

Kinetic Studies on Hexavalent Chromium Reduction

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Abstract

Cr(VI) is a known human carcinogen. It is a wide spread environmental contaminant as it is extensively used in different industry. The kinetic study of reduction of Cr(VI) by a known organic substance, 1-butanol in micellar media have been studied spectrophotometrically. The reduction of Cr(VI) to Cr(III) occurs in a micro-heterogeneous system in cell cytoplasm. As micelles are considered to mimic the cellular membranes, the reduction process occurring in the micellar system is considered as a model to obtain insight in to the reduction process prevailing in body systems. Micellar media is also a probe to establish the mechanistic paths of reduction of Cr(VI) to Cr(III) and the effects of some electrolytes common to a biological systems are studied to establish the proposed reaction mechanism strongly. The overall reaction follows a first order dependency on substrate and hexavalent chromium and second order dependency on hydrogen ion. Suitable surfactant & suitable concentration of electrolyte enhance the rate of the reaction.

Keywords: Pollution, Carcinogen, Cr(VI), Oxidation; Kinetics, Surfactant, Electrolyte

1. Introduction

Water pollution by chromium is of considerable concern, as this metal has found widespread use in electro plating, leather tanning, metal finishing, nuclear power plant, textile industries and chromate preparation [1]. The effluents from these industries contain Cr(III) and Cr(VI) at concentrations ranging from ten to hundreds of mg/L [2]. The hexavalent form is 500 times more toxic than the trivalent [3]. Though chromium exists in nine valence states ranging from -2 to +6, Cr(III) and Cr(VI) are of major environmental significance because of their stability in the natural environment [4]. The chromate anion is highly soluble and therefore can overcome the cellular permeability barrier, entering via sulphate transport pathways since it bears structural similarity with SO_4^{2-} [5-7]. It has been reported that hexavalent chromium causes lung cancer, chromate ulcer, perforation of nasal septum and kidney damage in humans and it is also toxic to other organism as well [8,9]. Chromium in its trivalent form is an essential micronutrient for many microorganisms, relatively insoluble in water.

A number of treatment methods for removal of metal ions from aqueous solutions have been reported mainly reduction, ion exchange, solvent extraction, reverse osmosis, chemical precipitation and adsorption [10]. In the reduction followed by chemical precipitation method

[11], Cr(VI) is reduced to Cr(III) first, then lime is added to precipitate chromium as hydroxide.

In this paper, we studied kinetics and mechanism of Cr(VI) reduction to Cr(III) by an alcohol in presence of micelle and electrolyte because micelle [12-14] and electrolyte [15] substantiate the reaction mechanism. The outcome of such an exercise will certainly influence the detoxification methods.

2. Experimental

2.1. Materials and Reagents

Butan-1-ol (AR, Merck, India), $\text{K}_2\text{Cr}_2\text{O}_7$ (AR, BDH, India), N-cetyl pyridinium chloride (CPC) (AR, SRL, India), Sodium dodecyl sulphate (SDS) (AR, SRL, India), TX-100 (AR, SRL, India), NaCl (AR, Merck, India), NH_4Cl (AR, Ranbaxy, India) and other chemicals used were of highest purity available commercially. Solutions were prepared in double distilled water.

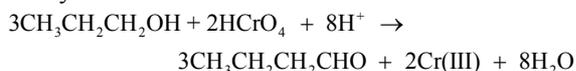
2.2. Procedure and Kinetic Measurements

Under the kinetic conditions, solutions of the oxidant and mixtures containing the known quantities of the substrate(s) (*i.e.*, butan-1-ol) (under the conditions $[\text{S}]_{\text{T}} \gg [\text{Cr(VI)}]_{\text{T}}$), acid and the other necessary chemicals were

separately thermostated ($\pm 0.1^\circ\text{C}$). The reaction was initiated by mixing the requisite amounts of the oxidant with the reaction mixture. Zero time was set when half of the required volume of the oxidant 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(SHIMADZU)]. Quartz cuvettes of path length 1 cm were used. The observed pseudo-first-order rate constants [$k_{\text{obs}}(\text{s}^{-1})$] 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, $r \geq 0.998$) were obtained for each reaction run. A large excess (≥ 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 investigated and the rate of decomposition in this path was found to be kinetically negligible.

2.3. Product Analysis and Stoichiometry

Under the kinetic condition (*i.e.*, $[\text{butanol}]_{\text{T}} \gg [\text{Cr(VI)}]_{\text{T}}$) butanol oxidizes to butanal and estimation of the reaction products was carried by gravimetrically as 2,4-dinitrophenylhydrazone. In a typical experimental set, 10ml of $0.06 \text{ mol}\cdot\text{L}^{-1}$ Cr(VI) in $1.0 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 was added to 40 mL of $0.2 \text{ mol}\cdot\text{L}^{-1}$ butanol and the reaction was allowed to proceed to completion. Completion of the reaction was indicated by the disappearances of Cr(VI) color. Then the reaction mixture was added slowly with stirring to 60 mL of a saturated solution of 2,4-dinitrophenylhydrazine in $2.0 \text{ mol}\cdot\text{L}^{-1}$ HCl. After storing for about 1 h in an ice-bath, the precipitate was collected weighed sintered glass crucible, washed with $2.0 \text{ mol}\cdot\text{L}^{-1}$ HCl followed by water and dried to a constant weight at $100\text{-}105^\circ\text{C}$ and recrystallized from ethanol. The hydrazone showed melting point $123\text{-}125^\circ\text{C}$ [16]. The found ratio, $[\text{Cr(VI)}]_{\text{T}}/[\text{Carbonyl compound}]_{\text{T}} \approx 2/3$ (from 3 independent determinations) supports the following Stoichiometry:



3. Results and Discussion

3.1. Dependence on Cr(VI)

Under the experimental condition, $[\text{Butan-1-ol}]_{\text{T}} \gg [\text{Cr(VI)}]_{\text{T}}$, the rate of disappearance of Cr(VI) shows a first order dependency on Cr(VI). This dependence is also maintained in the presence of cationic surfactant (CPC), anionic surfactant (SDS) and neutral surfactant (TX-100) (Figure 1).

3.2. Dependence on [Substrate]_T *i.e.*, [Butan-1-ol]_T

From the plot of k_{obs} vs $[\text{Butan-1-ol}]_{\text{T}}$ (Figure 2), it is established that the path shows a first order dependency on $[\text{substrate}]_{\text{T}}$, *i.e.*, $[\text{butan-1-ol}]_{\text{T}}$.

$$k_{\text{obs}} = k_s[\text{S}]_{\text{T}}$$

The above first order dependence on $[\text{substrate}]_{\text{T}}$ is also maintained in the presence of surfactant like CPC, SDS, TX-100.

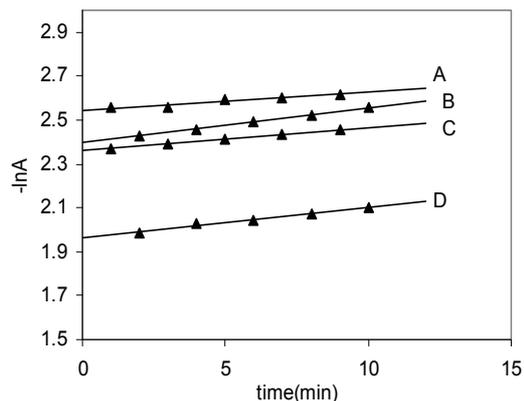


Figure 1. Some representative first-order plots to evaluate the pseudo-first-order rate constants (k_{obs}) for the Cr(VI) oxidation of 1-butanol at 30°C . Dependence of absorbance of Cr(VI) on time (min) for the oxidation of 1-butanol at 30°C . $[\text{Cr(VI)}] = 5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[\text{1-butanol}] = 1500 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[\text{H}_2\text{SO}_4] = 0.50 \text{ mol}\cdot\text{L}^{-1}$. A: $[\text{SDS}]_{\text{T}} = 0 \text{ mol}\cdot\text{L}^{-1}$, $[\text{CPC}]_{\text{T}} = 2 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, $[\text{TX-100}]_{\text{T}} = 0 \text{ mol}\cdot\text{L}^{-1}$. B: $[\text{SDS}]_{\text{T}} = 0 \text{ mol}\cdot\text{L}^{-1}$, $[\text{CPC}]_{\text{T}} = 0 \text{ mol}\cdot\text{L}^{-1}$, $[\text{TX-100}]_{\text{T}} = 2 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$. C: $[\text{SDS}]_{\text{T}} = 0 \text{ mol}\cdot\text{L}^{-1}$, $[\text{CPC}]_{\text{T}} = 0 \text{ mol}\cdot\text{L}^{-1}$, $[\text{TX-100}]_{\text{T}} = 0 \text{ mol}\cdot\text{L}^{-1}$. D: $[\text{SDS}]_{\text{T}} = 2 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, $[\text{CPC}] = 0 \text{ mol}\cdot\text{L}^{-1}$, $[\text{TX-100}]_{\text{T}} = 0 \text{ mol}\cdot\text{L}^{-1}$.

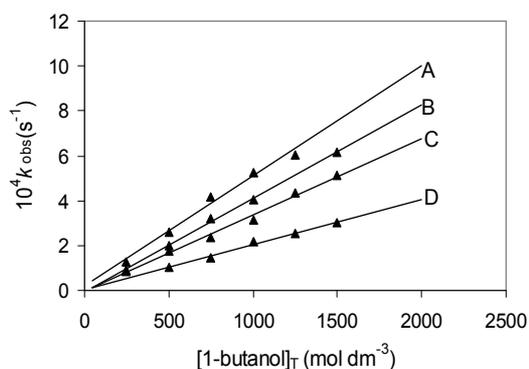


Figure 2. Dependence of k_{obs} on $[\text{1-butanol}]_{\text{T}}$ for the Cr(VI) oxidation of 1-butanol at 30°C . $[\text{Cr(VI)}] = 5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[\text{H}_2\text{SO}_4] = 0.50 \text{ mol}\cdot\text{L}^{-1}$. A: $[\text{SDS}]_{\text{T}} = 2 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, $[\text{CPC}]_{\text{T}} = 0 \text{ mol}\cdot\text{L}^{-1}$, $[\text{TX-100}]_{\text{T}} = 0 \text{ mol}\cdot\text{L}^{-1}$. B: $[\text{SDS}]_{\text{T}} = 0 \text{ mol}\cdot\text{L}^{-1}$, $[\text{CPC}]_{\text{T}} = 0 \text{ mol}\cdot\text{L}^{-1}$, $[\text{TX-100}]_{\text{T}} = 2 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$. C: $[\text{SDS}]_{\text{T}} = 0 \text{ mol}\cdot\text{L}^{-1}$, $[\text{CPC}]_{\text{T}} = 0 \text{ mol}\cdot\text{L}^{-1}$, $[\text{TX-100}]_{\text{T}} = 0 \text{ mol}\cdot\text{L}^{-1}$. D: $[\text{SDS}]_{\text{T}} = 0 \text{ mol}\cdot\text{L}^{-1}$, $[\text{CPC}] = 2 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, $[\text{TX-100}]_{\text{T}} = 0 \text{ mol}\cdot\text{L}^{-1}$.

3.3. Dependence on $[H^+]_T$

The acid dependence was followed in aqueous $HClO_4$ medium at fixed $Cr(VI)$ and $[substrate]$. From the experimental fit (Figure 3), the observation is

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

Thus the acid variation shows a second order dependence on $[H^+]$ ion. The above second order dependency is also maintained in presence of surfactants.

3.4. Effects of Surfactants

3.4.1. Effects 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 [17] in the oxidation of ferrocene by ferric salt salts in the presence of cationic

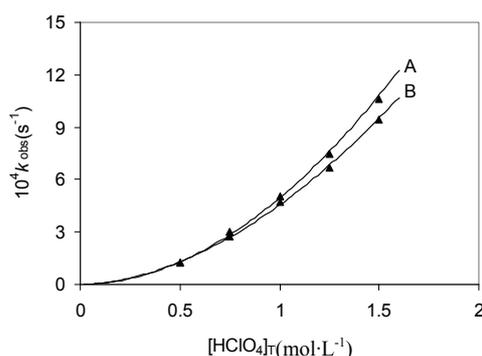


Figure 3. Dependence of k_{obs} on $[H^+]_T$ for the $Cr(VI)$ oxidation of 1-butanol at $30^\circ C$. A: $[Cr(VI)] = 5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[1\text{-butanol}] = 500 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[SDS] = 2 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$. B: $[Cr(VI)] = 5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[1\text{-butanol}] = 500 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[SDS] = 0 \text{ mol}\cdot\text{L}^{-1}$.

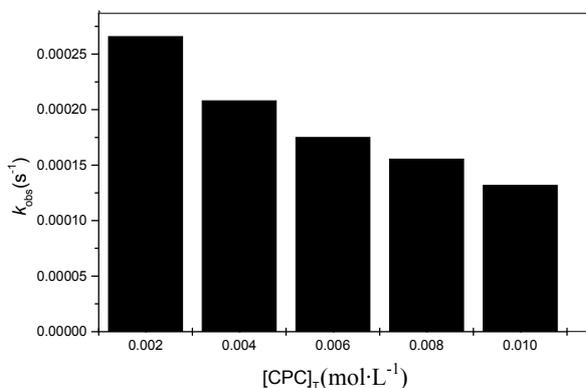


Figure 4. Dependence of k_{obs} on $[CPC]_T$ for the $Cr(VI)$ oxidation of 1-butanol at $30^\circ C$. $[Cr(VI)] = 5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[1\text{-butanol}] = 1000 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[H_2SO_4] = 0.50 \text{ mol}\cdot\text{L}^{-1}$.

surfactant cetyl trimethyl ammonium bromide (CTAB).

3.4.2. Effects of SDS

Sodium dodecyl sulphate (SDS, a representative anionic surfactant) accelerates the reaction path. The plot of k_{obs} vs $[SDS]_T$ (Figure 5) shows a continuous increase up to the concentration of SDS.

3.4.3. Effects 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 6 shows a continuous increase up to the concentration of TX-100.

3.4.4. Test for Acrylonitrile Polymerization

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

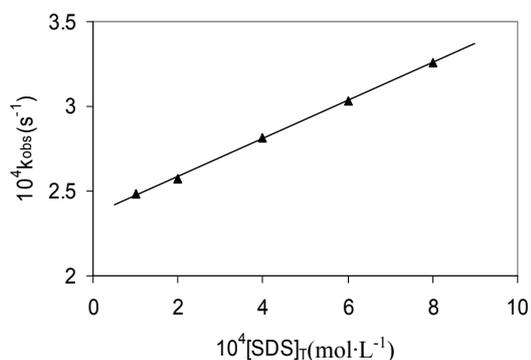


Figure 5. Dependence of k_{obs} on $[SDS]_T$ for the $Cr(VI)$ oxidation of 1-butanol at $30^\circ C$. $[Cr(VI)] = 5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[1\text{-butanol}] = 500 \text{ mol}\cdot\text{L}^{-1}$, $[H_2SO_4] = 0.50 \text{ mol}\cdot\text{L}^{-1}$.

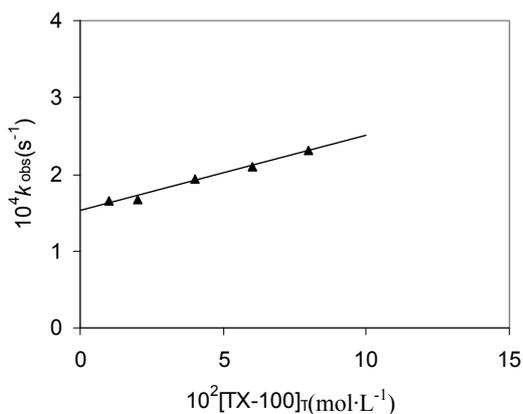
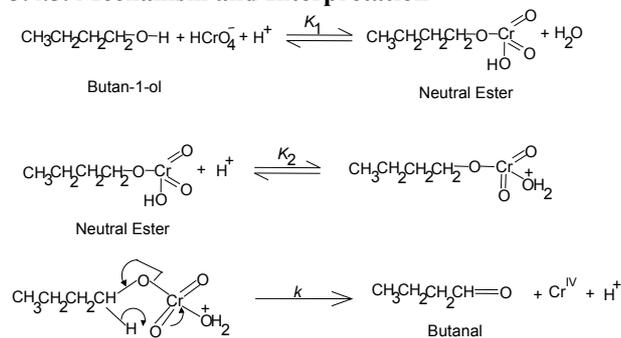


Figure 6. Dependence of k_{obs} on $[TX-100]_T$ for the $Cr(VI)$ oxidation of 1-butanol at $30^\circ C$. $[Cr(VI)] = 5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[1\text{-butanol}] = 500 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[H_2SO_4] = 0.50 \text{ mol}\cdot\text{L}^{-1}$.

3.4.5. Mechanism and Interpretation



Scheme 1. Cr(VI) reduction by butan-1-ol.

Scheme 1 leads to the following rate law

$$k_{\text{obs}} = (2/3) k K_1 K_2 [\text{S}]_T [\text{H}^+]^2$$

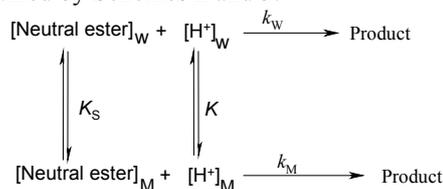
The pseudo-first-order rate constants (k_{obs}) in the presence of various concentrations of different types of surfactants, SDS, CPC, TX-100 are represented in **Figures 4-6**. The pseudo phase ion-exchange (PIE) [18] model is applied most widely in micellar catalysis. The basic assumption of the PIE 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.

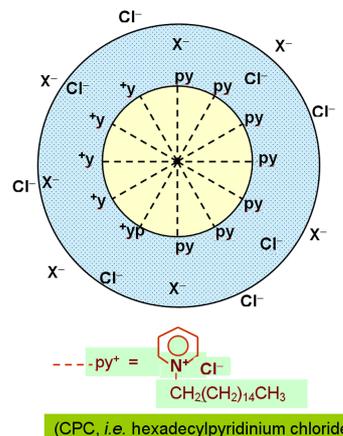
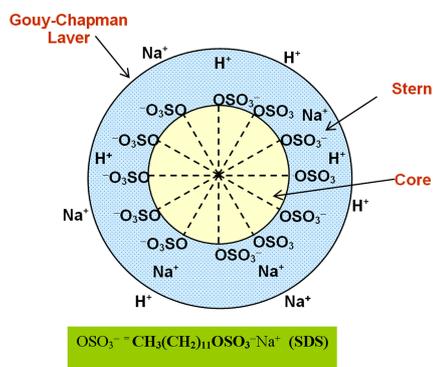
2) The reaction in the micellar pseudo phase occurs mainly at micelle surface.

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 whereas 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.

Ever since J. W. Mc Bain proposed the presence of molecular aggregates in soap solution on the basis of the unusual changes in electrical conductivity observed with changing soap concentration [19], the structure of micellar aggregates has been a matter of discussion. G. S. Hartley proposed that micelles are spherical with charged groups situated at the micellar surface [20], whereas Mc Bain suggested that lamellar and spherical forms coexist [21]. X-ray studies by Harkins *et al.*, [22,23] then suggested the sandwich or lamellar model. Later, P. Debye and E. W. Anacker proposed that micelles are rod-shaped rather than spherical or disk like [24]. The cross section of such a rod would be circular, with the polar heads of the detergent lying on the periphery and the hydrocarbon tails filling the interior. The ends of the rod would almost certainly have to be rounded and polar. In 1956, Hartley's spherical micelle model was established by I. Reich [25] from the view point of entropy, and the spherical form is now generally accepted as approximating the actual structure. 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 [26].

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 attach to the Stern layer of micelle through the substrate. The reaction takes place only in aqueous media, which is depleted in the substrate concentration.

3.4.6. Effect of Added Electrolyte

Experimental evidence has shown that electrolyte inhibition of micellar catalysis is a general phenomenon [27-29] with one apparent exception [30]. Here we report a system which connects inhibition and enhancement. The proposed study has taken into consideration for better understanding of Cr(VI) carcinogenicity. The added electrolytes are common to biological systems. 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 [31]. Enhancement of micellar catalysis by added salt is caused by their changing the shape or reducing the charge density of the micelle. Salts decrease the cmc (critical micelle concentration) and increase the aggregation number of ionic micelles [31-33] probably because increased screening by the counter ions decreases the effective charge density of the micelle. Added salts are very common sodium chloride (NaCl) and ammonium chloride (NH_4Cl). In SDS medium the rate is retarded up to $0.7 \text{ mol}\cdot\text{L}^{-1}$ solution of NH_4Cl and $0.8 \text{ mol}\cdot\text{L}^{-1}$ solution of NaCl. After that the rate is increased (Figure 7). Up to $0.7 \text{ mol}\cdot\text{L}^{-1}$ of NH_4Cl counter ion competition is important and after that micellar shape is important. The reason is same for NaCl up to $0.8 \text{ mol}\cdot\text{L}^{-1}$.

4. Conclusions

Kinetics and mechanism of chromic acid reduction by butan-1-ol in aqueous acid media have been studied under the conditions $[\text{butan-1-ol}]_T \gg [\text{Cr(VI)}]_T$. Under the kinetic conditions, the monomeric species of Cr(VI) has been found kinetically active. Cr(VI)-substrate ester experiences a redox decomposition through 2 electron transfer at the rate determining step. The reaction shows both 1st order dependency on $[\text{butan-1-ol}]_T$ and $[\text{Cr(VI)}]_T$

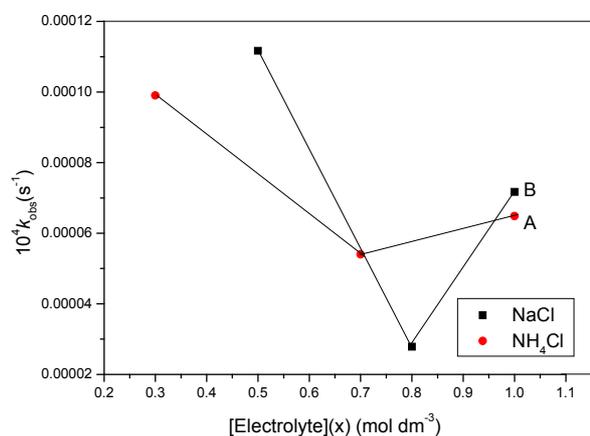


Figure 7. Dependence of k_{obs} on $[\text{electrolyte}(x)]$ for the Cr(VI) oxidation of 1-butanol at 30°C in SDS medium. $[\text{Cr(VI)}] = 5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[\text{1-butanol}] = 1500 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[\text{H}_2\text{SO}_4] = 0.50 \text{ mol}\cdot\text{L}^{-1}$. A: $x = [\text{NH}_4\text{Cl}]$. B: $x = [\text{NaCl}]$.

and second order dependency on $[H^+]$ ion. In the presence of non-functional surfactant, the order of the reaction remains unaltered. CPC has been found to retard the rate while SDS and TX-100 shows rate acceleration effect. The effect of added electrolyte is inhibition followed by enhancement in the rate.

5. Acknowledgements

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