone
AC	Activated complex
n	Number of molecules of solvent 1 in the solvent cage of transition state that are replaced by the same number of solvent 2 molecules in the transition state
mc	mechanism change
$k_{mc(i-1)}$	Rate constant at the mc_{i-1} point
k_{bm}	Observed rate constant
v	Reaction rate

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Subscripts

bm Binary mixture
ter Ternary mixture
i The *i*th zone

1 Introduction

Solvent effects on reactivity may be very large. Alcohols, as cosolvents, can change the rates of chemical reactions [1–5]. Malachite green (MG^+) is a triphenylmethane dye. These dyes represent a class of dyes of commercial and analytical importance [6, 7]. 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 [8]. In continuation of our earlier works [9, 10], in this work, we studied the MG^+ alkaline fading in ternary mixtures of water with different weight percentages of ethanol and ethylene glycol at 283–303 K. The MG^+ fading is a one-step reaction [11, 12].

2 Experimental

2.1 Chemicals

Malachite green oxalate (for analysis), ethanol ($\geq$99.9 %), ethylene glycol ($\geq$99 %), and NaOH were purchased from Merck.

2.2 Procedure

The fading of MG^+ was followed at its maximum wavelength (λ_{Max}) values in a thermostatted cell compartment of a Shimadzu UV–1650PC spectrophotometer. The experiments were conducted at 283, 293 and 303 K ($\pm$0.1 K) in a stoppered cell. All of the kinetic runs were carried out at least in triplicate. To perform each kinetic run, a 100 μL aliquot of 1.38×10^{-4} mol·L^{-1} MG^+ solution was added by a microsyringe into 2.9 mL of a solution containing 5.4×10^{-4} mol·L^{-1} sodium hydroxide and a certain concentration of the alcohols. The reaction between MG^+ and hydroxide ion is very fast and thus the reaction was studied at 283–303 K and very low concentrations of NaOH. This reaction is bimolecular, first order with respect to each reactant, and pseudo-first-order conditions (excess alkali) were used in all cases (Fig. 1).

We used the second-order reaction rate constants in our calculations. Ethanol and ethylene glycol have one and two hydroxyl groups, respectively, and the effect of ethylene glycol on the rate of this reaction is much greater than that of ethanol.

In this work, we investigated the simultaneous effect of various concentrations of ethanol and ethylene glycol on the kinetics of MG^+ fading.

3 Results and Discussion

3.1 Effect of Ethylene Glycol on MG^+ Fading in Constant Concentrations of Ethanol

These experiments were carried out in solutions containing 5, 10, 15, 20 and 25 weight percentages of ethanol and variable concentrations of ethylene glycol. As seen in Fig. 2, with increase in weight percentage of ethylene glycol, the λ_{Max} value of MG^+ is red shifted.

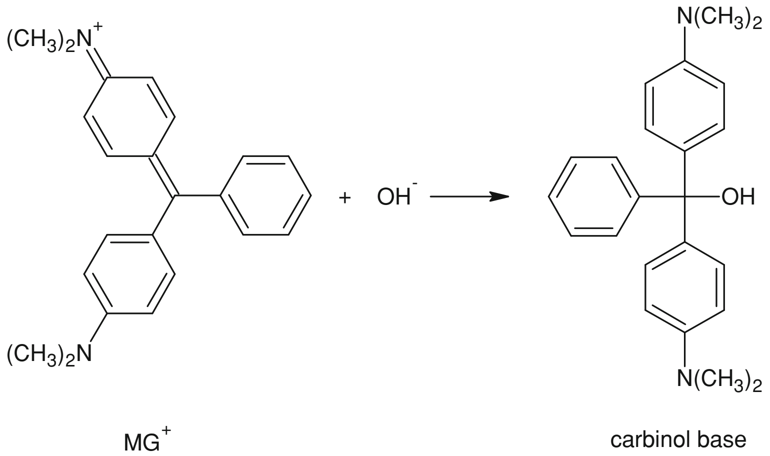

Fig. 1 Schematic representation of the MG^+ fading reaction

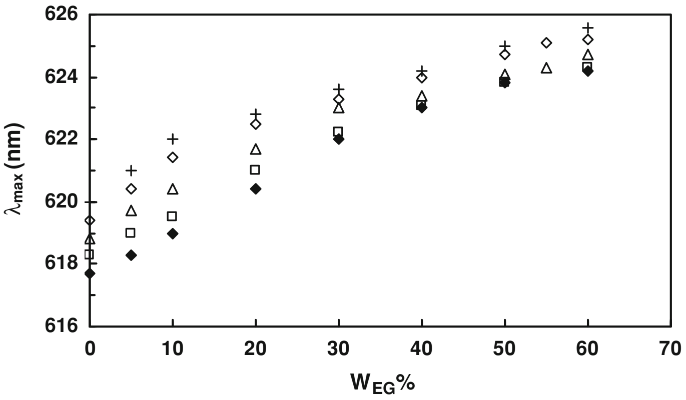

Fig. 2 λ_{Max} values of the MG^+ versus weight percentages of ethylene glycol in ternary mixtures of water–ethanol–ethylene glycol under alkaline conditions at room temperature. Weight percentages of ethanol in these solutions are: *filled diamond*, 5 %; *open square*, 10 %; *open triangle*, 15 %; *open diamond*, 20 % and +25 %

The red shift has been previously reported for other compounds upon going from polar to apolar solvents, as a result of hydrophobic interaction [13]. Comparison of these data to results obtained from the ethylene glycol–water binary mixtures [10] shows that, especially in low concentrations of ethanol, λ_{Max} values of MG^+ change similarly to their trend in binary aqueous ethylene glycol mixtures.

Reaction of MG^+ fading is an electrophile–nucleophile combination reaction. As shown in Tables 1, 2, 3, 4, 5 and Fig. 3, with increasing content of ethylene glycol, the rate constant of the reaction increases and then levels off over a small concentration range of ethylene glycol in the presence of 5 and 10 weight percentages of ethanol.

Alcohols have a lower dielectric constant than water and due to their hydrophobicity, according to Hughes–Ingold rules for solvent effects in nucleophilic substitution reactions [14–16], formation of the neutral carbinol base from two oppositely charged reactants (MG^+ and OH^-) becomes more favorable in higher weight percentages of alcohol in aqueous binary mixtures [17–19] and similar results are observed in this work.

As previously reported [10], in a series of alcohol–water binary mixtures, at the same mole fractions and temperatures, the rate constants of the MG^+ fading reaction at the low mole ratios of alcohols change as follows:

$$k_{\mathrm{W}} < k_{2-\mathrm{PrOH}} \approx k_{\mathrm{EtOH}} < k_{1-\mathrm{PrOH}} \approx k_{\mathrm{PrD}} < k_{\mathrm{Gl}} < k_{\mathrm{EG}} \leq k_{\mathrm{MeOH}} \tag{1}$$

where $k_{\mathrm{MeOH}}, k_{\mathrm{EG}}, k_{\mathrm{Gl}}, k_{\mathrm{PrD}}, k_{1-\mathrm{PrOH}}, k_{\mathrm{EtOH}}, k_{2-\mathrm{PrOH}}$ and k_{W} are the observed rate constants of the MG^+ fading reaction in aqueous mixtures of methanol, ethylene glycol, glycerol, 1,2-propanediol, 1-propanol, ethanol, 2-propanol and in water, respectively. Alcohols are hydrogen-bond donating solvents and the observed trend in relation 1 is similar to the trend of changes in hydrogen bond donor (α) and polarizability (π^*) parameters of the alcohols [20]. This shows that the role of hydrogen bonding in interaction between MG^+ and alcohol molecules is similar to that previously reported for interaction of dyes with protic solvents [21, 22].

In high mole fractions of these alcohols, due to the high viscosity of ethylene glycol, glycerol, and 1,2-propanediol, reaction rates change as follows:

$$k_{\mathrm{W}} < k_{\mathrm{Gl}} < k_{\mathrm{PrD}} \leq k_{\mathrm{EG}} < k_{2-\mathrm{PrOH}} \leq k_{\mathrm{EtOH}} < k_{1-\mathrm{PrOH}} < k_{\mathrm{MeOH}} \tag{2}$$

3.2 Proposed Reaction Mechanism

Data of Tables 1, 2, 3, 4 and 5 were analyzed by the SESMORTAC model. In the SESMORTAC model [9], a range of solvent composition in which the equation of logarithm of reaction rate constant, $\log_{10} k$, versus reciprocal of dielectric constant of the solution,

Table 1 k_{obs} and E_a values of MG^+ fading in water–ethanol (5 %)–ethylene glycol ternary solutions at 283–303 K

W_{EG} %	[EG]	[H_2O]	k_{obs} ($\mathrm{L \cdot mol^{-1} \cdot min^{-1}}$) at			E_a
	($\mathrm{mol \cdot L^{-1}}$)		283 K	293 K	303 K	($\mathrm{kJ \cdot mol^{-1}}$)
0.0	0.000	50.398	40.01 ± 2.45	76.43 ± 1.98	151.05 ± 6.71	47.3 ± 2.0
2.5	0.397	49.236	58.69 ± 3.02	121.03 ± 2.79	234.76 ± 4.36	49.4 ± 1.0
5.0	0.790	47.735	86.45 ± 3.88	165.96 ± 2.18	307.42 ± 3.59	45.2 ± 0.9
6.5	1.024	47.359	**102.07 ± 1.23**	**196.25 ± 1.04**	**353.11 ± 4.51**	44.3 ± 2.8
8.0	1.261	46.310	109.75 ± 2.62	213.58 ± 3.02	378.80 ± 8.68	44.2 ± 1.4
10.0	1.582	45.748	113.80 ± 2.69	233.09 ± 2.98	409.88 ± 10.02	45.7 ± 2.4
15.0	2.381	42.920	**133.30 ± 2.45**	**275.45 ± 10.91**	454.40 ± 3.76	43.8 ± 3.9
20.0	3.192	40.873	131.38 ± 2.66	274.75 ± 5.41	**485.14 ± 5.65**	46.6 ± 2.7
25.0	4.002	35.824	132.83 ± 2.34	275.12 ± 7.28	481.09 ± 11.77	45.9 ± 2.7
30.0	4.695	35.971	130.80 ± 1.39	277.43 ± 9.22	484.70 ± 10.42	46.8 ± 3.2
40.0	6.497	30.065	**133.85 ± 1.43**	**278.82 ± 4.90**	**531.12 ± 10.25**	49.1 ± 1.3
45.0	7.348	26.180	140.52 ± 2.08	308.30 ± 6.36	575.98 ± 26.14	54.1 ± 2.5
50.0	8.212	25.128	152.06 ± 5.52	338.69 ± 14.57	640.29 ± 8.56	51.3 ± 2.6
55.0	9.084	20.864	164.21 ± 8.58	364.21 ± 6.49	706.16 ± 7.77	52.0 ± 2.0
60.0	9.957	17.864	174.76 ± 2.13	384.53 ± 3.85	738.26 ± 10.24	51.4 ± 2.1
65.0	10.832	17.159	193.43 ± 2.78	434.53 ± 1.26	818.19 ± 14.62	51.5 ± 2.8
70.0	11.713	14.244	206.75 ± 2.96	483.32 ± 3.91	894.46 ± 16.99	52.3 ± 3.9

In these series of experiments, the concentration of ethanol is 1.005 $\mathrm{mol \cdot L^{-1}}$ (≈ 5 %). k_{mc} values are shown in bold. Zones 1, 2, 3 and 4 are in the range of (0–6.5 %, 6.5–15 %, 20–30 % and 40–70 %) at 283 and 293 K and in the range of (0–6.5 %, 6.5–20 %, 20–30 % and 40–70 %) at 303 K, respectively

Table 2 k_{obs} and E_a values of MG^+ fading in water–ethanol (10 %)–ethylene glycol ternary solutions at 283–303 K

W_{EG} %	[EG]	$[H_2O]$	k_{obs} ($L \cdot mol^{-1} \cdot min^{-1}$) at			E_a
	($mol \cdot L^{-1}$)		283 K	293 K	303 K	($kJ \cdot mol^{-1}$)
0.0	0.000	47.120	51.12 ± 1.08	100.85 ± 2.98	195.08 ± 7.10	47.7 ± 1.1
1.5	0.238	46.791	72.45 ± 1.32	126.52 ± 7.47	272.99 ± 7.20	47.2 ± 5.4
2.5	0.392	45.856	84.25 ± 2.34	159.93 ± 1.45	299.21 ± 6.52	45.2 ± 1.2
3.5	0.548	45.666	**95.26 ± 1.59**	**176.37 ± 4.99**	**335.78 ± 8.85**	44.9 ± 1.7
5.0	0.793	44.746	100.83 ± 2.36	184.75 ± 2.90	358.61 ± 12.41	45.2 ± 2.3
6.5	1.022	44.047	109.22 ± 1.33	207.55 ± 2.94	381.27 ± 6.73	44.6 ± 1.0
10.0	1.579	42.573	120.22 ± 1.72	244.87 ± 3.93	456.81 ± 13.93	47.6 ± 1.3
12.5	1.978	41.526	**134.09 ± 1.91**	280.94 ± 1.58	**523.00 ± 3.97**	48.5 ± 1.8
15.0	2.378	40.327	135.1 1 ± 2.33	**292.00 ± 1.20**	524.61 ± 7.87	48.4 ± 3.0
20.0	3.193	37.455	136.50 ± 3.98	296.28 ± 3.15	521.94 ± 3.09	47.9 ± 3.5
25.0	3.999	35.334	133.23 ± 1.71	296.67 ± 7.57	522.66 ± 4.10	48.8 ± 4.0
30.0	4.822	32.797	134.43 ± 2.07	297.39 ± 5.83	**545.50 ± 3.49**	50.0 ± 3.0
40.0	6.501	27.131	**144.67 ± 2 .96**	**341.09 ± 6.95**	640.24 ± 21.70	53.1 ± 3.8
45.0	7.345	24.575	158.89 ± 1.18	366.46 ± 5.56	706.92 ± 8.86	53.3 ± 2.8
50.0	8.202	22.115	176.62 ± 1.85	404.24 ± 4.01	755.86 ± 20.66	51.9 ± 3.3
55.0	9.075	19.271	192.3 6 ± 3.05	432.31 ± 6.39	812.24 ± 23.55	51.4 ± 2.9
60.0	9.940	16.973	212.48 ± 3.64	466.96 ± 9.99	891.51 ± 29.31	51.2 ± 2.2
65.0	10.834	13.794	244.29 ± 8.57	506.28 ± 2.73	951.04 ± 19.46	48.5 ± 1.4

In these series of experiments, the concentration of ethanol is 1.980 $mol \cdot L^{-1}$ ($\approx$ 10 %). k_{mc} values are shown in bold. Zones 1, 2, 3 and 4 are in the range of (0–3.5 %, 3.5–12.5 %, 12.5–30 % and 40–65 %), (0–3.5 %, 3.5–12.5 %, 15–30 % and 40–65 %) and (0–3.5 %, 3.5–12.5 %, 12.5–25 % and 30–65 %) at 283, 293 and 303 K, respectively

D^{-1}, is linear [23–27], is called a "zone" and a solvent composition in which a zone finishes and another zone starts is called "mechanism *c*hange point" (or abbreviated as *mc* point). Considerating a mechanism on the basis of point charge on a dielectric continuum suggests that plots of $\log_{10} k$ against D^{-1}, should be linear. The failure of the simple electrostatic interpretation shows the importance of hydrogen bonding and other non-electrostatic medium effects in controlling the reactivity of the substrates [26–28].

In the SESMORTAC model, variations in the mechanism are followed through the study of changes in the microenvironment (or solvent cage) of the activated complex. Dielectric constants of the aqueous ethanol and ethylene glycol binary solutions were obtained from the work of Åkerlof [29].

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

$$[(MG^+ + OH^-)]_{cage} \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} \underset{AC}{\left[\left(MG^{\delta+} - OH^{\delta-}\right)\right]^{\neq}_{cage}} \xrightarrow{k'_2} \text{Product} \quad (3)$$

where AC is an abbreviation for activated complex and k'_1, k'_{-1} and k'_2 are the fundamental rate constants of the MG^+ fading reaction in the pure solvent and we cannot determine

Table 3 k_{obs} and E_{a} values of MG^+ fading in water–ethanol (15 %)–ethylene glycol ternary solutions at 283–303 K

W_{EG} %	[EG]	[H_2O]	k_{obs} ($\mathrm{L{\cdot}mol^{-1}{\cdot}min^{-1}}$) at			E_{a}
	($\mathrm{mol{\cdot}L^{-1}}$)		283 K	293 K	303 K	($\mathrm{kJ{\cdot}mol^{-1}}$)
0.0	0.000	44.415	80.13 ± 1.79	141.50 ± 2.17	273.57 ± 3.76	43.7 ± 2.9
2.5	0.392	43.508	90.33 ± 1.52	173.76 ± 2.79	325.37 ± 4.28	45.7 ± 1.0
5.0	0.794	42.322	107.87 ± 2.62	205.31 ± 7.25	385.57 ± 7.47	45.4 ± 1.1
9.0	1.426	40.434	122.44 ± 1.49	251.78 ± 1.93	468.68 ± 7.99	47.9 ± 1.5
10.0	1.573	39.652	**130.56 ± 1.84**	269.36 ± 2.50	488.35 ± 5.37	47.1 ± 2.0
12.5	1.975	38.528	135.36 ± 1.21	**292.09 ± 4.00**	**534.69 ± 9.76**	49.0 ± 2.6
15.0	2.373	37.505	138.04 ± 2.52	301.92 ± 7.27	556.66 ± 2.71	49.8 ± 2.7
20.0	3.183	35.186	145.87 ± 2.39	319.79 ± 3.02	612.17 ± 7.98	51.2 ± 2.1
25.0	3.998	32.349	152.03 ± 1.68	327.07 ± 7.49	629.96 ± 18.58	50.7 ± 1.6
30.0	4.823	29.837	158.39 ± 2.78	340.51 ± 6.25	660.56 ± 5.03	50.9 ± 1.5
35.0	6.066	26.294	**164.85 ± 3.30**	**351.46 ± 16.89**	**707.19 ± 9.05**	51.9 ± 1.1
40.0	6.494	24.796	182.07 ± 4.70	392.59 ± 5.98	779.50 ± 23.19	51.9 ± 1.2
45.0	7.345	21.803	199.75 ± 2.58	431.25 ± 3.10	863.69 ± 15.87	52.2 ± 1.1
50.0	8.205	19.198	216.17 ± 2.73	483.78 ± 4.59	990.14 ± 14.39	54.3 ± 1.3
55.0	9.073	16.898	231.75 ± 10.92	537.36 ± 8.38	1091.56 ± 20.99	55.3 ± 2.0

In these series of experiments, the concentration of ethanol is 2.93 $\mathrm{mol{\cdot}L^{-1}}$ ($\approx$ 15 %). k_{mc} values are shown in bold. Zones 1, 2 and 3 are in the range of (0–10 %, 10–35 % and 35–55 % at 283 K and 0–10 %, 12.5–35 % and 35–55 %) at 293 and 303 K, respectively

Table 4 k_{obs} and E_{a} values of MG^+ fading in water–ethanol (20 %)–ethylene glycol ternary solutions at 283–303 K

W_{EG} %	[EG]	[H_2O]	k_{obs} ($\mathrm{L{\cdot}mol^{-1}{\cdot}min^{-1}}$) at			E_{a}
	($\mathrm{mol{\cdot}L^{-1}}$)		283 K	293 K	303 K	($\mathrm{kJ{\cdot}mol^{-1}}$)
0.0	0.000	41.830	89.53 ± 2.22	176.39 ± 8.37	310.00 ± 4.48	44.3 ± 1.7
5.0	0.804	39.216	117.00 ± 2.59	232.52 ± 3.69	440.60 ± 10.79	47.3 ± 0.9
10.0	1.571	36.942	144.80 ± 2.54	294.64 ± 1.33	550.56 ± 7.04	47.6 ± 1.2
12.5	1.985	35.467	**154.40 ± 3.73**	**320.97 ± 5.49**	**603.30 ± 2.17**	48.6 ± 1.5
15.0	2.389	34.379	158.22 ± 3.83	330.20 ± 7.06	639.38 ± 8.17	49.8 ± 1.1
20.0	3.191	32.041	167.31 ± 1.77	353.05 ± 7.23	659.70 ± 13.89	48.9 ± 1.8
25.0	4.003	29.457	170.50 ± 2.47	383.92 ± 6.71	752.40 ± 18.08	53.0 ± 2.1
30.0	4.828	26.793	182.19 ± 2.41	409.07 ± 14.46	807.80 ± 15.70	53.1 ± 1.9
35.0	5.646	23.345	190.57 ± 3.12	439.39 ± 4.36	865.53 ± 11.37	54.0 ± 2.4
40.0	6.497	21.475	**200.70 ± 1.76**	**472.86 ± 10.59**	**928.85 ± 19.28**	54.7 ± 2.9
45.0	7.374	18.903	230.50 ± 2.49	513.47 ± 15.29	1071.71 ± 15.51	54.8 ± 1.1
50.0	8.202	16.316	261.80 ± 1.59	587.39 ± 3.44	1210.00 ± 17.75	54.6 ± 1.3
55.0	9.115	13.046	299.35 ± 8.12	666.78 ± 14.81	1345.09 ± 12.51	53.6 ± 1.4

In these series of experiments, the concentration of ethanol is 3.86 $\mathrm{mol{\cdot}L^{-1}}$ ($\approx$ 20 %). k_{mc} values are shown in bold. At all temperatures, zones 1, 2 and 3 are in the range of (0–12.5 %, 12.5–40 and 40–55 %), respectively

Table 5 k_{obs} and E_a values of MG^+ fading in water–ethanol (25 %)–ethylene glycol ternary solutions at 283–303 K

W_{EG} %	[EG]	[H_2O]	k_{obs} ($L \cdot mol^{-1} \cdot min^{-1}$) at			E_a
	($mol \cdot L^{-1}$)		283 K	293 K	303 K	($kJ \cdot mol^{-1}$)
0.0	0.000	38.539	95.19 ± 1.31	200.65 ± 1.27	389.03 ± 2.36	50.2 ± 1.2
1.5	0.237	38.515	110.60 ± 2.33	219.29 ± 2.17	418.80 ± 3.59	47.5 ± 1.0
2.5	0.395	37.365	123.79 ± 1.96	242.42 ± 8.06	463.96 ± 5.21	47.1 ± 1.0
3.5	0.549	37.192	130.32 ± 2.23	263.10 ± 8.99	500.14 ± 4.92	47.9 ± 1.0
5.0	0.799	36.365	**139.15 ± 1.24**	**293.95 ± 4.52**	544.16 ± 7.88	48.6 ± 2.0
6.5	1.024	35.377	145.03 ± 1.96	305.71 ± 2.28	**579.44 ± 3.94**	49.4 ± 1.6
10.0	1.565	33.755	156.04 ± 2.31	333.59 ± 5.96	635.50 ± 9.08	50.1 ± 1.7
12.5	1.982	32.635	160.12 ± 3.28	350.99 ± 4.63	695.04 ± 6.16	52.4 ± 1.4
15.0	2.375	31.394	165.90 ± 2.70	363.18 ± 7.81	716.66 ± 4.43	52.2 ± 1.5
20.0	3.184	29.288	181.20 ± 1.28	397.80 ± 6.46	787.99 ± 6.79	52.4 ± 1.5
25.0	4.004	26.714	201.78 ± 4.01	428.74 ± 4.26	877.17 ± 10.24	52.4 ± 1.1
30.0	4.822	23.673	212.86 ± 1.54	479.69 ± 12.32	983.90 ± 8.20	54.6 ± 1.4
35.0	5.648	21.924	236.06 ± 14.22	547.52 ± 6.85	1106.7 1 ± 15.29	55.1 ± 2.1
40.0	6.496	18.433	252.78 ± 16.47	605.69 ± 3.11	1168.62 ± 18.61	54.6 ± 3.6
45.0	7.349	15.896	286.13 ± 7.44	670.14 ± 6.14	1300.34 ± 34.97	54.0 ± 3.0
50.0	8.213	13.156	304.86 ± 8.04	731.30 ± 15.85	1436.07 ± 48.38	55.3 ± 3.2

In these series of experiments, the concentration of ethanol is 4.93 $mol \cdot L^{-1}$ (≈ 25 %). k_{mc} values are shown in bold. Zones 1 and 2 are in the range of (0–5 % and 5–50 %) at 283 and 293 K and in the range of (0–6.5 % and 6.5–50 %) at 303 K, respectively

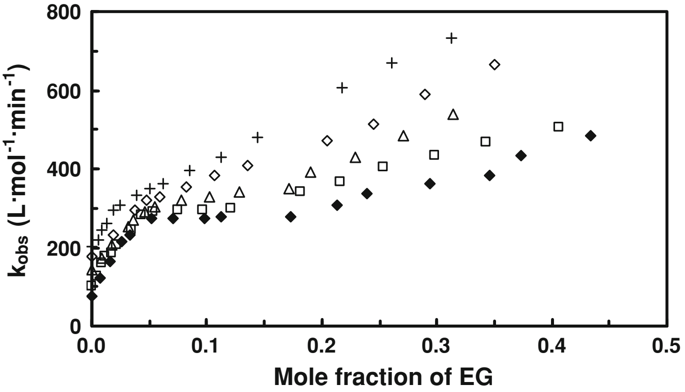

Fig. 3 k_{obs} values of MG^+ fading reaction versus mole fractions of ethylene glycol in ternary mixtures of water–ethanol–ethylene glycol under alkaline conditions at 293 K. Weight percentages of ethanol in these solutions are: *filled diamond*, 5 %; *open square*, 10 %; *open triangle*, 15 %; *open diamond*, 20 % and +25 %

them. But, in these series of ethanol–water binary mixtures there is an *mc* point. The reaction proceeds according to the second mechanism and the related rate equation, v_1, is written as follows:

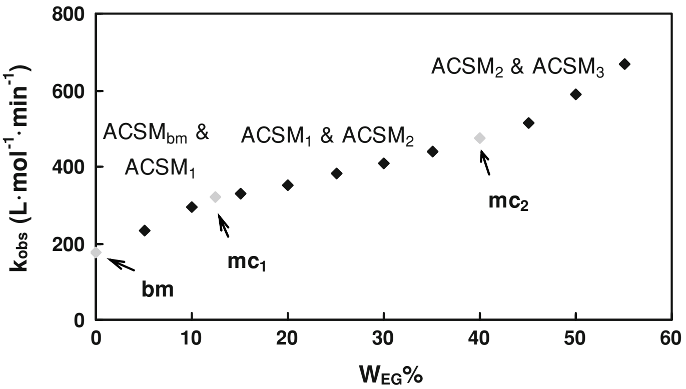

Fig. 4 Typical representation of the SEEMORTAC model for ethanol–ethylene glycol–water ternary mixtures involving a constant weight percentage of ethanol

$$v_1 = k_{bm}[\mathrm{MG}^+][\mathrm{OH}^-] \tag{4}$$

where k_{bm} is the observed rate constant in the ethanol–water binary solution. Thus, at this point rather than AC an ACSM forms. ACSM is an abbreviation for "Activated Complex formed in the Second Mechanism". This ACSM is called ACSM$_{bm}$ which is an abbreviation for "ACSM formed in binary mixture", Fig. 4.

Adding an organic solvent to a solvent (for example ethanol to water) or a binary mixture (for example ethylene glycol to aqueous ethanol) involving reactants results in formation of ACSM and affects the reaction rate. The mechanism of the reaction in these mixed solvents is written as follows:

$$[(\mathrm{MG}^+ + \ \mathrm{OH}^-)n\mathrm{H_2O}]_{\mathrm{cage}} + n\mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \left[\underset{\mathrm{ACSM}}{\left(\mathrm{MG}^{\delta+}{-}\mathrm{OH}^{\delta-}\right)n\mathrm{S}}\right]^{\neq}_{\mathrm{cage}} + n\mathrm{H_2O} \xrightarrow{k_2} \mathrm{Product} \tag{5}$$

where ethanol molecules in water–ethanol solvents or ethylene glycol molecules in water–ethanol–ethylene glycol 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. The solvent cage is the microenvironment of the MG$^{\delta+}$–OH$^{\delta-}$ contact pair and, in each zone, n molecules of water can be replaced by n molecules of ethylene glycol. 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 ethylene glycol molecules of its surrounding (n order in solvent molecules). As seen in Table 6, the values of n are different in each zone.

In each ternary mixture, the structure of the 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 ethylene glycol from its surrounding that decreases dielectric constant of the microenvironment of (MG$^{\delta+}$–OH$^{\delta-}$) in ACSM while the formation of neutral product, MGOH, becomes more favorable and results in an increase in the rate of the fading reaction. In the first zone, an increase in ethylene glycol weight percentage increases the concentration ACSM formed in this zone (shown as ACSM$_1$) and decreases the

Table 6 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–ethylene glycol ternary mixtures at constant concentrations of ethanol obtained from the SESMORTAC model at 283–303 K

T (K)	n				k_1 ($L^{(n+1)}\cdot mol^{-(n+1)}\cdot min^{-1}$)				k_{-1} ($L^n\cdot mol^{-n}\cdot min^{-1}$)				k_2 (min^{-1})				$E_a(k_1)$ ($kJ\cdot mol^{-1}$)			
	1st	2nd	3rd	4th	1st	2nd	3rd	4th	1st	2nd	3rd	4th	1st	2nd	3rd	4th	1st	2nd	3rd	4th
Water–ethanol(5 %)–ethylene glycol																				
283	1.241	0.951	–	1.555	60.80	23.12	–	8.21	1.24E−3	1.96E−2	–	7.61E4	1.51E6	6.97E6	–	1.16E7				
293	1.359	0.888	–	1.201	179.60	62.82	–	27.11	9.13E4	1.39E4	–	4.87E−4	7.56E5	1.29E6	–	5.44E6	53.4	61.8	–	69.0
303	1.141	1.019	–	1.149	270.07	130.62	–	56.58	6.06E4	1.33E5	–	8.28E3	5.78E5	7.98E5	–	3.23E6				
Water–ethanol(10 %)–ethylene glycol																				
283	0.869	1.034	–	1.280	74.52	26.09	–	14.81	1.23E−4	6.42E−3	–	6.69E−4	8.02E5	3.44E6	–	3.36E6				
293	1.147	1.237	–	1.093	155.49	69.27	–	33.06	4.79E−3	1.20E4	–	9.43E−5	7.18E5	1.90E6	–	2.73E6	57.0	54.0	–	46.4
303	1.022	1.268	–	1.122	369.43	118.23	–	54.27	8.92E4	4.64E−4	–	1.28E−5	3.11E5	1.06E6	–	2.83E6				
Water–ethanol(15 %)–ethylene glycol																				
283	1.003	1.034	0.724	–	31.70	10.94	29.88	–	6.39E3	1.64E5	2.20E−3	–	1.91E6	4.84E6	2.36E6	–				
293	0.990	0.934	0.887	–	79.92	25.71	68.81	–	6.86E−4	1.36E5	1.98E−3	–	1.12E6	2.30E6	1.59E6	–	55.4	61.6	53.7	–
303	1.079	0.881	0.954	–	149.51	61.59	134.44	–	2.16E4	4.73E4	2.53E−4	–	8.35E5	1.67E6	1.22E6	–				
Water–ethanol(20 %)–ethylene glycol																				
283	1.502	1.111	1.101	–	49.53	8.62	34.14	–	1.28E5	9.01E−4	1.88E−4	–	1.81E6	4.27E6	2.63E6	–				
293	1.404	1.173	1.776	–	90.03	26.92	54.83	–	6.30E4	4.27E3	4.68E4	–	1.36E6	2.41E6	3.67E6	–	44.7	70.5	58.3	–
303	0.996	1.329	1.126	–	173.88	62.11	176.82	–	2.75E4	1.95E4	2.18E4	–	1.00E6	1.59E6	9.43E5	–				
Water–ethanol(25 %)–ethylene glycol																				
283	0.758	1.192	–	–	53.46	15.09	–	–	7.32E−3	7.96E−4	–	–	2.07E6	6.84E6	–	–				
293	1.522	1.276			187.82	33.74	–	–	5.72E4	4.47E−4	–	–	4.39E5	4.95E6			63.1	63.3	–	–
303	1.465	1.133			311.09	86.41	–	–	4.13E4	3.05E−4	–	–	3.19E5	3.81E6						

E_a (k_1) values are the activation energy of k_1

concentration of $ACSM_{bm}$, and finally at mc_1 only $ACSM_1$ forms. A similar situation occurs in the second zone and with increasing ethylene glycol weight percentage, the concentration of $ACSM_1$ decreases and the concentration of $ACSM_2$ (ACSM formed in the second zone) increases, Fig. 4. In the first zone, assuming that a steady-state concentration of $ACSM_1$ is reached in the ternary mixtures, we have:

$$[\mathrm{ACSM}_1] = \frac{k_1^1[\mathrm{MG}^+][\mathrm{OH}^-][\mathrm{S}]^n}{k_{-1}^1\left([\mathrm{H_2O}]_{bm} - [\mathrm{H_2O}]\right)^n + k_2^1} \quad (6)$$

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

The effect of ethylene glycol molecules on the reaction rate equation in the first zone, v_2, is as follows:

$$v_2 = k_2^1[\mathrm{ACSM}_1] = \frac{k_1^1 k_2^1[\mathrm{MG}^+][\mathrm{OH}^-][\mathrm{S}]^n}{k_{-1}^1([\mathrm{H_2O}]_{bm} - [\mathrm{H_2O}])^n + k_2^1} \quad (7)$$

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

$$v = v_1 + v_2 = k_{\mathrm{obs}}[\mathrm{MG}^+][\mathrm{OH}^-] = \left(k_{bm} + \frac{k_1^1 k_2^1[\mathrm{S}]^n}{k_{-1}^1([\mathrm{H_2O}]_{bm} - [\mathrm{H_2O}])^n + k_2^1}\right)[\mathrm{MG}^+][\mathrm{OH}^-] \quad (8)$$

$$\text{where} \quad k_{\mathrm{obs}} = k_{bm} + \frac{k_1^1 k_2^1[\mathrm{S}]^n}{k_{-1}^1([\mathrm{H_2O}]_{bm} - [\mathrm{H_2O}])^n + k_2^1} \quad (9)$$

In the second zone, $v_1 = k_{mc1}[\mathrm{MG}^+][\mathrm{OH}^-]$ and Eq. 7 is replaced by:

$$v_2 = k_2^2[\mathrm{ACSM}_2] = \frac{k_1^2 k_2^2[\mathrm{MG}^+][\mathrm{OH}^-]\left([\mathrm{S}] - [\mathrm{S}]_{mc1}\right)^n}{k_{-1}^2\left([\mathrm{H_2O}]_{mc1} - [\mathrm{H_2O}]\right)^n + k_2^2} \quad (10)$$

In this zone, Eq. 9 is replaced by:

$$k_{\mathrm{obs}} = k_{mc1} + \frac{k_1^2 k_2^2\left([\mathrm{S}] - [\mathrm{S}]_{mc1}\right)^n}{k_{-1}^2\left([\mathrm{H_2O}]_{mc1} - [\mathrm{H_2O}]\right)^n + k_2^2} \quad (11)$$

$$\text{where} \quad k_{mc1} = k_{bm} + \frac{k_1^1 k_2^1[\mathrm{S}]_{mc1}^n}{k_{-1}^1([\mathrm{H_2O}]_{bm} - [\mathrm{H_2O}]_{mc1})^n + k_2^1} \quad (12)$$

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

$v_1 = k_{mc(i-1)}[\mathrm{MG}^+][\mathrm{OH}^-]$ and Eq. 7 is replaced by:

$$v_2 = k_2^i[\mathrm{ACSM}_i] = \frac{k_1^i k_2^i[\mathrm{MG}^+][\mathrm{OH}^-]\left([\mathrm{S}] - [\mathrm{S}]_{mc(i-1)}\right)^n}{k_{-1}^i\left([\mathrm{H_2O}]_{mc(i-1)} - [\mathrm{H_2O}]\right)^n + k_2^i} \quad (13)$$

and Eq. 9 is replaced by:

$$k_{\mathrm{obs}} = k_{mc(i-1)} + \frac{k_1^i k_2^i \left([\mathrm{S}] - [\mathrm{S}]_{mc(i-1)}\right)^n}{k_{-1}^i \left([\mathrm{H_2O}]_{mc(i-1)} - [\mathrm{H_2O}]\right)^n + k_2^i} \tag{14}$$

$$\text{where} \quad k_{mc(i-1)} = k_{mc(i-2)} + \frac{k_1^{i-1} k_2^{i-1} ([\mathrm{S}]_{mc(i-1)} - [\mathrm{S}]_{mc(i-2)})^n}{k_{-1}^{i-1} ([\mathrm{H_2O}]_{mc(i-2)} - [\mathrm{H_2O}]_{mc(i-1)})^n + k_2^{i-1}} \tag{15}$$

$k_{mc(i-1)}$ is the rate constant at the mc_{i-1} point, ACSM_i is the ACSM formed in the ith zone and k_1^i, k_{-1}^i and k_2^i are the fundamental rate constants of the MG^+ fading reaction in the ith zone. In this reaction, k_{obs} in the third zone of 5 and 10 % ethanol is approximately constant, $k_{\mathrm{obs}} = k_{mc2}$.

It has been shown that k_1 values in each zone obey the Arrhenius equation [9] and the related activation energy, $E_{\mathrm{a}}(k_1)$, values are given in Table 6. The observed rate constants in the first, second, third and fourth zones were fitted suitably with Eqs. 9, 11 and 14 and the results are given in Table 6. It was observed that at constant concentration of ethanol and variable concentrations of ethylene glycol, with increasing temperature the k_1 values increase whereas the k_2 values decrease, Table 6. Ethylene glycol has two hydroxyl groups and its viscosity is more than ethanol's [30] and thus the fundamental rate constants of MG^+ fading in ethylene glycol binary mixtures are different from those of ethanol–water binary mixtures [10] (Table 6). It is found that in the ethylene glycol concentration range used, with increasing ethanol concentration, the number of zones of water–ethanol–ethylene glycol solutions decreases from four to two (Tables 1, 2, 3, 4, 5) and the trend of variation of k_{obs} values becomes more similar to those of ethanol–water binary mixtures.

In 5 and 10 % ethanol, the reaction rate remains constant in the third zone and in the fourth zone. It seems that there is a competition between the increase in viscosity of the solution and the interaction between ethylene glycol and MG^+. Due to the presence of ethanol in the process of ACSM formation, the reaction is zone-three in 15 and 20 % ethanol and is zone-two in 25 % ethanol (Tables 1, 2, 3, 4, 5). Comparison of rate constants of MG^+ fading in low concentrations of ethylene glycol, zones 1 and 2 in 5–20 % ethanol and zone 1 in 25 % ethanol (Tables 1, 2, 3, 4, 5), to those in ethanol–water and ethylene glycol–water binary mixtures shows [10] that

$$k_1^{\mathrm{EG}} > k_1^{ter} > k_1^{\mathrm{EtOH}}, n^{\mathrm{EG}} < n^{ter} < n^{\mathrm{EtOH}} (\text{in the most cases}), k_2^{\mathrm{EG}} < k_2^{ter} < k_2^{\mathrm{EtOH}} \tag{16}$$

where superscripts EG, EtOH and *ter* are used for n, k_1 and k_2 values in binary mixtures of ethylene glycol–water, ethanol–water and ternary mixtures of water–ethanol–ethylene glycol solutions, respectively. k_1 values in relation (16) show that formation of ACSM in ethylene glycol–water binary mixtures is more favorable than its formation in these ternary mixtures. It seems that in low concentrations of ethylene glycol, hydrogen bonding between ethanol and ethylene glycol molecules competes with interactions of ethylene glycol molecules with MG^+ molecules.

In higher concentrations of ethylene glycol, zone 4 in 5 and 10 % ethanol, zone 3 in 15 and 20 % ethanol and zone 2 in 25 % ethanol, the k_1 and k_2 values become greater and the n values become lesser than those in water–ethanol or water-ethylene glycol binary solutions [10] and formation of ACSM in these ternary mixtures is more favorable than its formation in ethylene glycol–water binary mixtures. It seems that with increasing weight percentage of ethanol, its concentration in the microenvironment of ACSM increases and acts as a solvent for better dissolution of ethylene glycol molecules in ACSM.

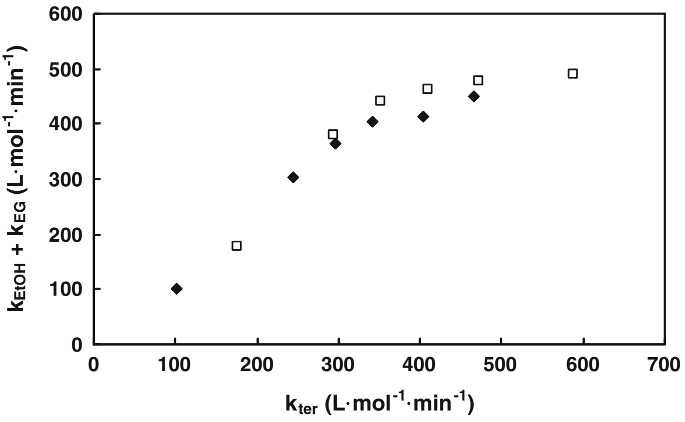

Fig. 5 Sum of the MG^+ fading rate constants in ethanol–water and ethylene glycol–water binary mixtures versus the observed rate constants in ternary water–ethanol–ethylene glycol mixtures containing: *filled diamond*, 10 %; and *open square*, 20 % ethanol and different weight percentages of ethylene glycol at 293 K

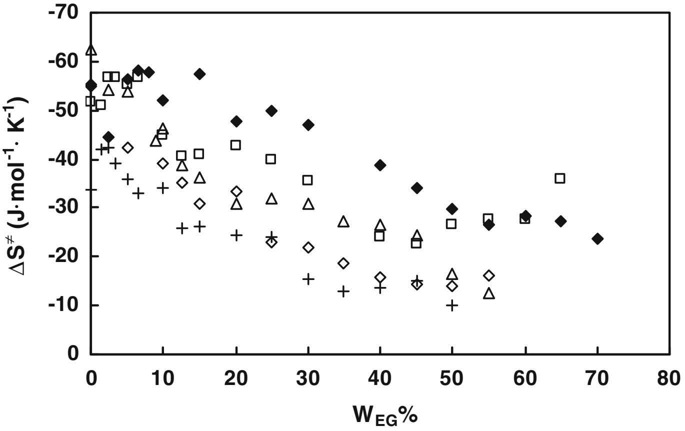

Fig. 6 $\Delta S^{\neq}$ values of the MG^+ fading reaction versus weight percentages of ethylene glycol in ternary mixtures of water–ethanol–ethylene glycol under alkaline conditions. Weight percentages of ethanol in these solutions are: *filled diamond*, 5 %; *open square*, 10 %; *open triangle*, 15 %; *open diamond*, 20 % and +25 %

To confirm these results, the sum of MG^+ fading rate constants in ethanol–water [10] (k_{EtOH}) and ethylene glycol–water (k_{EG}) binary mixtures are greater than the observed rate constants in ternary water–ethanol–ethylene glycol mixtures (k_{ter}) containing similar ethanol and ethylene glycol weight percentages in low concentrations of ethylene glycol, and are less than those values in high concentrations of ethylene glycol, respectively (Fig. 5).

As seen in Figs. 6 and 7, the $\Delta S^{\neq}$ and $\Delta H^{\neq}$ values of the fading reaction are negative and positive, respectively, which is due to dissolution of ethylene glycol molecules in the solvent cage and hydrogen binding and hydrophobic interactions [31] between MG^+ and ethylene glycol molecules when ACSM forms, and the formation of ACSM is enthalpy driven.

As shown experimentally, dissolution of hydrocarbons in water is exothermic and results in a more ordered structure of water around the dissolved hydrocarbon molecules

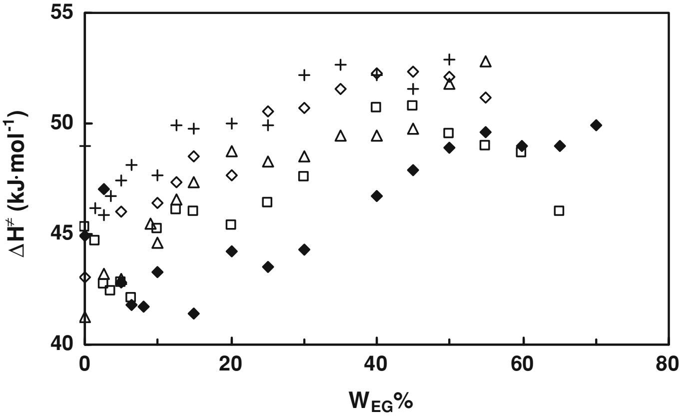

Fig. 7 $\Delta H^{\neq}$ values of the MG^+ fading reaction versus weight percentages of ethylene glycol in ternary mixtures of water–ethanol–ethylene glycol under alkaline conditions. Weight percentages of ethanol in these solutions are: *filled diamond*, 5 %; *open square*, 10 %; *open triangle*, 15 %; *open diamond*, 20 % and +25 %

[32]. 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 [32]. Also, dissolution of ethylene glycol in water is exothermic and increases the entropy of reaction. Therefore, with increase in ethylene glycol concentration the $\Delta S^{\neq}$ and $\Delta H^{\neq}$ values become less negative and more positive, respectively.

4 Conclusions

The rate constant of the MG^+ fading reaction increases in ternary mixtures of water–ethanol–ethylene glycol. The fundamental rate constants of MG^+ fading reaction in the used ternary solvent systems are obtained by the SESMORTAC model. It was observed that, at constant concentration of ethanol and variable concentrations of ethylene glycol, with increasing temperature, the k_1 values increase. The results show that formation of ACSM in these ternary mixtures is more favorable than its formation in the related alcohol–water binary mixtures. Analysis of the k_1 and k_2 values shows that, at low concentrations of ethylene glycol, interaction of ethanol and ethylene glycol affects the reaction rate and in high concentrations of ethylene glycol, ethanol acts as a solvent for ethylene glycol molecules. Hydrogen bonding and then hydrophobic interactions between MG^+ and alcohol molecules, result in an increase in the observed reaction rates.

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