Removal of hexavalent chromium by an aromatic alcohol

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ABSTRACT

Cr(VI) is a widespread environmental contaminant and a known human carcinogen. Biosorption is a very common method to remove toxic Cr(VI) from industrial waste water. In biosorption Cr(VI) is reduced to less toxic Cr(III) and adsorbed in biosorbent as Cr(III). Effective biosorbents contain hydroxy groups; it may be aliphatic or aromatic. Kinetics of reduction of Cr(VI) by an aromatic alcohol, benzyl alcohol, (which is an important volatile component of flowers of some night blooming plants) in micellar media have been studied spectrophotometrically. Micellar media is a probe to establish the mechanistic paths of reduction of Cr(VI) to Cr(III). Effects of electrolytes are studied to support the proposed reaction mechanism. Suitable surfactant & suitable concentration of electrolyte enhance the biosorption property.

Keywords: Biosorption; Carcinogen; Kinetics; Chromium (VI); Benzyl Alcohol; Non Functional Surfactants; Salt Effect
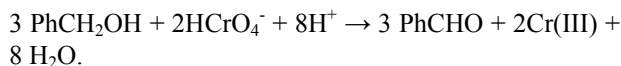
1. INTRODUCTION

Chromate [Cr(VI)] compounds are widely used in industry. Large amounts of toxic Cr(VI) are annually reintroduced into the environment through the discharge of chromium-containing industrial waste [1-4]. In the last few decades, the amount of chromium in aquatic and terrestrial eco-systems has increased a consequence of different human activities. Chromium is the new entry, after lead, cadmium and mercury in the major toxic metal series. In the Hinkley (a small desert town in San Bernardino Country, USA) case hexavalent chromium was used by Pacific Gas and Electric Company (PG & E) in cooling systems to prevent pipes from rusting. The runoff of hexavalent chromium contaminated water on the PG & E property, seeped into the ground and contaminated local water supplies. PG & E was required to compensate the plaintiffs $ 333 million, clean up the hexavalent chromium contamination, and stop using hexavalent chromium in their operation this is the highest amount of compensation in metal toxicity history. Various methods used for removal of Cr (VI) ions include chemical reduction and precipitation, reverse osmosis, ion exchange and adsorption on activated carbon or similar material [5]. But all these methods suffer from severe constraints, such as incomplete metal removal, high reagent or energy requirements, generation of toxic sludge or other waste products that require safe disposal. Some of the treatment methods involve high operating and maintenance cost. The high cost of the chemical reagents and the problems of secondary pollution also make the above physico-chemical methods rather limited in application. There is, therefore, a need for some alternative technique, which is efficient and cost-effective. The process of heavy metal removal by biological mate- rials is known as biosorption and the biological materials used are called biosorbents. Various biosorbents like bacteria, fungi, yeasts, agricultural by products, industrial wastes, etc have been used for biosorption. In this regard, considerable attention has been focused in recent years upon the field of biosorption for the removal of heavy metal ions from aqueous solutions [6]. Recently it is established that for chromium (VI) biosorption, chromium (VI) is first reduced to chromium (III) and then it is adsorbed as chromium (III) in the biosorbent [7]. Understanding of mechanism of chromium (VI) reduction to chromium (III) by some alcohol is important in this context. In this respect benzyl alcohol is ideal one. Benzyl alcohol is a volatile component of flower of a night blooming plant *Gaura drummondii* [8] and strawberry leaves [9]. The present investigations have been carried out in micro-heterogeneous systems to substantiate the proposed reaction mechanism as we carried out for other systems [10-17]. Effects of electrolytes are studied to support the proposed reaction mechanism.

2. THEORETICAL

It is expected that the reduction of Cr(VI) by benzyl al-

cohol in aqueous surfactant media is proceed through normal oxidation mechanism by chromate ester. Benzyl alcohol is oxidized to benzaldehyde and Cr(VI) is reduced to Cr(IV). The over-all reaction can be written as:

$$3\ PhCH_2OH + 2HCrO_4^- + 8H^+ \rightarrow 3\ PhCHO + 2Cr(III) + 8\ H_2O.$$

3. EXPERIMENTAL

3.1. Table for Materials and Reagents
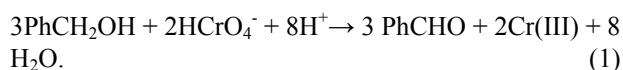
The materials and reagents are shown in **Table 1**.

3.2. Procedure and Kinetic Measurements

Under the kinetic conditions, solutions of the oxidant and mixtures containing the known quantities of the substrate(s) (*i.e*, benzyl alcohol) (under the conditions $[S]_T \gg [Cr(VI)]_T$), acid and the other necessary chemi- cals were separately thermostated ($\pm 0.1 ℃$). The reaction was initiated by mixing the requisite amounts of the oxidant with the reaction mixture. It is assumed that zero time was taken when half of the required volume of the oxidant solution had been added. The progress of the reaction was followed by monitoring the decay of oxidant [Cr(VI)] at 415 nm at different time intervals (2 minutes) with a UV-VIS spectrophotometer [UV-2450 (SHIMA-DZU)]. Quartz cuvettes of path length 1cm were used. The observed pseudo-first-order rate con- stants $[k_{obs}(s^{-1})]$ were determined from the linear part of the plots of $\ln(A_{415})$ versus time(t). Reproducible results giving first-order plots (co-relation co-efficient, $R^2 \geq 0.998$) were obtained for each reaction run. A large ex- cess ($\geq$ 15-fold) of reductant was used in all kinetic runs. No interference due to other species at 415 nm was verified. Under the experimental conditions, the possibility of decomposition of the surfactants by Cr(VI) was inves-

Table 1. Materials and reagents.

Materials	Brand
1. Benzyl alcohol	AR, Merck, India
2. $K_2Cr_2O_7$	AR, BDH, India
3. N-cetylpyridinium chloride (CPC)	AR, SRL, India
4. Sodium dodecylsulphate (SDS)	AR, SRL, India
5. TX-100	AR, SRL, India
6. NaCl	AR, Merck, India
7. NH_4Cl	AR, Ranbaxy, India

tigated and the rate of decomposition in this path was found to be kinetically negligible.

3.3. Product Analysis and Stoichiometry

Under the kinetic condition benzyl alcohol is oxidized to benzaldehyde and estimation of the reaction products was carried by gravimetrically as 2, 4-dinitrophenyl hydrazone [18]. In a typical experimental set, 10ml of 0.06 mol dm^{-3} Cr(VI) in 1.0 mol dm^{-3} H_2SO_4 was added to 40 ml of 0.2 mol dm^{-3} benzyl alcohol and the reaction was allowed to proceed to completion. Then the reaction mixture was added slowly with stirring to 60 ml of a saturated solution of 2,4-dinitrophenyl hydrazine in 2.0 mol dm^{-3} HCl. After storing for about 1hr in an ice-bath, the precipitate was collected weighed sintered glass crucible, washed with 2.0mol dm^{-3} HCl followed by water and dried to a constant weight at 100-105℃. The found ratio, $[Cr(VI)]_T/[Carbonyl\ compound]_T \approx 2/3$ (from 3 independent determinations) supports the fol- lowing Stoichiometry.

$$3PhCH_2OH + 2HCrO_4^- + 8H^+ \rightarrow 3\ PhCHO + 2Cr(III) + 8\ H_2O. \qquad (1)$$

4. RESULTS AND DISCUSSION

4.1. Dependence on $[Substrate]_T$ *i.e*, [Benzyl Alcohol]$_T$

From the plot of k_{obs} vs [benzyl alcohol]$_T$, it is established that the path shows a first order dependency on [substrate]$_T$ *i.e*, [benzyl alcohol]$_T$ *i.e*., with increasing substrate concentration the rate of the reaction increases in a straight line manner. (**Figure 1**).

$$\text{So, } k_{obs} = k_s[S]_T$$

The above first order dependence on $[S]_T$ also maintained in the presence of surfactant like CPC, SDS, TX-100.

4.2. Dependence on [H$^+$]

The acid dependence was followed in aqueous $HClO_4$ media at fixed Cr(VI) and $[S]_T$. From the experimental fit (**Figure 2**), the observation is

$$k_{obs} = k_H[H^+]^2$$

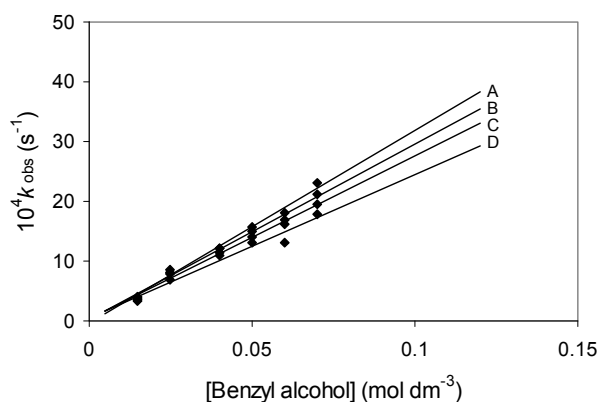The above second order dependency is also maintained in the presence of surfactant (e.g, SDS).
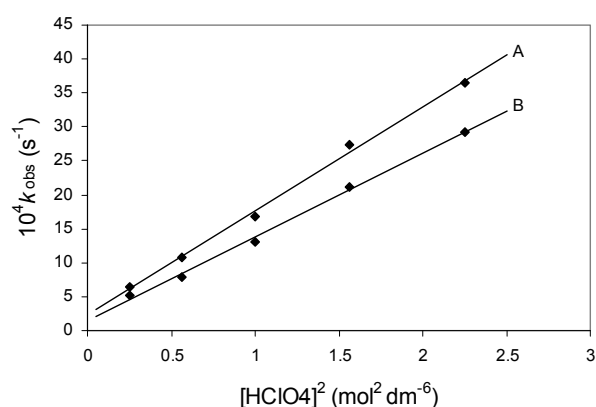
5. EFFECT OF SURFACTANTS

5.1. Effect of SDS

Sodium dodecyl sulphate(SDS, a representative anionic surfactant) accelerate the reaction path. The plot of k_{obs} vs $[SDS]_T$ [**Figure 3**] shows a continuous increase up to the concentration of SDS.
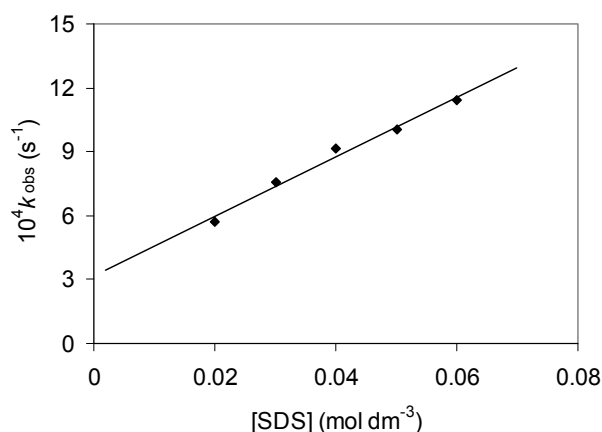
Figure 1. Dependence of k_{obs} on [benzyl alcohol] for the chromium (VI) oxidation of benzyl alcohol at 30℃. $[Cr(VI)]_T = 5 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.25$ mol dm^{-3}. A($[SDS]_T = 2 \times 10^{-2}$ mol dm^{-3}, $[CPC]_T = 0$ mol dm^{-3}, $[TX-100]_T = 0$ mol dm^{-3}), B($[SDS]_T = 0$ mol dm^{-3}, $[CPC]_T = 0$ mol dm^{-3}, $[TX-100]_T = 2 \times 10^{-2}$ mol dm^{-3}), C ($[SDS]_T = 0$ mol dm^{-3}, $[CPC]_T = 0$ mol dm^{-3}, $[TX-100]_T = 0$ mol dm^{-3}), D($[SDS]_T = 0$ mol dm^{-3}, $[CPC] = 2 \times 10^{-3}$ mol dm^{-3}, $[TX-100]_T = 0$ mol dm^{-3}).
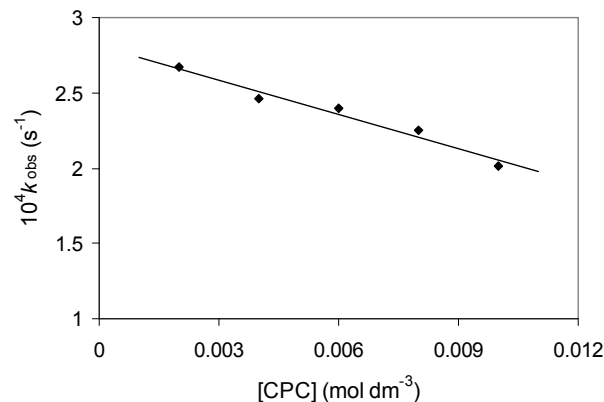

Figure 2. Dependence of k_{obs} on [H$^+$] for the chromium(VI) oxidation of benzyl alcohol at 30℃ in aqueous medium. $[Cr(VI)]_T = 5 \times 10^{-4}$ mol dm^{-3}, [benzyl alcohol]$_T = 150 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.25$ mol dm^{-3}. A($[SDS]_T = 2 \times 10^{-2}$), B($[SDS]_T = 0$).

5.2. Effect of CPC

Cetyl Pyridinium Chloride (CPC, a representative cationic surfactant is found to retard the reaction path. Plot of k_{obs} vs $[CPC]_T$ [**Figure 4**] shows a continuous decrease and finally it tends to level off at higher concentration of CPC. The observation is identical to that observed by Bunton and Cerichelli [19] in the oxidation of ferrocene by ferric salt salts in the presence of cationic surfactant cetyl trimethyl ammonium bromide (CTAB).

Figure 3. Dependence of k_{obs} on $[SDS]_T$ for the chromium (VI) oxidation of benzyl alcohol at 30℃. $[Cr(VI)]_T = 5 \times 10^{-4}$ mol dm^{-3}, [benzyl alcohol]$_T = 150 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.25$ mol dm^{-3}.

Figure 4. Dependence of k_{obs} on $[CPC]_T$ for the chromium(VI) oxidation of benzyl alcohol at 30℃. $[Cr(VI)]_T = 5 \times 10^{-4}$ mol dm^{-3}, [benzyl alcohol]$_T = 150 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.25$ mol dm^{-3}.
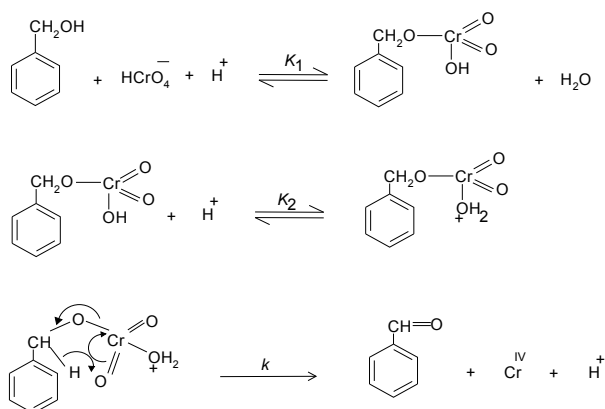
5.3. Effect of TX-100

Triton X-100(TX-100, a representative neutral surfactant) accelerates the reaction path. But the acceleration rate in TX-100 is less than that of SDS. The plot of k_{obs} vs $[TX-100]_T$ [**Figure 5**], shows a continuous increase up to the concentration of TX-100.
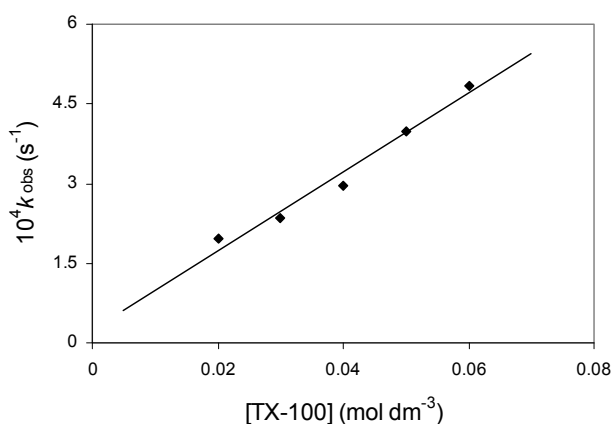
5.4. Test for Acrylonitrile Polymerization

Under the experimental conditions, the existence of free radical was indicated by polymerization of acrylonitrile under a nitrogen atmosphere.

5.5. Mechanism and Interpretation

Scheme 1 leads to the flowing rate law:
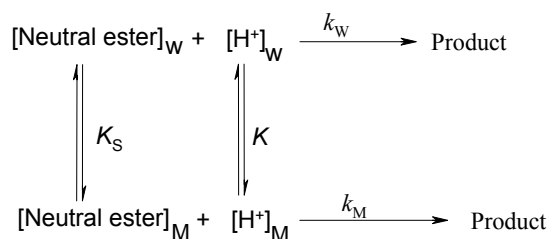
Scheme 1. Cr(Vl) reduction of Benzyl alcohol.

Figure 5. Dependence of k_{obs} on [TX-100]$_T$ for the chro- mium (VI) oxidation of benzyl alcohol at 30℃. [Cr(VI)]$_T$ = 5 × 10^{-4}mol dm^{-3}, [benzyl alcohol]$_T$ = 150 × 10^{-4}mol dm^{-3}, [H$_2$SO$_4$] = 0.25 mol dm^{-3}.

$$k_{obs} = (2/3)\, kK_1K_2[S]_T[H^+]^2 \qquad (2)$$
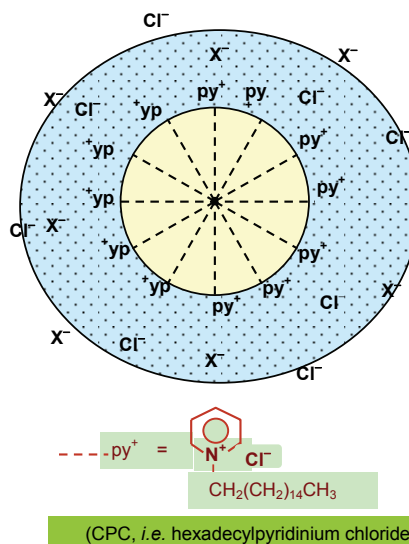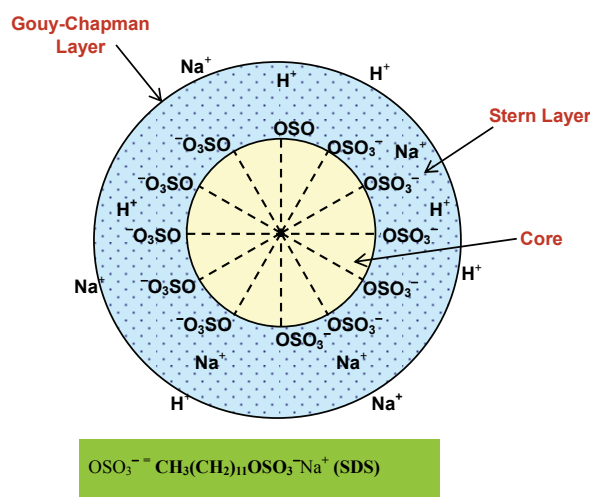
The pseudo-first-order rate constants (k_{obs}) in the presence of various concentrations of different types of surfactants, SDS (Sodium dodecyl sulfate, a representative anionic surfactant), CPC (N-cetyl pyridinium chloride, a representative anionic surfactant) and TX-100 (Trian X-100, a neutral surfactant) are presented in **Figures 4-6**. The pseudo phase ion-exchange (PIE) [20] model is applied most widely in micellar catalysis. The basic assumption of the PIE is as follows:

1) Micelles act as a separate phase from water, all reactants are distributed quickly between water and micellar phase, and the reaction rate can be considered as the sum of that in two phases.

2) The reaction in the micellar pseudo phase occurs mainly at micelle surface.

3) The reactant ions and the inert ions compete at the charged micellar surface.

The data reveal that SDS and TX-100 accelerate the rate where as CPC decreases the rate. The rate acceleration is higher in the case of SDS than TX-100. This can be explained by **Schemes 2** and **3**.

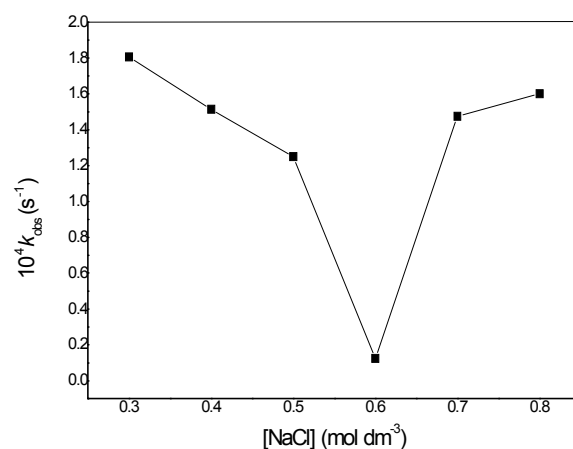**Scheme 2.** Partitioning of the reactive species between the aqueous and micellar phases.

Scheme 3. Structural representation of anionic & cationic surfactants.

The formation of micelles by ionic surfactants is ascribed to a balance between hydrocarbon chain attraction and ionic repulsion. The net charge of micelles is less than the degree of micellar aggregates, indicating that a large fraction of counter ions remains associated with the micelle; these counter ions form the Stern layer at the micellar surface. For nonionic surfactants, however, the hydrocarbon chain attraction is opposed by the requirements of hydrophilic groups for hydration and space. Therefore, the micellar structure is determined by equilibrium between the repulsive forces among hydrophilic groups and the short-range attractive forces among hydrophobic groups. For bimolecular reactions inhibition arises from incorporation of one reactant into the micellar pseudo phase and exclusion of the other from it. Catalysis is apparently caused, for the most part, by concentration of the two reactants into a small volume in the micellar Stern layer [21].
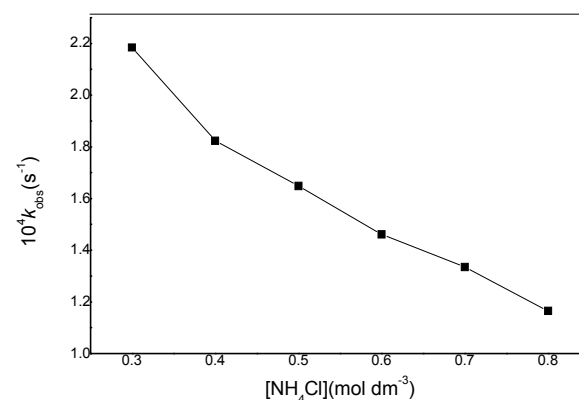
The substrate is partitioned in the Stern layer of the micellar phase. SDS being an anionic surfactant, owing to the electrostatic attraction between the positively charged $[H^+]$ species and negatively charged micellar head groups. $[H^+]$ easily attaches to the Stern layer of the micelle. The reaction takes place in both the micellar and aqueous media. The observed rate acceleration is due to the favored reaction in the micellar phase, where both H^+ and the neutral ester are preferably accumulated. In the case of TX-100, H^+ also attaches to the Stern layer of the micelle, but the amount is less compared to SDS because TX-100 is a neutral surfactant, so no electrostatic attraction takes place. CPC is a cationic surfactant and consequently due to the electrostatic repulsion between the positively charged $[H^+]$ species and positively charged micellar head group, $[H^+]$ does not attaches to the Stern layer of micelle through the substrate. The reaction takes place only in aqueous media, which is depleted in the substrate concentration.

5.6. Effect of Added Electrolyte

Experimental evidence has shown that electrolyte inhibition of micellar catalysis is a general phenomenon [22-24] with one apparent exception [25]. The proposed study has taken into consideration for better under standing of reduction mechanism. Electrolyte inhibition is rationalized by assuming that a counter ion competes with an ionic reagent (e.g., OH^-, H_3O^+, and X^-) for a site on the ionic micelle [26]. When NH_4Cl is added the inhibition phenomena comes into play (**Figure 7**). But for the case of NaCl inhibition followed by enhancement takes place which is interesting (**Figure 6**). Enhancement of micellar catalysis by added salt is caused by their changing the shape or reducing the charge density

Figure 6. Dependence of k_{obs} on [NaCl] for the chromium(VI) oxidation of benzyl alcohol at 30^0C in SDS medium. $[Cr(VI)]_T$ = 5×10^{-4} mol dm^{-3}, [benzyl alcohol]$_T$ = 150×10^{-4} mol dm^{-3}, $[H_2SO_4]$ = 0.25 mol dm^{-3}.

Figure 7. Dependence of k_{obs} on [NH$_4$Cl] for the chromium(VI) oxidation of benzyl alcohol at 30^0C in SDS medium. $[Cr(VI)]_T$ = 5×10^{-4} mol dm^{-3}, [benzyl alcohol]$_T$ = 150×10^{-4} mol dm^{-3}, $[H_2SO_4]$ = 0.25 mol dm^{-3}.

of the micelle. Salts decrease the cmc (critical micelle concentration) and increase the aggregation no of ionic micelles [27-28] probably because increased screening by the counter ions decreases the effective charge density of the micelle.

6. CONCLUSIONS

Kinetics and mechanism of Cr(VI) reduction by benzyl alcohol in aqueous acid media have been studied under the conditions [benzyl alcohol]$_T$>>[Cr(VI)]$_T$. under the kinetic conditions, the monomeric species of Cr(VI) has been found kinetically active. Cr(VI)-substrate ester experiences a redox decomposition through 2e$^-$ transfer at

Table 2. Presentation of rate constants values (k_{obs}) of benzyl alcohol oxidation in different surfactant medium.

[benzyl alcohol]$_T$ (mol dm^{-3})	[SDS]$_T$ (mol dm^{-3})	$10^4 k_{obs}$(s^{-1})	[CPC]$_T$ (mol dm^{-3})	$10^4 k_{obs}$(s^{-1})	[TX-100]$_T$ (mol dm-3)	$10^4 k_{obs}$(s^{-1})
1500×10^{-4}	0.02	5.68 ± 0.002	0.002(M)	2.668 ± 0.001	0.02	1.95 ± 0.003
1500×10^{-4}	0.03	7.54 ± 0.002	0.004(M)	2.46 ± 0.002	0.03	2.36 ± 0.002
1500×10^{-4}	0.04	9.14 ± 0.002	0.006(M)	2.395 ± 0.001	0.04	2.95 ± 0.001
1500×10^{-4}	0.05	10.04 ± 0.003	0.008(M)	2.25 ± 0.001	0.05	3.98 ± 0.003
1500×10^{-4}	0.06	11.39 ± 0.002	0.01(M)	2.013 ± 0.002	0.06	4.85 ± 0.003

the rate determining step. The reaction shows both 1st order dependency on [benzyl alcohol]$_T$ and [Cr(VI)]$_T$ and 2nd order dependency on [H$^+$] ion. In the presence of some non-functional surfactants, the orders remain unchanged. CPC has been found to retard the rate while SDS and TX-100 shows the rate acceleration effect (**Table 2**). The effect of added electrolye gives different observations. Inhibition followed by enhancement is the effect of NaCl but for NH$_4$Cl inhibition is the only fate. So for waste water treatment with biosorbent, SDS or TX-100 and suitable concentration of NaCl may be used for quick result.

7. ACKNOWLEDGEMENTS

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