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Micellar Effects on the Chromium (VI) Oxidation on Various Substrates: Exploring Different Kinetic Models in Micellar System

Monirul Islam[1*], Debraj Roy[2*]

[1]Seth Anandram Jaipuria College, Kolkata, West Bengal 700005, India
[2]Sripat Singh College, Jiaganj, Murshidabad, West Bengal 742123, India

[*]Corresponding Author's E-mail: roydebraj29@gmail.com, michem989@gmail.com

Abstract

Chromium(VI), a potent and mighty oxidising agent, undergoes reduction to chromium(III) through various redox reactions. This process is significantly influenced by the choice of students and experimental parameters and often involves intermediate oxidation states such as Cr(V) and Cr(IV). The redox behaviour of Cr(VI) is highly relevant due to its carcinogenic and mutagenic activities, as well as its interaction with biologically active molecules during reduction. Cr(VI) typically exists as CrO_4^{2-} at neutral pH and can invade the cells, leading to toxicity associated with the intermediate state during the reduction to Cr(III). Electron transfer reactions in organised assemblies like micelles vesicles, and polyelectrolytes have been extensively studied, highlighting the role of hydrophobic and electrostatic interactions in reaction kinetics. Micellar systems, which emulate cellular membranes, provide insights into electron transfer mechanisms in heterogeneous environments. These systems are crucial for understanding biochemical processes, including drug-membrane interactions and photochemical energy storage. In pharmaceutical applications, micelles enhance drug bioavailability, prevent degradation and enable targeted delivery to regions with leaky blood vessels, highlighting their importance in therapeutic and biomedical research.

Keywords: *Chromate Toxicity; Electron Transfer Kinetics; Micelles; Vesicular Structure*

Introduction

Chromium(VI) as a powerful oxidising agent serves in various redox reactions, during which it is reduced to Cr(III). The Cr(VI) is reduced to Cr(III) significantly depending on the type of reductant used and the choice of specific experimental parameters (Codd *et al*, 2001; Das, 2004; Mahanti & Banerji, 2002; Mitewa & Bontchev, 1985). Sometimes Cr(V) and Cr(IV) are determined and explained as intermediates within many reactions. Understanding these subtle variations, the researchers have thoroughly studied Cr(VI) in the context of redox kinetics. Cr(VI) appeared as a hazardous one because of its carcinogenic and mutagenic activity (Arslan, Beltrame & Tomasi, 1987; Costa, 1997; De Flora, 2000; Katz, Ballantyne & Salem, 2005.; Rossi & Wetterhahn, 1989). The kinetics and mechanism of Cr(VI) oxidation are biologically relevant as a reducing agent, making them relevant for the biochemists and inorganic chemists (Codd *et al*, 2001; Das, 2004). In its intermediate oxidation states, chromium, i.e., Cr(VI) → Cr(III), could potentially engage with bioactive compounds and lead

to harmful effects. Considering chromate toxicity, it's reasonable to suggest that reducing agents significantly influence and modulate its various effects Codd *et al* (2001). At neutral pH, via non-specific anion carriers, Cr(VI) predominantly exists as CrO_4^{2-}. It can enter inside the cells (Arslan, Beltrame & Tomasi, 1987), where it gains an electron to Cr(III), producing various states of transition in chromium during the Cr(VI) → Cr(III) electron acceptance process. The intermediates of DNA bases are very often kinetically labile (Köster & Beyersmann, 1985), which can induce chromate toxicity.

The organised structures or assemblies influence electron transfer rate, and reactions have been explored by different research workers (Bhalekar & Engberts, 1978; Cavasino, 1985). The influence of structured gatherings on the reaction rate is thought to arise as a consequence of their interactions (Bhalekar & Engberts, 1978; Cavasino, 1985) from hydrophobic and electrostatic forces of interactions, which attribute reactants within the system. Many redox reactions in the biochemical model, which involve the transfer of electrons, take place in systems that contain both a water-based (aqueous) part and a fat-like (lipophilic) part. Studies have documented occurrences of electron transfer processes (Bhalekar & Engberts, 1978; Cavasino, 1985) at polyelectrolytes, cell vesicles, and micellar surfaces. In a simulated system, the micelle-based structures are considered to emulate the cellular membranes. These studies help us to comprehend the electron transfer mechanism in a partially mixed, small-scale, heterogeneous environment. Kinetic equilibria on electron transfer reactions in micellar systems are very crucial (Minero *et al*, 1983) for understanding various events; phenothiazine derivatives exhibit diverse therapeutic activities, including antitumor, antibacterial, and antioxidant effects. They interact with cellular surface membranes, altering lipid composition and tri-layered membrane integrity, which can disrupt cancer cell functions. Additionally, compounds with photo-redox properties are utilised in photochemical energy storage systems, often within micellar structures, enhancing their efficiency and stability. Micelles have potent utility in pharmacy and act as a tool for numerous applications (Rangel-Yagui *et al*, 2005), like in drug delivery, drug degradation and loss, and preventing harmful side effects by solubilising the poorly soluble drugs to enhance their bioavailability. Micelles can house in the bloodstream for a long period of time, allowing them up slowly and sequentially in the target area. The size also enables them to gather in regions with leaky blood vessels.

Attributions of Micelles in Aqueous Solutions

Surfactants possess diphilic moieties, with the head region constituted from a hydrophilic or polar moiety and the tail region from a hydrophobic component. Surfactant head can be charged, anionic or cationic, dipolar (zwitter ionic) or charge-less (non-ionic). Ionic surfactants are represented as RX, where "R" denotes a hydrocarbon chain consisting of 8 to 18 carbon atoms. This "R" group may be part of an alkyl or aromatic radical, or it could be another form of hydrophobic structure (Hait & Moulik, 2002; Im *et al*, 2003). Therefore, the moiety, that is, ionic X taking both anionic and cationic parts. The surfactants are cation-active and anion-active, contingent upon the nature of Charge on "X", and hydrophilic anion-active surfactants have phosphate, sulphonate, carboxylate or sulphate groups. For example, $(CH_3)(CH_2)_nSO_3^-M^+$, $(CH_3)(CH_2)_nSO_3$-M^+, $(CH_3)(CH_2)_nCO_2^-M^+$ (where, M^+= Li^+,

Na^+, K^+, and MMe^{4+} etc. Here, *n*= 8-18 carbon chain number) and many more are listed. One can relay that the best example is sodium dodecyl sulphate (SDS) $C_{12}H_{25}OSO_3^-Na^+$ in all experimental cases, whereas for the surfactants that are cation active parts, attract water (hydrophilic moiety), made up either of a quaternary ammonium, pyridinium, or phosphonium group (Montalvo & Khan, 2002). Few lists are provided herewith: $(CH_3)(CH_2)_n^+N(CH_3)_3B^-$, $(CH_3)(CH_2)_n^+N(CH_3)_3B^-$, $(CH_3)(CH_2)_n^+N(C_2H_5)_3B^-$, etc. (Here, B^- = Cl^-, Br^-, OH^-, etc.; and n = 8-18). Various studies support the best example of cetyltrimethylammonium bromide (CTAB), $C_{16}H_{33}N^+Me_3Br^-$; cetylpyridinium chloride (CPC) $C_{16}H_{33}N^+(C_5H_5)Cl^-$for their best activity and less chemical jargon (Im *et al*, 2003). Non-ionic surfactants can often be represented as RX, where the component X, which is electrically neutral, typically signifies a polyoxyethylene group (Dwars, Paetzold & Oehme, 2005).

When any surfactants act as solutes, taken into solution, the solute particles naturally aggregate on their own, forming thermodynamically stable particles that fall within the colloidal size range. At lower concentrations, the surfactant acts like an ordinary solute; when the concentration reaches a certain threshold, they come together, with an aggregation number, denoted as N, ranging from twenty to a hundred depending on the conditions, to create micelles (Figure 1). Micelles are like cellular membranes, and the minimum concentration that starts micellisation is called the critical micelle concentration (CMC). Aggregation of surfactant molecules occurs among the hydrocarbon chains due to their hydrophobic interaction. The enlargement of micelles and the separation of surfactants into a micro-phase depend on factors like hydrophilic group hydration, electrostatic repulsion for ionic reactants, steric hindrance, and entropy losses, which prevent the formation of a micellar pseudo-phase.

The transformation between micelles and surfactant molecules that occurs quickly and can easily reverse itself takes place within milliseconds. As long as the surfactant concentration drops below the CMC, the resultant micelles can be broken down to a basic surfactant solution by simple dilution.

At a given temperature, all surfactants have a definite CMC. The value of CMC depends on the length of the hydrocarbon chains. For the shorter hydrocarbon chain, higher is its CMC value due to a small decrease in free energy during the micellisation process. Any CMC value of a particular surfactant depends on the chemical composition of the solution in which micellisation is carried out. For the ionic surfactants, the factors that minimise the electrostatic repulsion among the hydrophilic moieties favour micellisation. An increase in the concentration of counterions lowers the CMC value. Essentially, more counterions make micelle formation easier, so it requires a low surfactant concentration. Counterions reduce the electrostatic repulsion among the head groups, thereby stabilising a micelle formation. The higher alcohols, which can reduce the surface charge density, diminish the CMC of ionic surfactants. Micellisation of non-ionic surfactants is promoted by the increase in the temperature, as it reduces the hydration of their hydrophilic groups. Micellisation occurs within a specific concentration range near the critical CMC, where solution properties like viscosity, electrical conductivity, surface tension, light scattering, etc. change significantly. Micelles can take various shapes, like spheres or rods, but they all share a common

structure: their hydrophobic hydrocarbon ends cluster inside, while their hydrophilic ends extend outward, interacting with the surrounding solvent.

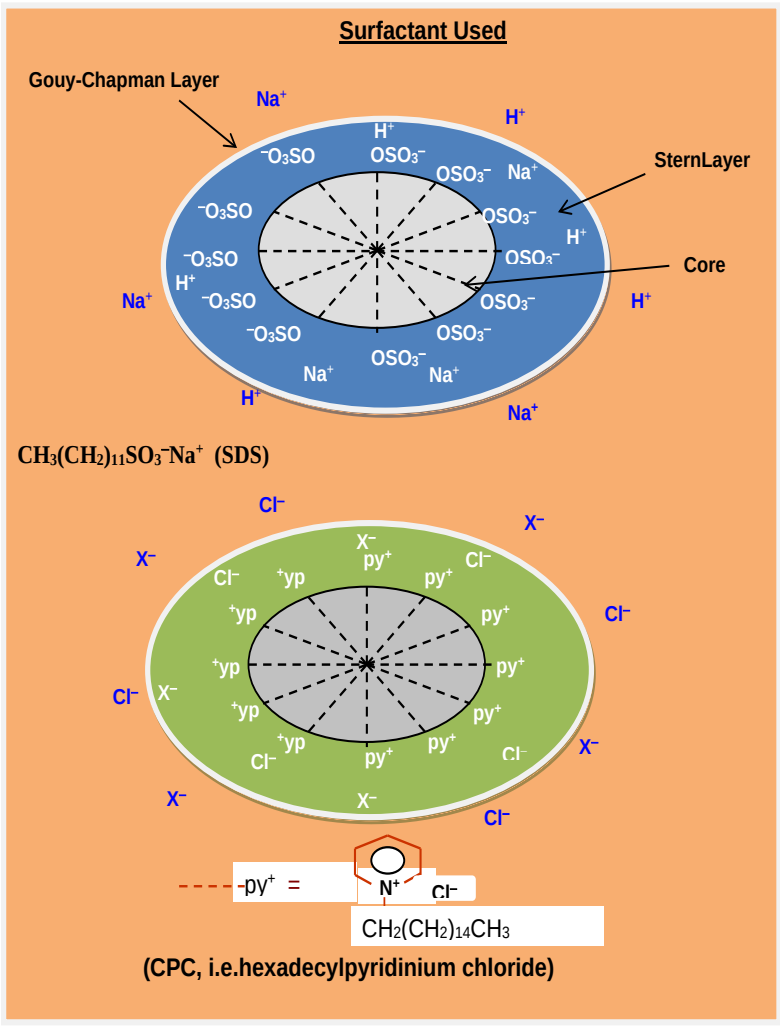


Figure 1: Schematic Representation of the Micellar System Involving Cationic Surfactant CPC and Anionic Surfactant SDS (*Source: Author*)

The Stern layer contains the ionic head groups of surfactants, neutralising 60-70 per cent of the micellar charge along with some gegenions. The leftover counterions from a diffuse (Bhalekar & Engberts, 1978; Cavasino, 1985) layer balance the remaining charge. Counterions that attach to neutralise the micellar head group charge, creating electrical double layers. The micelles create electrical double layers that influence the stability, particularly in colloidal and interfacial systems.

Dwars, Paetzold and Oehme (2005) have explained the amphiphile aggregates' shape and formation in water that balance the two forces in opposite directions: the hydrophobic

attraction between the alkyl chains and the polar repulsion of head groups. The alkyl chain attraction is mainly driven by entropy. Over an extensive span of temperatures, the Gibbs energy (free energy) associated with the formation process displays negligible fluctuation, reflecting a sharp and precise equilibrium between enthalpic and entropic contributions. Aggregates of amphiphilic molecules, such as micelles, have the capability to assemble within solvents exhibiting polar characteristics and hydrogen-bonding tendencies akin to those of water.

Different Kinetic Models of Micellar Effect

(A) Cooperative Model

Surfactants influence the reaction rates, and such reactions are very much similar to the models of enzyme-catalysed interactions. Piszkiewicz (1977) used a mechanistic model, very nearly a similar Hill model, to explain how micelles influence bimolecular reactions. Micelles, which are aggregates formed by surfactants, can alter reaction rates by creating unique microenvironments. This model helps explain the cooperative behaviour observed in such systems. to explain the micellar effect on bimolecular reactions. In Scheme 1, the model proposes that S (Substrate) and D (Detergent) molecules combine to form active micelles (D_nS).

$$nD + S \underset{}{\overset{K_D}{\rightleftharpoons}} D_nS \xrightarrow{k_M} \text{Product} \quad (1)$$

$$S \xrightarrow{k_W} \text{Product} \quad (2)$$

Scheme 1

The dissociation constant, K_D expresses the equilibrium between the micelle and its free components. The above scheme helps to explain the expression for the observed rate constant (k_{obs}).

$$k_{obs} = (k_M[D]^n + k_W K_D)/(K_D + [D]^n) \quad (3)$$

$$\text{or, } \log(k_{obs} - k_W)/(k_M - k_{obs}) = \log(G) = n\log[D] - \log K_D \quad (4)$$

[Where $G = (k_{obs} - k_w)/(k_M - k_{obs})$]

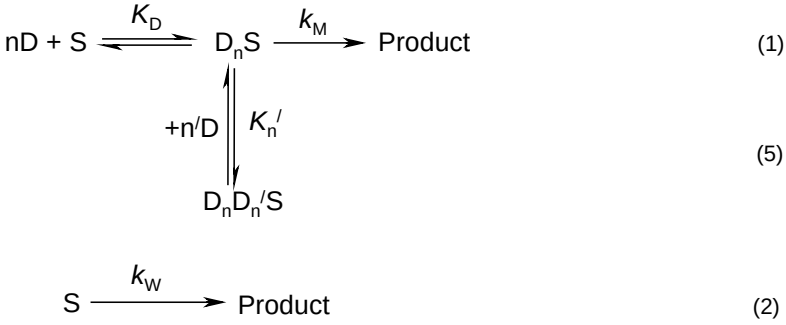
The constants, *K*D, n (measure of cooperativity), and $\log[D]_{50} = (\log K_D)/n$ (= The logarithmic value of the detergent concentration required to achieve half of the maximum velocity) are determined graphically. For analysing the data, *k*w refers to the observed rate constants without detergents, while k_M proposed the rate constant if the detergent is present. The analysis mainly focused on the detergent concentration range, showing an initial sigmoid relevance of k_{obs} (the observed constant of the rate) on the detergent concentration. It didn't account for higher detergent concentrations where *k*obs tends to decrease in bimolecular reactions due to the reactants getting diluted in the micellar phase. The Piszkiewicz model is advantageous because it does not rely on knowing the CMC of the detergent, which can be difficult to determine under experimental conditions. The value of n typically ranges from 1 to 3, which is much smaller than the aggregation number of micelles, usually between 20

and 100. Low values of n suggest that catalytically active micelles begin to form even at low concentrations, in the permicellar range. The non-integral nature of n implies that multiple equilibria might be involved in the formation of these active premicelles. From analogy with the enzyme-catalysed reactions, a value of n > 1 indicates positive cooperativity.

Piszkiewicz model (Matos & Gehlen, 2004) has been extended to explain: In bimolecular reactions, detergents can act as catalysts, speeding up the reaction by helping the reactants interact more effectively. However, when the concentration of detergent becomes very high, it starts to interfere with the reaction instead of helping it. This is called the "rate retarding effect". Essentially, the detergent molecules crowd the system, making it harder for the reactants to collide and react.

In Scheme 2, $n^{/}$ gives the additional number of detergent molecules which are associated with the catalytically active micelle (D_nS) to form the completely inactive species ($D_nD_n^{/}S$); $K_n^{/}$ is the corresponding binding constant.

The proposed model is outlined below (Scheme 2).



Scheme 2

The k_2 is the second-order rate constant of a bimolecular reaction: obtained from the above scheme, it is as follows:

$$k_2 = (k_M[D]^n + k_W K_D)/(K_D + [D]^n + K_n^{/}[D]^n[D]^{ń}) \quad (6)$$

At low concentration of detergent, Eqn. 6 reduces to Eqn. 3, while at higher concentration of detergent, Eqn. 6 reduces to:

$$k_2 = k_M/(1 + K_n^{/}[D]^{ń}) \quad (7)$$

$$\text{or, } \log[(k_M/k_2) - 1] = \log K_n^{/} + n^{/}\log[D] \quad (8)$$

(B) Ion Exchange Model (Pseudo-phase):

The model called as pseudo-phase ion exchange (PIE) (Bunton *et al*, 1991; Das *et al*, 2001a), surface of the micelles is assumed to be the selectively saturated counter ions exchangers. If the reactant is a species with a +2 charge (such as R^{2+}), then when sodium dodecyl sulphate (SDS) micelles are present, both the R^{2+} ions and Na^{+} ions will exhibit behaviour influenced by the micellar environment.

$$R_W^{2+} + 2Na_M^{+} \rightleftharpoons R_M^{2+} + 2Na_W^{+} \quad (9)$$

k_W k_M

Product Product (10)

Scheme 3

The observed pseudo-first-order rate constant (k_ψ) is given by:

$$k_\psi = (k_W + k_M K_{ex}/YF)/(1 + K_{ex}/YF) \quad (11)$$

The pseudo-phase ion exchange equilibrium constant (K_{ex}) is given by:

$$K_{ex} = [R_M^{2+}]YF/[R_W^{2+}] \quad (12)$$

$$\text{Where, } Y = ([Na_W^{+}]/[Na_M^{+}])^2 \quad (13)$$

$$F = \gamma_W^2(Na^+)/\gamma_W(R^{2+}) \quad (14)$$

For the micellar pseudo-phase, the ratio of activity denoted as $\gamma_W^2(Na^+)/\gamma_M(R^{2+})$, reasonably be regarded as constant and equal to one. The activity coefficient factor, F, is determined using the Davies equation (Davies & Waind, 1950), considering the total micellar surface charge to be compensated by the bound ions, *i.e.,* Na^+ and R^{2+}, the binding parameter (β refers to the proportion of the micellar surface charge that is balanced by the ions attached to it) is given by:

$$\beta = ([Na_M^{+}]/[D_n]) + (2[R_M^{2+}]/[D_n]) = m_{Na} + 2m_R \quad (15)$$

$$\text{Where } [D_n] = [SDS]_T - CMC \quad (16)$$

$$Y = [(\beta - 2_{mR})[D_n]/\{[Na^+]_T - (\beta - 2_{mR})[D_n]\}]^2 \quad (17)$$

(C) Menger- Portnoy Model

The Menger-Portnoy model (Menger & Portnoy, 1967) focuses on the distribution of a single reactant, such as A, between the micellar phase and an aqueous phase (as depicted in Scheme 4).

$$A_W + B \longrightarrow \text{Product} \quad (18)$$

K_A

$$A_M + B \xrightarrow{k_M} \text{Product} \quad (19)$$

Scheme 4

Scheme 4 derived the following rate law;

$$k = \frac{k_M K_A C + k_W}{1 + K_A C} \quad (20)$$

Here, K_A represents the binding constant for the micellized surfactant. k_m and k_w are the first-order rate constants in the micellar and aqueous phases, respectively, incorporating the concentration of reactant 'B' in these pseudo-phases. C denotes the concentration of the micelle.

(D) Berezin's Model

Berezin model (Berezin, Martinek & Yatsimirskii, 1973) suggests the system consists of two phases: one for the aqueous and the other for the micellar pseudo-phase at the above CMC. The quantitative rate equation for a bimolecular reaction involving the reactants A and B is as follows:

$$\text{rate} = k_M[A]_M[B]_M CV + k_M'[A]_M[B]_W CV + k_M''[A]_W[B]_M CV + k_W[A]_W[B]_W(1 - CV) \quad (21)$$

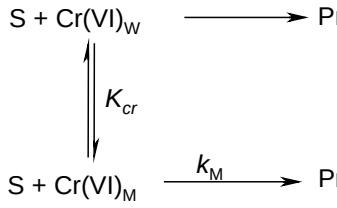
Here, $C = [D]_T - CMC$; where $[D]_T$ represents the total surfactant concentration (molarity), some authors have defined $C = ([D]_T - CMC)/N$ where N gives the aggregation number. V is the partial molar volume of the surfactant in the micelle (≈ 0.3 mol dm^{-3}) (Berezin, Martinek & Yatsimirskii, 1973); CV and (1 – CV) represent the fractions by volume of micellar phase and aqueous phase, respectively; the subscripts M and W stand for the quantities relating to the micellar phase and aqueous phase, respectively; k_M and k_W are the rate constants for the reaction occurring in the micellar phase and the aqueous phase respectively; k_M' stands for the rate constant of the reaction due to the encounter between the reactant A in the micellar phase and the reactant B in the aqueous phase; k_M'' refers to the exactly reverse situation.

Effects of Surfactants on the Kinetic Studies of Substrates by Hexavalent Chromium

Oxidation of malonic acid by Cr(VI), when exposed to the anionic surfactant SDS, the rate of the reaction is retarded. The slowing down of the reaction rate has been attributed to the partitioning behaviour of Cr(VI) species and the acid concentration across the aqueous and micellar phases. Findings suggest that the reaction takes place in the aqueous phase, where the H^+ concentration is significantly diminished.

To analyse the binding of one reactant (i.e. H_2CrO_4) to the micelle, the kinetic data has been interpreted using Berezin model (Berezin, Martinek & Yatsimirskii, 1973) (as depicted in Scheme 5).

The suggested reaction steps are shown in Scheme 5 is as follows:



Scheme 5

In the above Scheme Cr(VI) is H_2CrO_4 and 'S' is the organic substrate present at the interface. This rate law is given by

$$k_\Psi = (k_W + k_M K_{Cr} C)/(1 + K_{Cr} C) \quad (24)$$

The plot of $1/k_\Psi$ *vs* C gives that $k_W >> k_M K_{Cr} C$. Using Menger-Portnoy model (Menger & Portnoy, 1967), a proposed type of conclusion could be drawn. It is noted that the affinity of binding constant value of Cr(VI) is increased for the upscale value increase of H^+ concentrations. The Cr(VI) oxidation of cyclohexanol (Acharjee *et al*, 2019) in water acidic media was found to be catalysed by SDS.

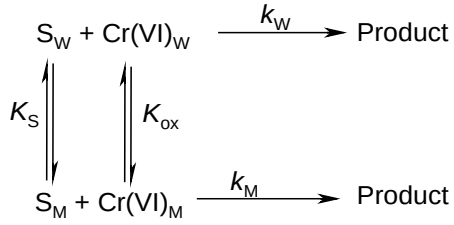
The rate enhancement phenomenon likely arises from the solubilisation of both the oxidant and substrate within the micellar phase of both the oxidant and substrate within the micellar phase, where the reaction predominantly occurs. The catalytic effect can be attributed to the increased solubilisation of the protonated Cr(VI)-cyclohexanol complex, positively charged micellar pseudo-phase through electrostatic attraction.

The kinetic data has been interpreted using Berezin's phase separation model, which is relevant when both reactants- $H_3CrO_4^+$ (consider kinetically active) and cyclohexanol- are strongly associated with the micellar phase. Graphical methods were used to estimate binding and rate constants. High binding constants and partition coefficients suggest that the substrate and oxidant bind to the micelle through hydrophobic and electrostatic interactions. However, the existence of $H_3CrO_4^+$ as a species is debatable.

In a water acid media kinetic analysis for Cr(VI) oxidation on lactic acid (Saha, Islam & Das, 2006) and dl-mandelic acid are performed by Sahu and Panigrahi (1996) with an anionic surfactant of Sodium dodecyl sulphate (SDS).

At CMC, oxidation rate is increased with the increase of surfactant concentration and decreased if further surfactant concentration is increased. The experimental findings indicate that the Menger-Portnoy model (Menger & Portnoy, 1967) fails to provide an adequate explanation.

Instead, by taking into account the distribution of the reactants- namely the organic substrates and H_2CrO_4, which are considered kinetically active-between the bulk aqueous phase and the micellar pseudo-phase, the kinetic data has been interpreted using Berezin's model. The proposed reaction mechanism is outlined below.



Scheme 6

In Scheme 6, the organic substrate 'S' represents lactic acid or *dl*-mandelic acid respectively and the active species H_2CrO_4 is represented byCr(VI). According to Berezin's approach, the rate equation is given by

$$k_\Psi = (k_W + k_M K_S K_{OX} C)/\{(1 + K_S C)(1 + K_{OX} C)\} \quad (27)$$

The symbols maintain their conventional meanings. Various rates and binding constants can be determined using Equation 27. The observed reduction in the rate at high concentrations has been analysed for compatibility with Piszkiewicz model (Piszkiewicz, 1977), which is linked to Hill model commonly used in enzyme catalysis studies.

The anionic surfactant, sodium dodecyl sulphate (SDS), is progressive for Cr(VI) oxidation on dialkyl sulphides (Ganesan, Rajagopal & Bharathy, 2000), while the cationic surfactant, cetyltrimethylammonium chloride (CTAC), slows down the rate of activity. This type of finding is explained by considering the fact that the reaction occurs in water as well as in the micellar phase simultaneously. The enhancement of reaction rate of sodium dodecyl sulphate (SDS) occurs through enhanced concentration of the local reactants in the micellar phase. In an acid-catalysed reaction H^+ ions are preferred to concentrate around the anionic micellar phase. The cationic surfactant, CTAC, slowly reacts because the approach of H^+ ions on the cationic micellar surface (both the reactants are concentrated) is unfavoured. The oxidation of an organic sulphide is because the electron transfer from sulphide to Cr(VI) to buildup positive charge on sulphur is not favoured for interaction with the cationic micellar top edge groups. The picolinic acid and bipyridine catalysed Cr(VI) oxidation of dimethyl sulfoxide have been found to be accelerated by sodium dodecyl sulphate (SDS, an anionic surfactant), and the rate is retarded by *N* –cetylpyridinium chloride (CPC, cationic surfactant). A similar micellar effect has been found in the Cr(VI) oxidation of formic acid (Das, 1999) in the presence of picolinic acid catalyst. In the presence of surfactant the rate retardation has been explained by considering the applicability of Piszkiewicz model (Piszkiewicz, 1977). The rate of Cr(VI) oxidation of cyclopentanol (Sahu & Panigrahi, 1996) with sodium dodecyl sulphate (SDS) is found to be decreased monotonically with increasing SDS concentration after the CMC. This observation is explained correctly with the Menger-Portnoy model (Menger & Portnoy, 1967) and its modified form (Bunton & Robinson, 1969), which considers solubilisation of one reactant only into the micellar phase. This modified Menger-Portnoy equation, which neglects the k_M-path (reaction in the micellar phase), is:

$$1/k_\Psi = 1/k_W + KC/k_W \quad (28)$$

Here, *K* is a binding constant of the species that is partitioned between the two phases, that is, aqueous and micellar. This is identified as $H_3CrO_4^+$. By using Berezin's equation (the k_M is not considered, and the relationship with other micellar phases is considered) for the determination of the binding constant, it nicely agreed with that obtained from Eqn. 28. The k_Ψ decreases exponentially with increasing K_2SO_4 concentration. The presence of K^+ and SO_4^{2-} ions around the Stern layer may result in an increase of surface potential of the micelle, which in turn facilitates the preferential accumulation of the active chromium species (*i.e.* $H_3CrO_4^+$) in the micellar pseudo phase. The rate of retardation with increase of K_2SO_4 concentration is due to depletion of the active chromium species. However, the existence of the species, $H_3CrO_4^+$ is questioned.

Scientists have studied how a chemical called sodium dodecyl sulphate (SDS), which forms tiny structures called micelles, affects the speed of a reaction where Cr(VI) is involved in breaking down different alcohols. They found that for alcohols that dissolve in water (like butan-1-ol, propan-2-ol, benzyl alcohol), the reaction speed increases as $[SDS]_T$ is added but only up to certain point-after that, adding more SDS slows it down. This happens because of a balance between charged particles (ions) in the reaction and how they interact with the SDS micelles. Rodenas and Perez-Benito (1991) conducted a study on alcohols that do not mix well with water, and for the same alcohols, such as hexan-1-ol and octan-1-ol, the pattern may differ. These reactions need an acidic environment to work. Additionally, other studies have looked at how different types of surfactants (Chemicals that help liquids mix) affect the same kind of reactions with various compounds like sugars, acids, and alcohols. They observed that a negatively charged surfactant like SDS speeds up the reaction, while a positively charged surfactant, such as N-cetylpyridinium chloride (CPC), slows it down. Adding certain helpers (chelating agents) can also speed up these reactions.

The reactions are acid catalysed. Recently, the effects of both anionic (i.e. sodium dodecyl sulphate, SDS) and cationic (i.e. *N*-cetylpyridinium chloride, CPC) surfactants have been studied for the Cr(VI) oxidation of different substrates, e.g. hexitols (Saha *et al*, 2004), diols (Das *et al*, 2001b), D-glucose (Bayen *et al*, 2005), D-fructose (Das, Roy & Saha, 2001; Islam, Saha & Das, 2005), L-sorbose (Islam & Das, 2008b; Saha *et al*, 2004), maleic acid (Islam, Saha & Das, 2007), *dl*-mandelic acid (Islam & Das, 2008a), etc., in aqueous acid media in absence and presence of different chelating agents like 2,2´-bipyridyl (bipy), 1,10-phenanthroline (phen) and picolinic acid (PA). It has been observed that the cationic surfactant *N*-cetylpyridinium chloride (CPC) retards the reaction rate, while the anionic surfactant sodium dodecyl sulphate (SDS) accelerates the reaction rate.

Rodenas and Perez-Benito (1991) have investigated that anionic surfactant sodium dodecyl sulphate (SDS) reverse micelles in hexan-1-ol, octan-1-ol or butan-1-ol on the oxidation of corresponding alcohol by Cr(VI) in water-perchloric acid medium. To explain the experimental findings, it was required to consider the intermicellar exchange of the reactants. The interaction is influenced by the thickness of the layer containing the surfactant and alcohol, which was determined using fluorescence quenching techniques.

Kabir-ud-Din, Iqubal and Khan (2005) and Kabir-ud-Din, Morshed and Khan (2002) have studied the micellar effects on the Cr(VI) oxidation of sugars. They observed that the

increase in concentration of anionic surfactants, sodium dodecyl sulphate (SDS), and non-ionic surfactant, octylphenoxypolyethoxy ethanol (TX-100), the oxidation rate increases. Rate enhancement in SDS micelles is decreased in the presence of Li^+, Na^+, NH_4^+ ions. Rate inhibition due to the presence of those ions can be explained by electrostatic considerations.

Effect of ionic micelles that propel the oxidation of citric acid by chromium(VI) continued with some workers (Hartani & Khan, 2000). They have proposed a one-step, three-electron oxidation mechanism. The rate decreases with the increase in concentration of the cationic surfactants cetyl trimethylammonium bromide (CTAB) and cetyl pyridinium bromide (CPB), while the anionic surfactant, sodium dodecyl sulphate (SDS) has no effect on the rate. The activation parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$) are significantly affected in the presence of CTAB or CPB.

Interpretation for the effects of surfactants on the kinetic studies of some organic substrates by hexavalent chromium.

It has been observed that different natures of graphs for the kinetic studies of some organic substrates by hexavalent chromium in the presence of surfactants. These works have already been published in a reputed journal (Islam, Saha & Das, 2005). Some of these research works have been presented here for interpretation of the effects of surfactants on the kinetic studies.

(A) Interpretation cationic surfactant (N-cetylpyridinium chloride) CPC concentration variation over organic substrates-a kinetic study:

The compound N-cetylpyridinium chloride exhibits inhibitory effects on the catalysed pathways. Observations of kobs plotted against $[CPC]_T$ (Figure 2) reveal a progressive decline, eventually plateauing at higher concentrations of CPC. This behaviour mirrors findings reported by Bunton and Cerichelli (1980) and documents similar effects during the electron release of ferrocene by ferric salts in the presence of the cationic surfactant cetyl trimethyl ammonium bromide (CTAB).

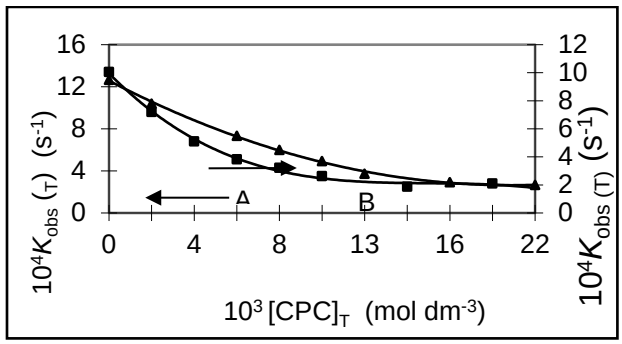
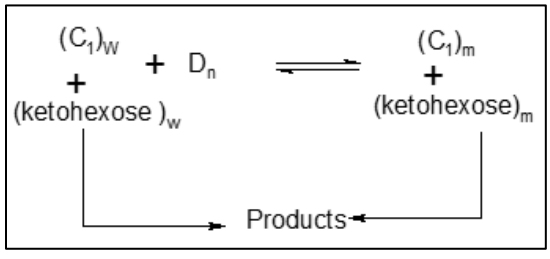


Figure 2: Effect of $[CPC]_T$ on $k_{obs(T)}$ for the Cr(VI) oxidation of D-fructose in the presence of bipy and phen in aqueous H_2SO_4 media (Islam, Saha & Das, 2005)

Experimental conditions:- $[Cr(VI)]_T$ = 4x10^{-4} mol dm^{-3}, $[H_2SO_4]$ = 0.5 mol dm^{-3}. (A) : $[phen]_T$ = 50x10^{-4} mol dm^{-3}, $[D\text{-fructose}]_T$ = 140x10^{-4} mol dm^{-3}, T = 40^{0}C. (B) : $[bipy]_T$ = 120x10^{-4} mol dm^{-3}, $[D\text{-fructose}]_T$ = 60x10^{-4} mol dm^{-3}, T = 50^{0}C.

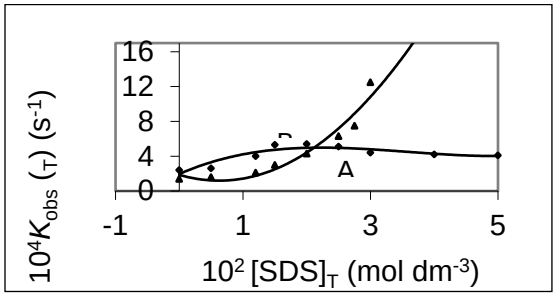
The findings align with the observations made by Sahu and Panigrahi (1996) regarding the oxidation of acetophenone by Ce(IV) in the presence of *N*-dodecyl pyridinium chloride (NDPC). In this process, cetylpyridinium chloride (CPC) limits the activity of the positively charged Cr(VI) catalyst complex, the active oxidising agent, in the water phase.

Consequently, the neutral substrate accumulated in the micellar phase (specifically, the Stern layer) does not contribute to the reaction. Therefore, the catalysed reaction is predominantly confined to the aqueous phase, where the substrate concentration diminishes due to its portioning into the Stern layer of the micelle. The portioning behaviour of the reactants between the aqueous phase and the micellar phase is illustrated in Scheme 7, where Dn signifies micellises surfactants, with 'n' denoting the aggregation number.



Scheme 7: Partitioning of the Reactive Species between the Aqueous and Micellar Phases

(B) Interpretation for the concentration variation of anionic surfactant, Sodium dodecyl sulfate (SDS) for the kinetic studies of organic substrates:



Source: Islam, Saha & Das, 2005

Figure 3: Effect of $[SDS]_T$ on $k_{obs(T)}$ for the Cr(VI) oxidation of D-fructose in the presence of bipy and phen in aqueous H_2SO_4 media

Experimental conditions:- $[Cr(VI)]_T$ = 4x10^{-4} mol dm^{-3}, $[H_2SO_4]$ = 0.25 mol dm^{-3}, T = 35^{0}C. (A) : $[D\text{-fructose}]_T$ = 50x10^{-4} mol dm^{-3}, $[phen]_T$ = 40x10^{-4} mol dm^{-3}. (B): $[D\text{-fructose}]_T$ = 60x10^{-4} mol dm^{-3}, $[bipy]_T$ = 40x10^{-4} mol dm^{-3}.

Sodium dodecyl sulphate (SDS) enhances the catalysed pathway by facilitating interactions between reactants and oxidants. The Cr(VI)-catalyst complex, a cationic species, is

considered the active oxidant, preferentially distributed in the micellar pseudo-phase of SDS due to electrostatic attraction. The presence of SDS starts a reaction for both micellar pseudo-phases for an increase of reactants, and the water phase promotes the rate of the observed reaction.

The plot of k_{obs} versus $[SDS]_T$ (*c.f.* Figs. 3) indicates continuous rate improvement for bipy-catalysed reactions with increasing SDS concentration. For phen-catalysed reactions, the rate initially rises with higher $[SDS]_T$, then reaches a limit followed by slight retardation. Rate acceleration is driven by preferential portioning of positively charged oxidants and neutral substrates into the Stern layer of micelles.

Conversely, at very high $[SDS]_T$ levels, rate retardation occurs due to reactant dilution within the micellar phase. Increased SDS concentration also raises micellar counterion (e.g., Na^+) levels, which could displace H^+ and Ox^{2+} ions from the micellar surface, affecting the reaction dynamics.

$$2Na^+_W + Ox^{2+}_M \rightleftharpoons 2Na^+_M + Ox^{2+}_W \quad (29)$$

$$Na^+_w + H^+_M \rightleftharpoons Na^+_M + H^+_w \quad (30)$$

The equilibria mentioned causes a reduction in the concentrations of $[HM]^+$ and $[OxM]^{2+}$, which in turn slows the reaction rate. These opposing effects influence the reaction rate in different ways. For the phen-catalysed pathway, the two effects essentially cancel each other out at higher surfactant concentrations, leading to rate saturation. However, in the bpy-catalyzed pathway, the solubilisation effect (first effect) dominates over the counterion effect (second effect) up to the maximum SDS concentration used.

Conclusion

The redox behaviour of chromium(VI) and its reduction to chromium(III), along with intermediate states, emphasises its biological significance and environmental impact. Understanding these reactions and their toxicological effects is essential for advancing safety measures and biochemical applications.

Furthermore, micellar systems and organised assemblies provide a valuable platform for studying electron transfer and reaction kinetics in heterogeneous environments. Their ability to emulate cellular membranes has profound implications for pharmaceutical science, enhancing drug delivery, bioavailability, and targeted therapy. Together, these fields underscore the importance of interdisciplinary research in chemistry, biology, and medical science to address pressing challenges and develop innovative solutions.

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