Micellar Catalytic Oxidation of Ascorbic Acid by Potassium Dichromate

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Abstract

The kinetic oxidation of ascorbic acid; vitamin C; (H_3As) by Potassium dichromate ($Cr_2O_7^{2-}$) has been investigated spectrophotometrically at λ = 360 nm in aqueous and in the presence of 10 mM of both an anionic surfactant sodium dioctylsulfosuccinate (AOT) and cationic surfactant cetyltrimethylammonium bromide (CTAB) at pH = 8 and temperature = 25°C. The reaction followed first-order kinetics with respect to [H_3As] and [$Cr_2O_7^{2-}$]. The k_{obs} values are found to be independent on pH values lower than pH = 6 and higher than pH = 9. Increased cationic CTAB concentration found to increase k_{obs} values whereas those of AOT decrease the k_{obs} values. The effect of added anions, such as chloride, bromide, and iodide has been studied and discussed. The activation parameters ΔH and ΔS* were also evaluated.*

Keywords: Oxidation, H_3As, $Cr_2O_7^{2-}$, pH, Micelles.

Introduction

Surfactants are considered as antibacterial compounds. They are useful because they form aggregated structures called micelles. They are used as environmental cleaning products. The application of surfactants is increasing in many fields such as cosmetic formulations and pharmaceuticals paint. The interesting properties of surfactants find enormous applications in material science, biology, chemistry, engineering, photochemical, photobiological, conversion of solar energy and other fields[1]. These molecules of such materials possess hydrophobic (non polar) and hydrophilic (polar) segments[2]. Surfactant and its micelle has the effect of creating of nonpolar regions in a total structure stable in polar aqueous solution. Because of nonpolar regions of micelles are able to solubilize nonpolar organic materials, solution of surfactants are able to dissolve materials that remain insoluble in pure water. The effects of surfactants and its micelle become the focus of research for chemists and biologests[3]. A large number of reports are available on the capability of micellar solutions and colloids to affect equilibria, the rate of the reactions, concentration or depletion of the reactants in the interfacial region[4-8].

Micellar solutions and colloids can form a simple system in which one can control chemical reactivity and equilibria in solution[9]. Micellar solutions play an important effect on chemical reactivity of the reactions; they can inhibit or catalyze the reactions by keeping the reactants apart or concentrating them at the colloid surfaces depending on ionic strength, temperature, pH , the chemical system, the kind of surfactant used and other factors[9]. Potassium dichromate is an important oxidizing agent in many inorganic and organic redox reactions. Different suggested mechanisms for different organic substrates by various authors are not similar, showing that a variety of mechanisms are possible[10].

Ascorbic acid which is an effective reducing agent belongs to endiol group and has two alcoholic groups with acidic character. It can be quantitatively and reversibly oxidized by different oxidizing agent in aqueous solutions. Ascorbic acid oxidation is very sensitive to the pH reaction media[11]. Its oxidation products in acidic solution by different oxidizing agent leads to the formation of dehydroascorbic acid, which can hydrolyze to form free carboxylic group[12]. The oxidation of ascorbic acid at different pH values (acidic/ basic), with a variety of oxidizing agents organic and inorganic[13.] have been reported. However, the reduction of organic dye stuff with ascorbic acid is rarely reported[14].

In this paper we present a study of the kinetics and the mechanism involved in the H_3As oxidation by $Cr_2O_7^{2-}$ in different micellar medium.

Material and Methods

Ascorbic acid (H_3As) and potassium dichromate, ($K_2Cr_2O_7$) BDH England. $K_2Cr_2O_7$ was finely ground and dried at 110°C. Cetyltrimethylammonium bromide (CTAB) was 99% pure from Fairlawn, NJ, USA and sodium dioctylsulfosuccinate (AOT) from Fluka Chemical Co. Switzerland were used as supplied. Water used to prepare the solutions was distilled twice. All other chemicals were used as provided.

A proper concentration of $Cr_2O_7^{2-}$ was taken from a freshly pre-prepared stock solution and was put in glass tube (A). Required volume of H_3As reagent mixture at pH = 8.0 aqueous medium or a required volume of H_3As + surfactant (AOT or CTAB) at pH = 8.0 micellar medium was put in another glass tube (B).

In order to make the total volume of the reaction mixtures in all experimental runs identical (10 mL) a measured quantity of distilled water was added to tube B. To attain thermal equilibrium both tubes (A) and (B) were thermostated at the desired temperature for 20 minutes pre mixing. To work under pseudo-first-order conditions the H_3As concentration was in large excess over $Cr_2O_7^{2-}$ concentration. As soon as tube B was added to tube A the time of the reaction was recorded by using stop watch. This procedure has been followed all through the experimental runs.

Kinetics and Instruments: The reaction rates of the reactants H_3As and $Cr_2O_7^{2-}$ in basic aqueous or micellar solutions were studied spectrophotometrically by monitoring the color fading of $Cr_2O_7^{2-}$ against time at 360 nm and 25.0 ^oC ± 0.1 ^oC using a Shimadzu-1601 UV–VIS spectrophotometer. All experimental runs were performed at pH = 8.0 .

pH values of solutions were adjusted using a microprocessor combined pH-meter and thermometer, model pH 211 by Hanna instruments.

The critical micelle concentration (CMC) values of the surfactants were measured conductometrically at 25^oC. The instrument employed is Hanna conductometer using a dip-type cell made of platinum black. The duplicate measurements were reproducible to ± 3%. CMC was identified as the break point in a plot of the measured specific conductivity against surfactant concentration[15-17]. The values obtained were in the vicinity of 0.85 mM, and 6.5 mM , for CTAB, and AOT respectively,
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which are considerably in consistent with the reported values of 0.90 Mm and 7.0 mM in water at 25^oC for previous surfactants respectively[18].

Results and Discussion

Effect of $[H_3As]$ **and** $[Cr_2O_7^{2-}]$ **on the reaction rate:** Rates of kinetic oxidation of *H_3As* by $Cr_2O_7^{2-}$ in aqueous basic media or micellar solutions was followed with respect to time under the experimental conditions. As shown in figure 1, the reduction follows a pseudo- first order model; where the natural logarithm of (C_o/C) has a straight line relation with time. Also the kinetics of oxidation of H_3As by $Cr_2O_7^{2-}$ was investigated in water and in 10 mM surfactant (AOT or CTAB) at different pH values and at 25^oC.

Observed rate constants (k_{obs}) were not affected on pH values lower than pH = 6 and higher than pH = 9 as shown in figure 2. Therefore, in the present experimental conditions the basic medium indicates that ascorbate (As$^-$) ion is considered as a reducing agent. The reducing property of the ascorbate (As$^-$) has been reported earlier for other processes[19]. The basic medium shifts the reaction in equation 1 to the right by decreasing H$^+$ concentration and makes the ascorbic acid in its anionic form (As$^-$).

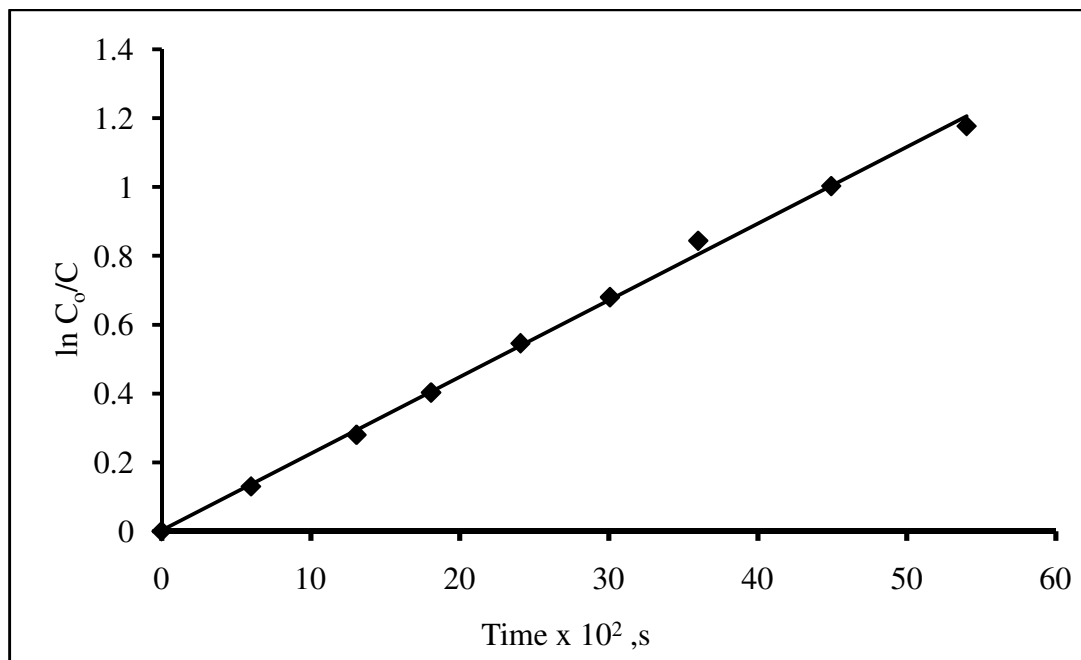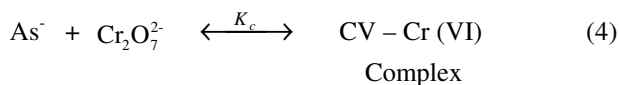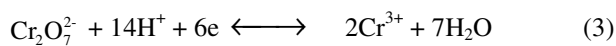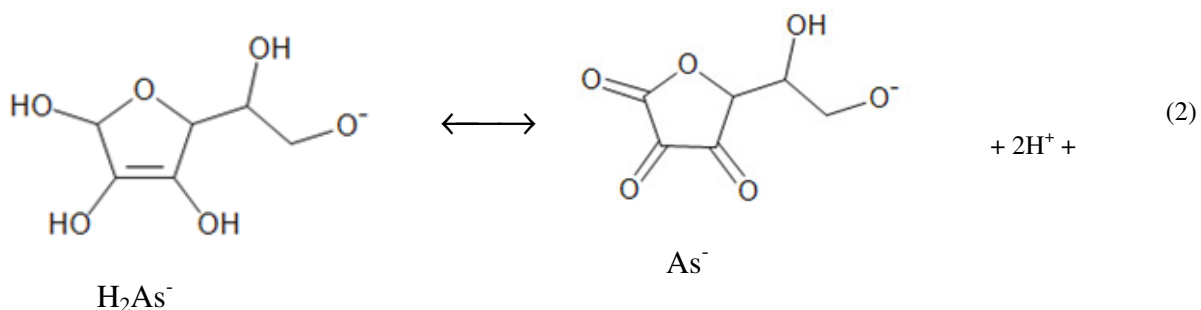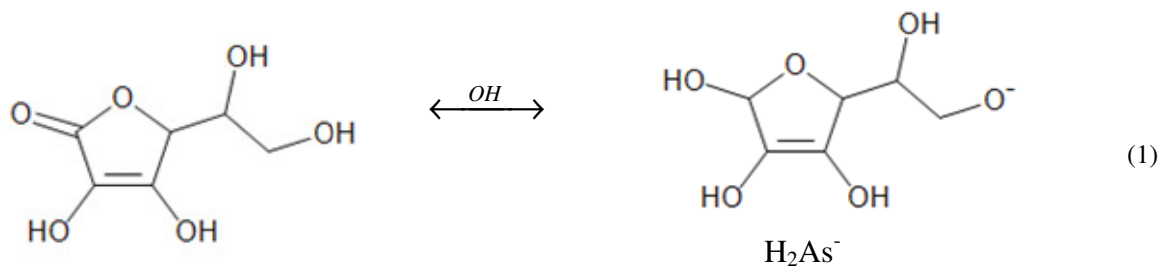The reduction of $Cr_2O_7^{2-}$ by As$^-$ can be followed by the following equations.

Figure-1
The relation between ln C^o /C vs. time to verify pseudo first order kinetics of H$_3$As/ $Cr_2O_7^{2-}$ reaction at 25^oC.

$$(1)$$

$$\text{H}_2\text{As}^-$$

$$(2)$$

$$+ 2\text{H}^+ +$$

$$\text{As}^-$$

$$\text{H}_2\text{As}^-$$

$$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e} \longleftrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \qquad (3)$$

$$\text{As}^- + \text{Cr}_2\text{O}_7^{2-} \xleftrightarrow{K_c} \text{CV} - \text{Cr (VI)} \qquad (4)$$
$$\text{Complex}$$

$$-\frac{d[\text{Cr}_2\text{O}_7^{2-}]}{dt} = k[\text{Cr}_2\text{O}_7^{2-}][\text{As}^-] \qquad (5)$$

As H_3As in excess

$$-\frac{d[\text{Cr}_2\text{O}_7^{2-}]}{dt} = k_{obs}[\text{Cr}_2\text{O}_7^{2-}] \qquad (6)$$
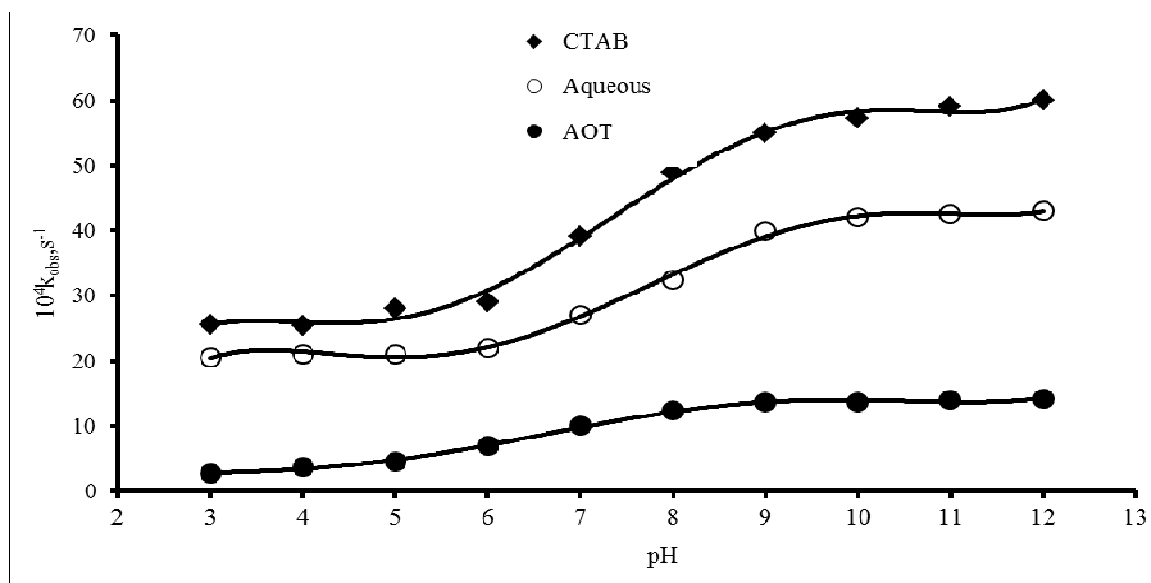
With $k_{obs} = k\,[\text{As}^-]$

Figure-2

Effect of variation of pH values on k_{obs} for $\text{H}_3\text{As}\,/\,\text{Cr}_2\text{O}_7^{2-}$ reaction in the aqueous and in 10 mM surfactant at 25$^\text{o}$C. [H$_3$As] = 0.6 mM, [$\text{Cr}_2\text{O}_7^{2-}$]= 0.1 mM,

Table 1 shows the effect of variation of reactants concentrations on the values of observed rate constant (k_{obs}). No significant change on k_{obs} values have been seen by changing the concentration of $Cr_2O_7^{2-}$ from 0.03 mM to 0.2 mM. This indicate a first order reaction with respect to $Cr_2O_7^{2-}$. Figure 3 shows the effect of variation of the ascorbic acid (H_3As) concentrations from 0.4 to 1.6 mM on observed rate constant. The data show that the rate constant (k_{obs}) increases linearly with increase of H_3As concentrations in aqueous and in 10 mM surfactant, indicating the reaction was first order in H_3As concentration in aqueous and micellar media as well. As a result of this behavior one can also suggests that the oxidation reduction reaction of H_3As and $Cr_2O_7^{2-}$ in surfactant concentration range from 1 to 50 mM, that the micellar surface area is still unsaturated with H_3As molecules.

Micellar catalysis: Rate of oxidation of H_3As by $Cr_2O_7^{2-}$ has been examined in the presence of two types of surfactants: anionic surfactant (AOT) and cationic surfactant (CTAB). It was found that the extent of H_3As oxidation vary in both surfactants anionic and cationic ones.

Table-1
Effect of [H_3As] and [$Cr_2O_7^{2-}$] on k_{obs} for H_3As / $Cr_2O_7^{2-}$
reaction in aqueous and in 10 mM surfactant and pH = 8.0 at 25°C

[$Cr_2O_7^{2-}$] (mM)	[H_3As] (mM)	$10^2 k_{obs}$ (s^{-1})		
		CTAB	**Aqueous**	**AOT**
0.03	0.60	47.7	31.3	10.6
0.05	0.60	48.0	31.7	10.8
0.08	0.60	48.5	32.0	11.1
0.10	0.60	49.0	32.4	11.4
0.13	0.60	49.3	32.6	11.7
0.15	0.60	49.8	32.9	11.8
0.20	0.60	50.2	3.0	12.0
0.10	0.40	30.6	19.3	6.90
0.10	0.50	38.3	26.8	10.0
0.10	0.60	49.0	32.4	11.7
0.10	0.80	70.0	49.8	16.0
0.10	1.00	92.0	59.8	20.2
0.10	1.20	110	83.5	23
0.10	1.40	150	97.2	30.
0.10	1.60	180	116	33.7

The oxidation was instantaneous in CTAB, slower in AOT i.e., rate$_{CTAB}$ >> rate$_{H2O}$ > rate$_{AOT}$. Figure 4 shows the effect of changing surfactant concentration on the observed rate constant (k_{obs}, s^{-1}) for the oxidation H_3As by $Cr_2O_7^{2-}$.

The oxidation of H_3As by $Cr_2O_7^{2-}$ can be discussed in terms of encounter probability[20-21] and the fractal nature of the micelle surface[22]. The type of the charges carried out by each reactant and micelle, played an important role of the nature of interaction between them[23,24-26]. Many organic and inorganic compounds bind to the micellar surfaces due to their interactions which might be electrostatic and/or hydrophobic[27]. In this case the rate of the reaction in the anionic micelle is expected to be the highest. However, it is found more significant increase on the reaction rate in the cationic micelles. This is due to the columbic attraction between the cationic micelles and the anions As$^-$ and $Cr_2O_7^{2-}$ where all possible types of interactions, electrostatic and hydrophobic are available. Whereas, in an anionic micellar medium because of charge similarities of the reacting species As$^-$ and $Cr_2O_7^{2-}$ with the anionic micelle, reacting ions are excluded from the surface of the anionic micelles, which lead to inhibit the collision between the reactants in the charged anionic micelle and cause the reaction rate to decrease to a considerable extent. So, the reaction rate took the following order: rate$_{CTAB}$ > rate$_{H2O}$ > rate$_{AOT.}$

Effect of temperature on the reaction rate: The rate constants oxidation of H_3As by $Cr_2O_7^{2-}$ in presence of different surfactants micelles were determined at different temperatures (10.0-40.0°C). It is shown in figure 5 the plot of (ln k_{obs}) against (1/T) which is linear and fit Eyring equation:[27-29]

The activation parameters ΔH* and ΔS* were evaluated by Eyring equation:

$$k_{obs} = \frac{k_B T}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT} \qquad (7)$$

Where R is the universal gas constant (= 8.314 J mol^{-1} K^{-1}), k_B is the Boltzman constant and h is Plank's constant. The values of ΔS* and ΔH*, were estimated from the result using a nonlinear squares method[28-30] and are tabulated in table 2.

These results indicated that values of ΔH* increase in the order AOT > aqueous > CTAB , which also accompanied with less negative ΔS* values. This signify that the negatively charged AOT micelles are not friendly with similar charge reactants As$^-$ and $Cr_2O_7^{2-}$. Thus, it will lead to repel both reactants to be adsorbed to AOT micelles. While negative charged reactants were adsorbed to positively charged CTAB micelles. So this makes high stabilization condition of the transition state[31].

Effect of additive salts: Effect of electrolytes such as KCl, KBr and KI on the reaction rate were also examined. Added salts in micellar system acquire a special place due to their ability to motivate structural changes which may, in turn , alter the substrate-surfactant interactions[32]. Inhibition effect of added electrolytes in the micellar catalysis is known phenomenon. The inhibition has been explained in terms of the competition of the counter ion with an ionic reactant species (e.g., OH$^-$, H_3O^+ , X$^-$)[33-34] for a site on the micelle. The larger the counter ion size greater is inhibition effect[35-37]. The repulsion of negatively charged AOT micelles with counter ions of salts , Cl$^-$, Br$^-$ and I$^-$

as well as the reacting species, As^-, $Cr_2O_7^{2-}$, cause the rate of reaction be diminishes according to sequence of lager ions as I^- > Br^- > Cl^-. But in cationic CTAB micelles, there is a competition of these ions with the ionic reactants for a site on the micelle as well as induce the micellar structure change. But

due to polarizability trend of these ions as I^- > Br^- > Cl^-, which may interact with the hydrophobic part of CTAB micelles. Sot this behavior may increases the rate of the reaction slightly as shown in figure 6.
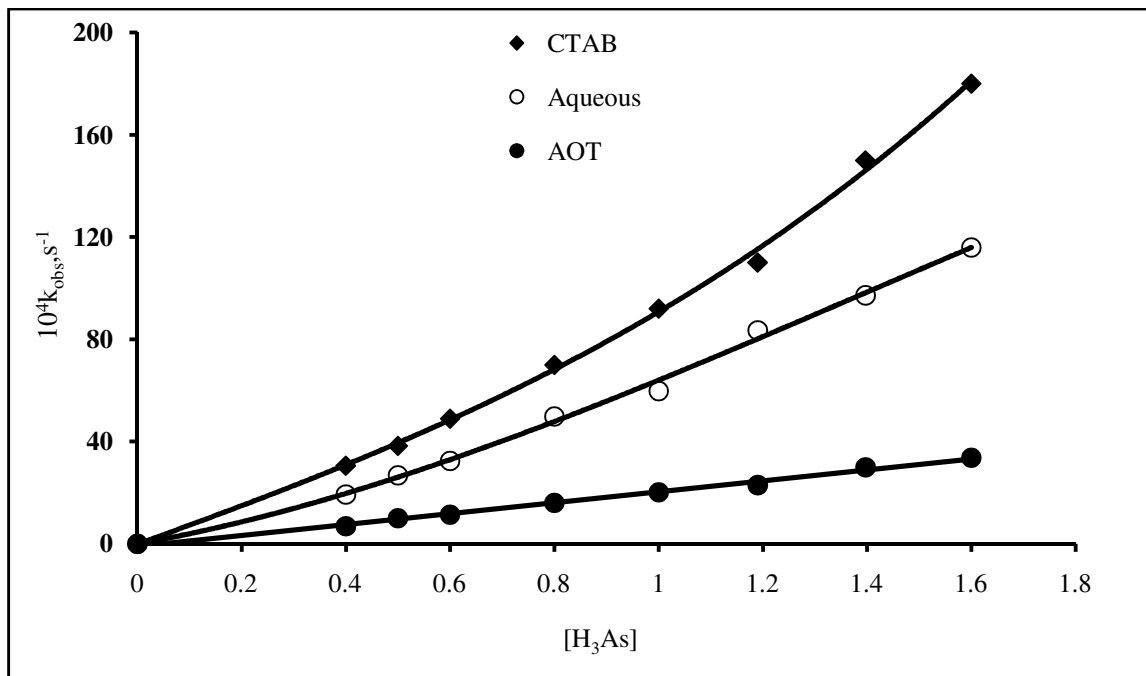

Figure-3
Effect of [H$_3$As] on k$_{obs}$ for H$_3$As /$Cr_2O_7^{2-}$ reaction in aqueous and in 10 mM surfactant at 25°C, [$Cr_2O_7^{2-}$]= 0.1 mM , pH = 8.0
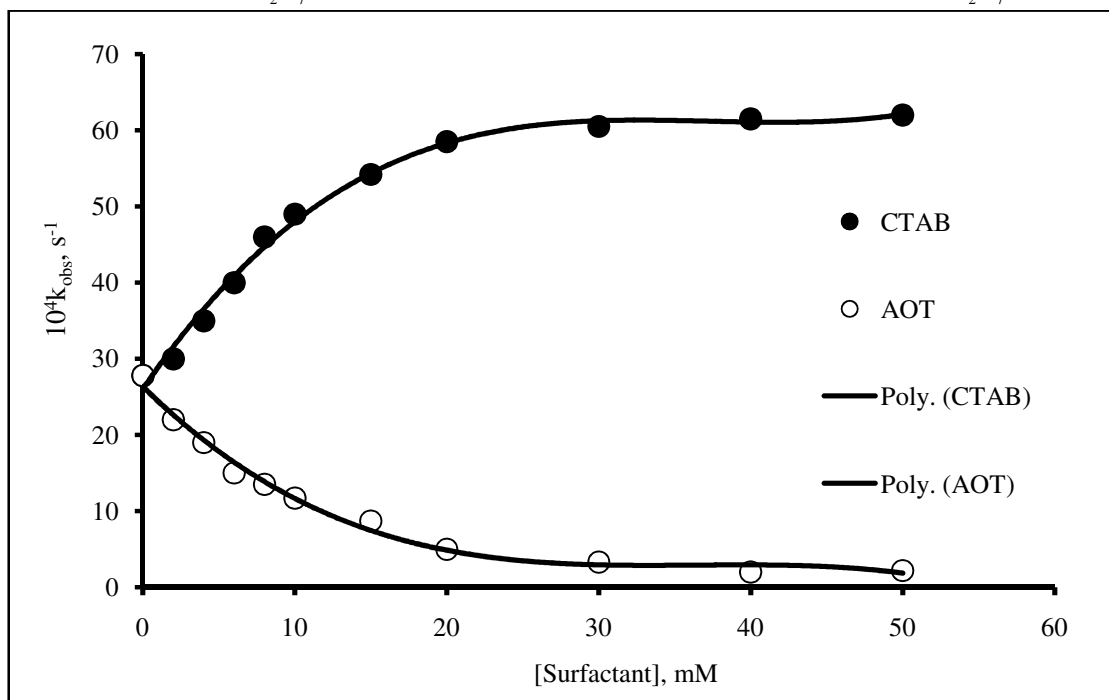
Figure-4
Effect of [surfactant] on k$_{obs}$ for H$_3$As /$Cr_2O_7^{2-}$ reaction at 25°C. [H$_3$As] = 0.6 mM, [$Cr_2O_7^{2-}$] = 0.1 mM, and pH = 8.0
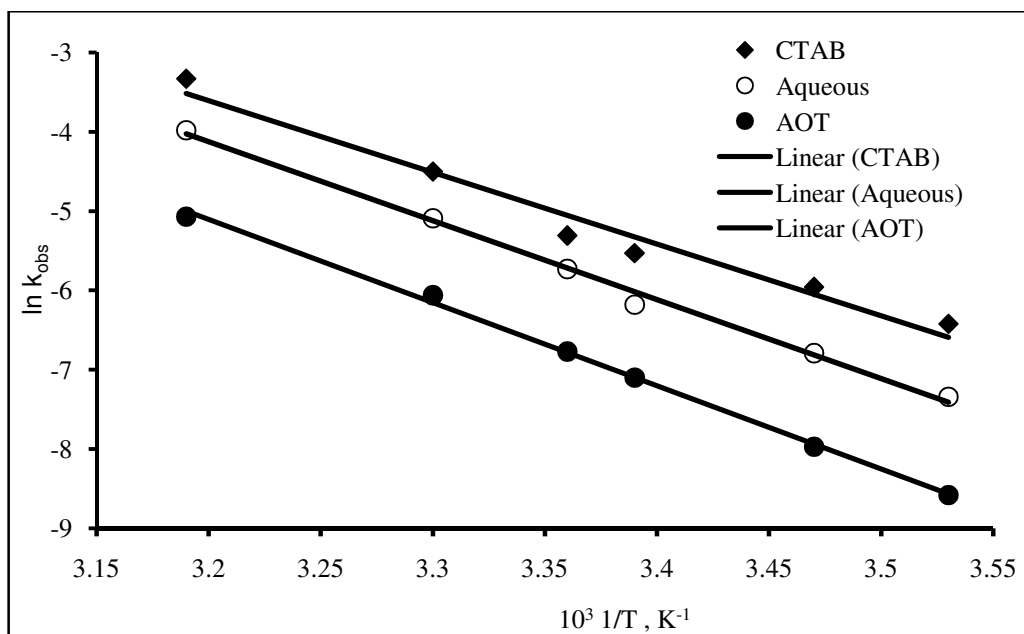
Figure-5
Plot of ln k_{obs} against 1/T for H_3As / $Cr_2O_7^{2-}$ reaction [H_3As] = 0.6 mM, [$Cr_2O_7^{2-}$] = 0.1 mM and pH = 8.0

Table-2
Activation parameters for H_3As / $Cr_2O_7^{2-}$ reaction in the aqueous and in the presence of 10 mM surfactant and pH = 8.0 at different temperatures

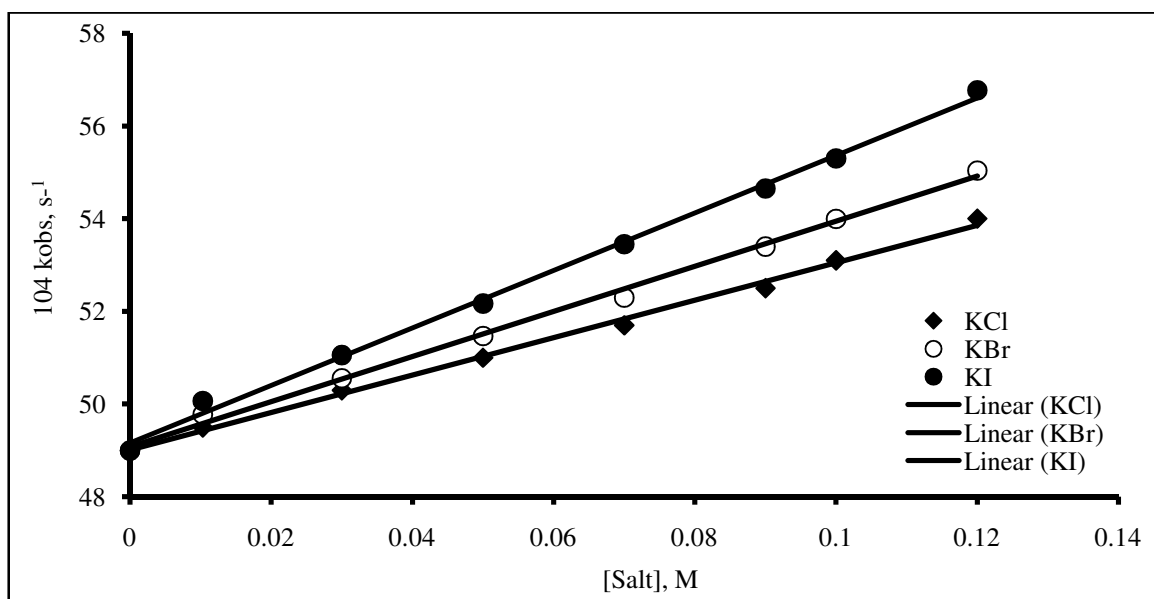| Reaction medium	Activation parameters	
	ΔH^* (kJmol^{-1})	ΔS^* (Jmol^{-1}K^{-1})
CTAB	75.01	-34.41
Aqueous	82.62	-14.38
AOT	87.02	-8.50

Figure-6
Effect of [salts] on k_{obs} for H_3As / $Cr_2O_7^{2-}$ reaction at 25°C. [H_3As] = 0.6 mM, [$Cr_2O_7^{2-}$] = 0.1 mM, [CTAB] = 10 mM and pH = 8.0

Conclusion

The kinetic oxidation of ascorbic acid; vitamin C; (H_3As) by Potassium dichromate ($Cr_2O_7^{2-}$) has been investigated   in aqueous and in the presence of an anionic surfactant sodium dioctylsulfosuccinate (AOT) and cationic surfactant cetyltrimethylammonium bromide (CTAB) at pH = 8 and temperature = 25^oC. The reaction followed the first-order kinetics with respect to [H_3As] and [$Cr_2O_7^{2-}$].

The rate constants, k_{obs}, were found to be independent on pH values lower than pH = 6 and higher than pH = 9. The basic medium indicates that the ascorbate ion (As$^-$) is responsible for the reduction of $Cr_2O_7^{2-}$ in the present experimental conditions. It is found a significant increase on the reaction rate in the presence of cationic micelles. But, in an anionic micellar medium the rate of the reaction decreased to a considerable extent due to charge similarties of the reacting species As$^-$ and $Cr_2O_7^{2-}$ with the anionic micelles.

Added salt inhibit the micellar catalysis. The larger the counter ion size the greater is the inhibition effect. But in cationic CTAB micelles a slight increase in the reaction rate have been observed.

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