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Kinetics and Mechanism of Oxidation of Caffeine by Permanganate ion in Aqueous Sodium Hydroxide Solution

M. K. Triveni [1], S. Bellappa [2], T. Shivalingaswamy [3] and I. Mallikarjuna[4]*

1. Department of Chemistry,Maharaja Institute of Technology-Mysore, **INDIA**
2. Department of Chemistry,GSSSIETW, Mysore, **INDIA**
3. P.G Department of Physics, Govt. College (Autonomous), Mandya, **INDIA**
4. Department of Chemistry, VHD Central institute of Home Science, Bangalore, **INDIA**
Email: mallikarjunahiremath4@gmail.com

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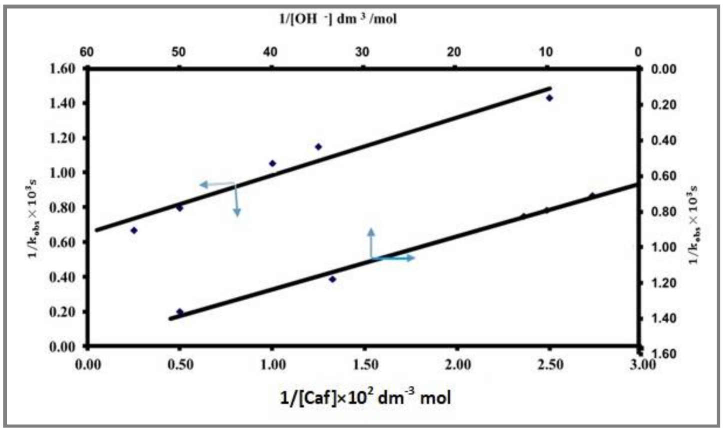
ABSTRACT

The kinetics of the oxidation of Caffeine by permanganate ion in aqueous sodium hydroxide medium was studied at 301K. The reactions followed kinetics with a first-order dependence of rate on permanganate ion and less than unit order dependence on both the alkali and caffeine concentrations. The reaction is catalyzed by OH^- ions. The reaction was studied at different temperatures and activation parameters were evaluated. The reaction constants involved in the mechanism were computed. The observed results have been explained in terms of a mechanism and a relevant rate law has been deduced.

Graphical Abstract



Variation of $1/k_{obs}$ versus 1/[Caf] and Variation of $1/k_{obs}$ versus $1/[OH^-]$

Keywords: Caffeine, Potassium permanganate, Kinetics and alkaline solution.

INTRODUCTION

Caffeine has been the subject of extensive research in recent years [1] inspired by its wide- spread occurrence in nature [2], long history of human consumption - possibly from Stone Age [3] and its overall affirmative effects [4]. A survey of literature reveals that reports [5-7] hardly describe the mechanism of oxidation of caffeine and therefore, no mechanistic information is available to distinguish between the mechanism of direct one-electron reduction to manganese (VI) and a mechanism in which a hypomanganate is formed in a two-electron reduction followed by rapid oxidation of the hypomanganate ion [8]. Against this background, we undertook the present investigation of the kinetics and mechanism of oxidation of caffeine by permanganate ion which is presumed to the most efficient and eco-friendly oxidizing agent in different alkaline media [9-10]. We proposed to investigate the reaction of caffeine in the presence of permanganate ion in alkaline medium and the oxidation mechanism of such drugs and their effect on human metabolism.

MATERIALS AND METHODS

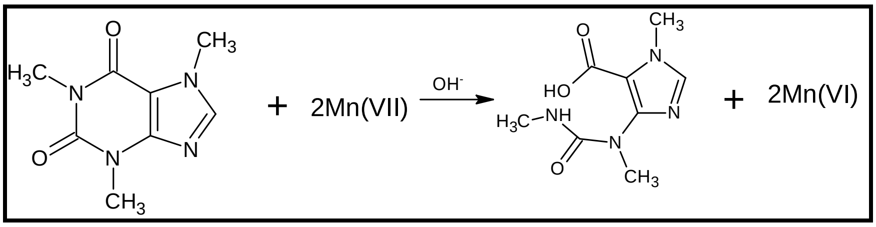
A stock solution of caffeine was prepared by dissolving the appropriate sample amount in doubly distilled H_2O.The solution of potassium permanganate was prepared and standardized against oxalic acid [11]. Carrington and Symons method was followed to prepare Potassium manganate solution [12]. A regression analysis of experimental data was undertaken with computer Core 2 Duo Processor in order to obtain the regression coefficient (r) and the standard deviation (S) of points from the regression line.

Kinetic Procedure: All kinetic measurements were recorded under pseudo - first order conditions with caffeine being at least thirty-fold molar excess over [MnO^-_4] ion at constant ionic strength (1.5 mol dm^{-3}). The reaction was initiated by mixing previously thermostated solutions of MnO^-_4 and caffeine, which also contained the required quantities of NaOH and $NaClO_4$. The temperature was maintained at 28 ± 0.1^0 C. The course of reaction was followed by monitoring the decrease in absorbance of MnO^-_4 in 1 cm quartz cell UV-visible spectrophotometer at its absorption maximum of 545 nm as a function of time. Earlier it was verified that negligible interference occurs from other reagents at this wavelength. The first order rate constants, k_{obs} were evaluated by plots of log [A_t-A_∞] versus time. Where, A_t refers to absorbance at any time t and A_∞ at infinite time, The first order plots in almost all cases were linear to 80% completion of the reaction and k_{obs} values were reproducible within ±10%. During the course of measurements the solution changed from violet to blue and then to green.

The effect of dissolved oxygen on the reaction rate was studied by preparing the mixture and following the reaction in an atmosphere of dinitrogen. No significant differences in results were observed either in the presence of nitrogen or in the presence of air. The effect of carbonate on the reaction was also studied in view of the ubiquitous contamination of basic solutions by carbonate. Addition of carbonate had no effect on the reaction rate. Nevertheless, fresh solutions were used while conducting kinetic experiments as a precautionary step. In view of the modest concentration of alkali used in the reaction medium, attention was also given to the effect of the surface of the reaction vessel on the kinetics. The use of polythene or acrylic ware and quartz or polyacrylate cells gave the same results indicating that the surface does not have any significant effect on the rate.

RESULTS AND DISCUSSION

Stoichiometry and Product Analysis: The reaction mixtures containing an excess of $KMnO_4$ over caffeine, in 1 mol dm^{-3} NaOH at a constant ionic strength of 1.0 mol dm^{-3} were allowed to react for 2 h at 28°C in an inert atmosphere. Acidified by HCl (5%) solution the reaction completes as shown below



The products were obtained when the product analysis was carried under pseudo-first order conditions for caffeine. The main product 4-(1,3-dimethylureido)-1-methyl-1H-imidazole-5-carboxylic acid was identified by spot test and confirmed by NMR analysis. ^{1}H-NMR: δ2.71 (s,3H,urea, N-CH_3), 3.36δ (S,3H,N-CH_3), δ 3.72(S,3H,immid,N-CH_3),δ 6.00(S,1H,NH),δ 7.98 (S,1H,imm.CH), δ 11(Broad,1H,COOH). A test for corresponding acid was positive. Stoichiometry of the reaction under kinetic study is derived as 1:2 in the above equation.

Reaction Order: The reduction of permanganate by caffeine in alkaline medium is with a measurable rate. The reaction orders have been determined from the slopes of log k_{obs} versus log (concentration) plots by varying the concentrations of caffeine and alkali in turn while keeping the others constant.

Effect of [$KMnO_4$]: The oxidant $KMnO_4$ concentration was varied from 0.8 × 10^{-4} to 8.0×10^4 mol dm^{-3} keeping all others conditions constant. Linearity of the plots of log [$KMnO_4$] versus time, for different initial concentrations of $KMnO_4$ indicated that the order in $KMnO_4$ was unity (Fig 1). This fact was also confirmed by varying [$KMnO_4$] which did not show any change in pseudo-first order constants k_{obs} (Table 1).

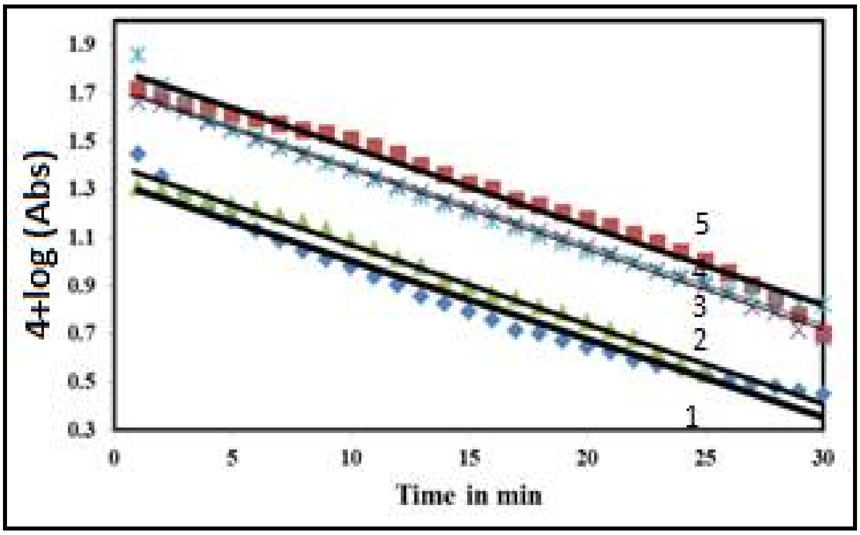


Figure 1. First order plots of oxidation of caffeine by $KMnO_4$ in alkaline medium at 28°C.

Dependence of Caffeine: The caffeine concentration was varied from 4 × 10^{-3} to 40 × 10^{-3} mol dm^{-3} at 28°C, keeping all other reactant concentrations and conditions constant. The rate constant k_{obs} increased with increase in concentration of caffeine indicating a less than unit order dependence on the substrate concentration (Table 1).

Effect of [Alkali]: The alkali concentration was varied in the range of 0.02 to 0.2 mol dm^{-3} at 28°C, keeping all other reactant concentrations and conditions constant (Table 1). The rate constant increases with the increase in [OH^-], the order with respect to [OH^-] and was found to be less than unity.

Table 1. Effect of variation of $KMnO_4$, Caffeine and NaOH on oxidation of caffeine by $KMnO_4$ in aqueous alkaline medium at 28^0C and Constant ionic strength is $1.0moldm^{-3}$.

$[KMnO4]\times10^{-4}$ mol dm^{-3}	$[Caf]\times10^{-3}$mol dm^{-3}	$[OH^-]$ mol dm^{-3}	$k_{obs}\times10^{-3}$
0.8	2	1	1.256
2	2	1	1.260
4	2	1	1.274
6	2	1	1.265
8	2	1	1.270
4	4	1	0.700
4	8	1	0.868
4	10	1	0.956
4	20	1	1.260
4	40	1	1.500
4	2	0.02	0.733
4	2	0.03	0.844
4	2	0.08	1.21
4	2	0.1	1.260
4	2	0.2	1.41

Effect of ionic strength and dielectric constant: The effect of ionic strength was studied by varying the sodium perchlorate concentration from 0.2 to 2.0 mol dm^{-3} at constant concentrations of $KMnO_4$, caffeine and alkali. It was found that the rate constants k_{obs} increased with increase in the concentration of sodium perchlorate. The plot of log k_{obs} versus $\sqrt{I}$ was linear with positive slope as shown in figure 4. The effect of relative permittivity (ε_T) was studied by varying t-butanol-water content in the reaction mixture with all other conditions being maintained constant. The rate constant k_{obs} increased with decrease in the dielectric constant of the medium. The plot of log k_{obs} versus $1/\varepsilon_T$ was linear with a positive slope as shown in figure 4.

Test for free radicals: Possible presence of free radicals in the reaction was examined. The reaction mixture, to which a known quantity of acrylonitrile scavenger had been initially added, was kept for 2 h in an inert atmosphere. After diluting the reaction mixture with methanol no precipitate was formed indicating the absence of free radicals in the reaction.

Effect of temperature: The reaction rate was measured at four different temperatures with varying concentrations of caffeine, alkali and keeping other conditions constant. The rate constant was found to increase with increasing temperature. The values of k_{obs} at different temperatures were calculated by plotting $1/k_{obs}$ v/s $1/[OH^-]$. The data were subjected to least square analysis and were tabulated in table 3 and figure 2. The activation parameters for the reaction were studied by using linear regression analysis [13].

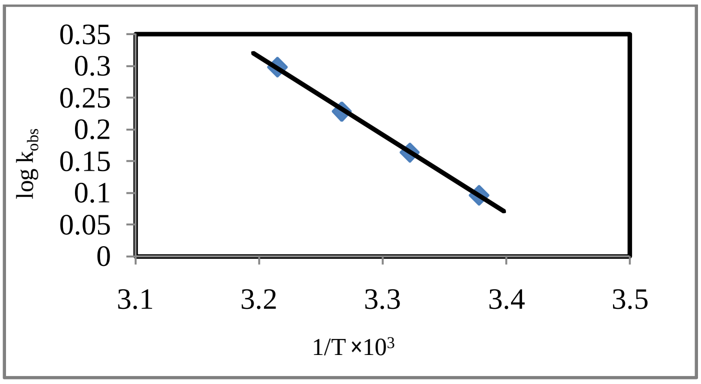
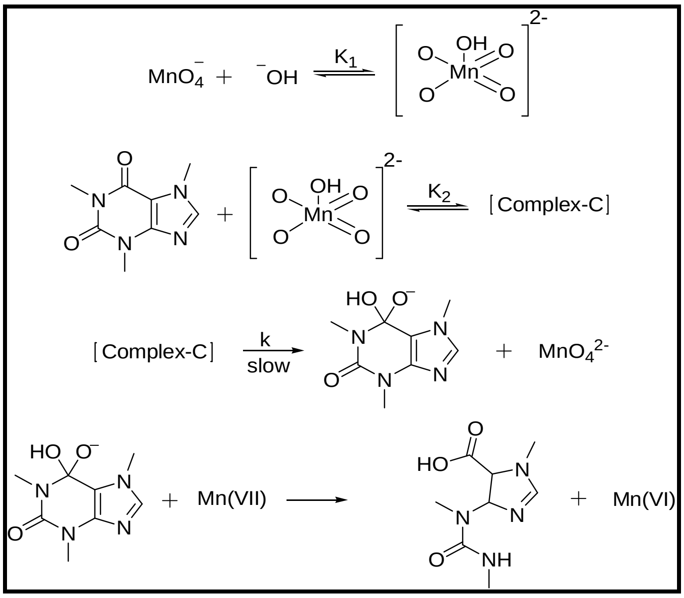


Figure 2. Effect of temperature on the slow step of the mechanism of caffeine by $KMnO_4$ in aqueous alkaline at 28°C.

Permaganate ion is a powerful oxidant in an aqueous alkaline medium. As it exhibits many oxidation states, the stoichiometric results and pH of the reaction media play an important role. Under the prevailing experimental conditions at pH > 12 the reduction product of manganese(VII) is stable and further reduction of manganese(VI) might be stopped [12, 13]. DARSS studies have shown that at pH > 12, the product of manganese (VII) is manganese (VI) and no further reduction was observed as reported by Simandi *et al* [14, 15]. However, on prolonged standing, manganese (VII) is reduced to manganese (VI) under our experimental conditions. The reaction between $KMnO_4$ and caffeine under study in alkaline medium has a 2:1 stoichiometry with a first order dependence on $[KMnO_4]$ and less than unit order dependence on both the $[OH^-]$ and [Caf]. The results suggest that the first alkali combines with $KMnO_4$ to form an alkali-$KMnO_4$ species $[MnO_4\ OH]^{2-}$ in a pre-equilibrium step which explains the less than unit order in alkali. Such type of alkali $KMnO_4$ species is observed in earlier work [16]. Caffeine reacts with MnO_4^{2-} species to form a complex (C). This complex (C) species, initially, passes through slow step while it further reacts with another $[MnO_4\ OH]^{2-}$ species in a fast step to yield products. The experimental results can be accommodated in scheme 1 as given below.



The evidence for complex formation is obtained by kinetic studies (i.e., from the Michaelis-Menten plot). The plot of $1/k_{obs}$ versus 1/[Caf], figure 3 is linear with a non zero intercept. Such type of substrate-oxidant complex formation has been reported previously [17]. This is also proved by spectral evidence with bathochromic shift, λ_{max}, of about 5nm from 273 to 278 nm is observed.

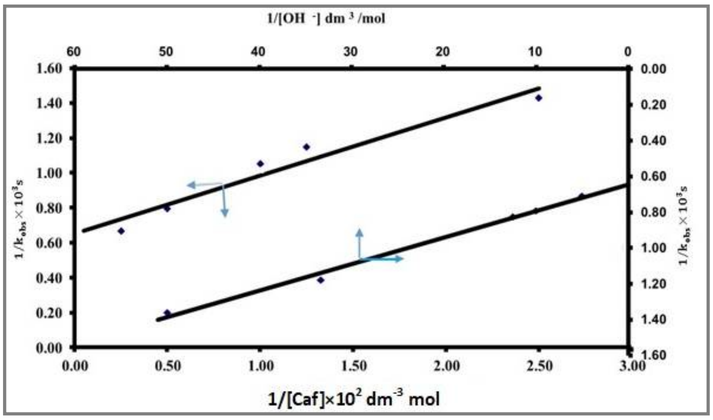


Figure 3. Variation of 1/kobs versus 1/[Caf] and Variation of 1/kobs versus $1/[OH^-]$.

The mechanism is also supported by moderate values of activation parameters (Table 3). A negative value of $\Delta S^{\#}$ suggests that the intermediate complex is more ordered than the reactants. The observed modest enthalpy of activation, relatively low value of the entropy of activation and higher rate constant for the slow step of the mechanism indicate that oxidation presumably occurs by an inner-sphere mechanism. This conclusion is supported by earlier work [18]. The $KMnO_4$ oxidation of caffeine in aqueous alkaline medium takes place at a measurable rate of $1/k_{obs}$ versus $1/[OH^-]$ be linear. From the slopes and intercepts of such plots the values of K_1, K_2 and k, were found to be 4.84 $dm^3\ mol^{-1}$, 56.259 $dm^3\ mol^{-1}$ and $1.260\times 10^3\ dm^3\ mol^{-}s^{-1}$ respectively. Using these values the rate constants under different experimental conditions were calculated by equation (7) (given in appendix) and compared with experimental data (Table 1 and 2). Experimental values and mathematically calculated values agreed reasonably well supporting the assumptions of scheme 1. The value of K_1 is in agreement with earlier work [19].

Table 2. Effect of temperature and calculation of activation parameters

T (K)	1/T (X)	$k_{obs}\times10^{-3}\ s^{-1}$	$Logk_{obs}$
296	0.003378	1.249	0.0965
301	0.003322	1.459	0.164
306	0.003268	1.693	0.2286
311	0.003215	1.989	0.2986

$[KMnO_4]= 4\times10^{-4}$ mol dm^{-3}; $[OH^-]= 1$ mol dm^{-3};
$[Caf]= 2\times10^{-2}$ mol dm^{-3} ;$[NaClO_4]= 1.5$ mol dm^{-3}

Table 3. Thermodynamic parameters

Parameters	Ea (kJ mol^{-1})	Log A	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ ($JK^{-1}\ mol^{-1}$)	$\Delta G^{\#}$ (kJ mol^{-1})
Values	23.602	0.2009	21.079	-59.584	39.161

The effect of increasing ionic strength on the rate qualitatively explains the reaction between two negatively charged ions as seen in scheme 1. The effect of solvent on the reaction rate is described [18]. A plot of log k_{obs} versus $1/\varepsilon_T$ gives a straight line with negative slope for a reaction between negative ions and a neutral molecule where as positive slope results for a positive ion and neutral molecule. In our present study, the plot of log k_{obs} versus $1/\ \varepsilon_T$ was linear with a positive slope as shown in figure 4, which is in accordance the involvement of negative ion as given scheme 1.

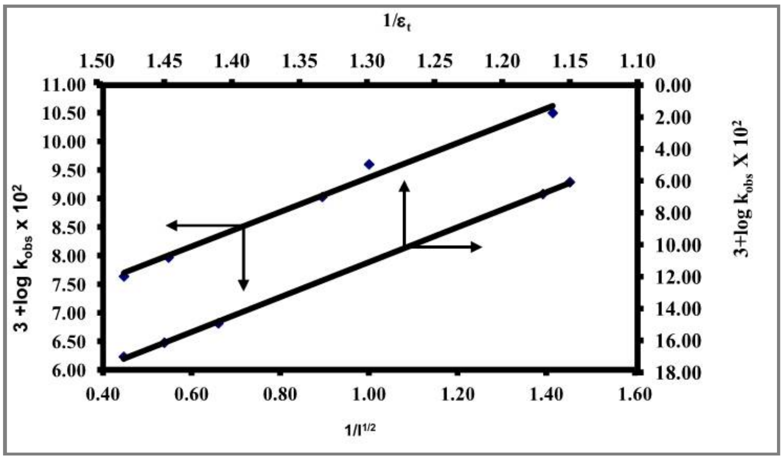


Figure 4. Effect of ionic strength and dielectric constant on the $KMnO_4$ oxidation of caffeine in aqueous alkaline medium.

Scheme 1 leads to the rate law as follows,

$$\text{Rate} = \frac{d[\text{MnO}_4^-]}{dt} = k[\text{C}][(\text{MnO}_4)(\text{OH})]^{2-}$$

$$= kK_2[\text{Caf}]_f K_1[\text{OH}^-]_f[\text{MnO}_4^-]_f$$

$$= kK_1K_2[\text{Caf}]_f[\text{OH}^-]_f[\text{MnO}_4^-]_f \qquad (1)$$

The total [MnO $_4^-$] is given by,(where t and f stands for total and free)

$$[\text{MnO}_4^-]_t = [\text{MnO}_4^-]_f + [\text{MnO}_4^-]_f[\text{OH}^-]_f$$

$$= [\text{MnO}_4^-]_f + K_1[\text{MnO}_4^-]_f[\text{OH}^-]_f$$

$$[\text{MnO}_4^-]_t = [\text{MnO}_4^-]_f\{1 + K_1[\text{OH}^-]_f\}$$

Therefore

$$[\text{MnO}_4^-]_f = \frac{[\text{MnO}_4^-]_t}{1+K_1[\text{OH}^-]_f} \qquad (2)$$

Similarly,

$$[\text{Caf}]_t = [\text{Caf}]_f + [\text{C}]$$

$$= [\text{Caf}]_f + K_2\,[\text{Caf}]_f$$

$$= [\text{Caf}]_f\ \{1 + K_2\} \qquad (3)$$

and

$$[\text{Caf}]_f = \frac{[\text{Caf}]_t}{1 + K_2}$$

Similarly,

$$[\text{OH}^-]_t = [\text{OH}^-]_f + [\text{MnO}_4.\text{OH}]^{2-}$$

$$= [\text{OH}^-]_f + K_1[\text{OH}^-]_f[\text{MnO}_4^-]_f$$

$$= [\text{OH}^-]_f\{1 + K_1[\text{MnO}_4^-]_f\}$$

Therefore,

$$[\text{OH}^-]_f = \frac{[\text{OH}^-]_t}{1+K_1[\text{MnO}_4^-]_f} \qquad (4)$$

Substituting equations (2), (3) and (4) in equation (1), we get

$$\text{Rate} = \frac{kK_1K_2\,[\text{Caf}]_t[\text{OH}^-]_t[\text{MnO}_4^-]_t}{(1 + K_1[\text{OH}^-] + K_1K_2[\text{OH}^-][\text{Caf}])}$$

$$\text{C} = \frac{1}{\{(1+K_1K_2[\text{MnO}_4^-][\text{OH}^-])(1+K_1[\text{MnO}_4^-]+K_1K_2[\text{MnO}_4^-][\text{Caf}])\}} \qquad (5)$$

The terms $(1 + K_1K_2[\text{MnO}_4^-][\text{OH}^-])$ and $(1 + K_1[\text{MnO}_4^-] + K_1K_2[\text{MnO}_4^-][\text{Caf}])$ in the denominator of equation (5) can be approximated to unity in view of low concentration of MnO_4^- used.
Therefore equation (5) becomes (omitting t and f subscripts)

$$k_{obs} = \frac{\text{Rate}}{\text{MnO}_4^-} = \frac{kK_1K_2\,[\text{Caf}][\text{OH}^-]}{(1+K_1[\text{OH}^-]+K_1K_2[\text{OH}^-][\text{Caf}])} \qquad (6)$$

Equation (6) can be rearranged to the following form, which is suitable for the verification of the rate law:

$$\frac{1}{k_{obs}} = \frac{1}{kK_1K_2\,[Caf][OH^-]} + \frac{1}{kK_2\,[Caf]} + \frac{1}{kK_2\,[OH^-]} + \frac{1}{k} \qquad (7)$$

APPLICATION

The results have been explained in terms of a mechanism and a relevant rate law has been deduced. Rate constants of slow step and other equilibrium constants involved in the mechanism were evaluated and activation parameters with respect to slow step of the reaction were computed.

CONCLUSION

The kinetic data for the oxidation of caffeine by permanganate ion has been carried out in alkaline medium (NaOH). Order with respect to all the reactants was found out and the effect of ionic strength, dielectric constant and temperature on the rate of the reaction was computed. Other thermodynamic parameters were also studied. Rate constants of slow step and other equilibrium constants involved in the mechanism were evaluated and activation parameters with respect to slow step of the reaction were computed.

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