Summary

Surfactants, surface active agents or detergents are amphiphilic, organic or organometallic compounds which form association colloids or micelles in solution. Surfactants adsorb at an air-water or oil-water interface and at the surface of solids. The molecules of surfactants have two parts:

(i) Polar or hydrophilic group, and
(ii) Non-polar group or hydrophobic group

which can be a hydrocarbon chain or long alkyl chain joined with an aromatic ring. The polar group of the surfactants forms hydrogen bond with water molecules hence it is pulled by the aqueous media. The non-polar part is not attracted by water but it has affinity for organic substances like oil, fats and grease.

Micellar catalysis and inhibition of reaction can be divided into two types of reaction occurring e.g., base-catalyzed and acid catalyzed hydrolysis, oxidation in terms of mechanisms, e.g., position of reactive group in micelle, attraction of counter ions to an oppositely charged micellar surface, protection by solubilization within non-ionic micelles etc.

This thesis summarizes the oxidation of triphenyl methane dyes (AG, MV, BG, CV and AV), aromatic azo dyes (MR and MO) and indigo carmine by V (V) in aqueous sulphuric acid media in the absence and presence of cationic, anionic and non-ionic surfactants at different temperatures. The rate constant for the oxidation of various dyes with V (V) are pseudo first-order when \([V (V)] >> [\text{Dyes}]\). The pseudo first-order rate constant increases with increase in the concentration of V (V). The pseudo first order rate constants are independent of the initial concentration of dyes. The rate increases with the increase in \([\text{H}^+]\) ion concentration. The result shows the effect of temperature tended to pronouncedly increase the oxidation of different dyes. The observation remains unaltered in presence of added surfactants.

The pseudo first-order rate constants for SDS and SDES catalyzed reaction for oxidation of dyes (AG, MV, BG, CV, AV, MR, MO and IC) do not vary linearly as the reaction in aqueous phase. The pseudo first-order rate constant \((k_{obs})\) increases, reaches the maximum and thereafter it decreases with the increase in the concentration of the surfactant. The increase in rate may be due to mixed micelle formation of the dye molecules and surfactant molecules which bears a negative charge thereby attracting the \([V (OH)_3\text{HSO}_4]^{+}\) species. It has been shown that concentration of reactants into a small bulk at the micellar surface is a major source of
enhancement of bimolecular reactions. Thus with increase in the concentration of SDS and SDES, the rate increases and attains a maximum value. With further increase in the concentration of SDS and SDES produces increase in the concentration of unreactive counter ions Na\(^+\), that displaces the H\(^+\) or [V (OH)\(_3\)HSO\(_4\)]\(^+\) ion in the proximity of the bound dye molecules in the micelles. This may be accounted for the decrease in the rate constant at higher surfactant concentration. The effect of varying the concentration of V (V) has been studied in presence of fixed surfactants concentration for various dyes. It indicates that overall catalysis factor slowly increases.

The rate constant of the SDS and SDES catalyzed reaction in presence of added salts viz., KCl, NaCl, KBr and Na\(_2\)SO\(_4\) has also been studied. Various salts strongly retarded the oxidation of anionic catalysed dyes. It is found that initially rate decreases and become almost constant with increase in the concentration of salts. The order of retardation with respect to anion is as follows:

\[
\text{SO}_4^{2-} > \text{Br}^- > \text{Cl}^- > \text{no salt.}
\]

Hence the observed retardation in the presence of electrolytes may be due to the interaction between anion of the salt with the positively charged species [V (OH)\(_3\)HSO\(_4\)]\(^+\) and a less reactive species may be formed.

The kinetics of the oxidation of TPM dyes has also been studied in presence of cationic surfactants (C\(_{16}\)TABr, TTABr and CPyBr). The rate constant decreases as the concentration of the surfactant increases. In presence of cationic surfactants, inhibitory effect may be due to non approachability of [V (OH)\(_3\)HSO\(_4\)]\(^+\) ion to the bounded substrate in the cationic micelle of similar charge. At very low cationic surfactant concentration well below the CMC, the inhibition rate for the oxidation of TPM dyes are explained in terms of “monomeric-dye-cationic surfactants oligomer” interacted product [110]. The retardation in the reaction rate by cationic surfactants in the premicellar concentration region may be assumed with the formation of “monomeric-dye-cationic surfactants oligomer”. At lower concentration of cationic surfactants bearing a positive charge on it which would repel the attacking [V (OH)\(_3\)HSO\(_4\)]\(^+\) species Hence the cationic surfactants retarded reaction rate in the premicellar region. The decrease in the rate of the reaction is in following order:

\[
\text{CTAB} < \text{TTAB} < \text{CPyB}
\]
Non-ionic surfactants (Triton X-100, Triton X-102, Tween-80, Pluronic-68, Pluronic-88 and Pluronic-98) inhibited the rate of oxidation of various dyes (AG, MV, BG, CV, AV, MR, MO and IC) by V (V). The rate decreases rapidly and then becomes almost constant with the increase in the non-ionic surfactant concentration. It has been found that non-ionic surfactants have good affinity for these dyes, to form complex, the nonionic surfactant does not carry any ionisable groups so that the binding has to be accomplished by inter molecular forces, possibly consisting of mixed micelles, involving both dye and surfactant. The fast decrease in the rate may be due to the strong complex formation between the dye and surfactant. The decrease in the rate constant is in the following order.

Triton X-100 < Triton X-102 < Tween-80
Pluronic-98 < Pluronic-88 < Pluronic-68

The effect of various solvents viz., acetic acid and acetone on different dyes have been studied at fixed concentration of various surfactants, at fixed concentration of dye and V (V) ion. In the micellar environment of cationic surfactants viz., CTAB, TTAB and CPyB, the extent of inhibition diminishes with increasing solvent percentage in the reaction system. The extent of reducing the overall inhibition for the reaction is more for acetone than acetic acid.

Acetic acid < Acetone

Complete destruction of catalytic micelle by solvents may also be ruled out in the presence of solvent the electrostatic as well as hydrophobic interactions among the species present in the reaction system would continue to exist, and also the concentration of solvent in the reaction system is too low to cause such effects. It appears more probable that some reorganization in the structure of catalytic micelles might take place. In the formation of new catalytic aggregates, substrate, surfactant and solvent molecules might participate resulting in reorganization of reactants’ concentrations at the reaction sites and a modification in the thermodynamic parameters of the reactions, which is manifested in diminishing the effectiveness of cationic surfactant on the reaction rate. Breaking of water and consequent destabilization of [V(OH)\textsubscript{3}HSO\textsubscript{4}]\textsuperscript{+} ion may be another contributory factor for such effects. However, the destabilization and selective solvation reaction plays an important role in affecting the rate.
It may be seen that the addition of acetone and acetic acid with different dyes (AG, MV, BG, CV, AV, MR, MO and IC) to the reaction system reduces the overall catalysis by SDS and SDES. It may be noted that acetic acid is more effective than acetone in reducing the overall catalysis of these reactions by SDS and SDES.

\[
\text{Acetic acid} \quad < \quad \text{Acetone}
\]

The kinetics of the reaction of varying concentration of solvent-water mixture in presence of fixed concentration of non-ionic surfactants and the substrate has been studied at 30°C. It is observed from these kinetic data that the addition of solvents to micelle-affected reaction markedly diminishes the overall inhibition caused due to presence of non-ionic surfactants. The effectiveness of solvents reduced the extent of overall inhibition is found to increase in the following order:

\[
\text{Acetone} \quad < \quad \text{Acetic acid}
\]

The participation of solvent molecules in reorganizing the structure of micellar aggregates seems to be responsible for the observed effect, which result in the reorganization of \([V (OH)_3 HSO_4]^{+}\) at reaction sites.

The effect of temperature on the reaction of different dyes (AG, MV, BG, CV, AV, MR, MO and IC) with V (V) ion has been studied at fixed concentrations of surfactant, substrate and V (V). The reaction is found to obey Arrhenius equation. The plot of log \(k_{\text{obs}}\) versus \(1/T\) in absence and presence of surfactants are linear. The values of activation parameters viz., \(E_a^\#, \text{ frequency factor } Z, \Delta S^\#, \Delta H^\#, \Delta G^\#\) have been calculated. The values of activation energies obtained from the slopes of Arrhenius plots for SDS and SDES catalysed reaction and for CTAB, TTAB, CPyB and Triton X-100, Triton X-102, Tween-80, Pluronic-68, Pluronic-88 and Pluronic-98 inhibited reactions in aqueous solutions suggest that a decrease in activation energy in presence of anionic surfactants (SDS and SDES) relative to aqueous medium is one of the factors responsible for the catalysis and a higher activation energy in presence of cationic (viz., CTAB, TTAB, CPyB) surfactants and non-ionic (viz., Triton X-100, Triton X-102, Tween-80, Pluronic-68, Pluronic-88 and Pluronic-98) surfactants as compared to those in absence are consistent with the fact that the reaction is inhibited in presence of cationic and non-ionic surfactants. Nearly same values of \(\Delta G^\#\) in absence and presence of surfactants shows that similar mechanism for oxidation is operative in aqueous and micellar media. The values of \(\Delta S^\#\) in all systems are negative indicating that the reaction is occurring between ionic species. Micelles do
not alter the mechanism of the reaction but only effect the reaction rate. The values of $\Delta S^\#$ and $E_a^\#$ follow the order.

Anionic surfactants < Without surfactants < Non ionic surfactants

The value of frequency factor in presence and in absence of ionic and non ionic surfactants shows that the large number of collisions are required to produce the forward reaction in the presence of cationic (viz., CTAB, TTAB and CPyB) and non ionic surfactants (viz., Triton X-100, Triton X-102, Tween-80, Pluronic -68, Pluronic -88, Pluronic -98) where as lesser number of collision result in forward reaction in the presence of anionic surfactants (viz., SDS & SDES).

The kinetic results of enhancement of the rate constant by anionic surfactant (SDS, SDES) and retardation of the rate constant by cationic surfactant (viz., CTAB, TTAB and CPyB) and non-ionic surfactants (viz., Triton X-100, Triton X-102, Tween-80, Pluronic-68, Pluronic-88 and Pluronic-98) surfactants have been rationalized on the basis of a model proposed by Bruice et. al. and applied by Piszkiewicz. A plot of $\log (k_w - k_{obs}) / (k_{obs} - k_m)$ versus $\log [C_D]$ is found linear with a slope ($n$) called the index of co-operativity. Values of $\log [D]_{50}$ represent the concentration of detergent required for half maximal catalysis or inhibition of reaction. This demonstrates the existence of function sub-micellar aggregates involving detergent and substrate molecules of varying stoichiometries. The value of $n >1$ indicates positive co-operativity, which implies the stimulation of additional molecule by interaction of the first molecule with the micelle. The values of binding constants ($K_b$ which is reciprocal of $K_D$) for non ionic surfactants are higher than anionic and cationic surfactants. In presence of SDS and SDES catalysed effect is observed due to approachability $[\text{V (OH)}_3\text{(HSO)}_4]^+$ to the strongly bound substrate in the catalytic aggregate of opposite charge and due to the stabilization of ground state of dyes.

However in presence of cationic surfactants (viz., CTAB, TTAB and CPyB) inhibitory effect is observed due to the non approachability of $[\text{V (OH)}_3\text{HSO}_4]^+$ active species to the strongly bound substrate in the catalytic aggregate of similar positive charge.

However the inhibition in case of Triton X-100, Triton X-102, Tween-80, Pluronic-68, Pluronic-88 and Pluronic-98 may be due to strongly bound substrate in
the catalytic aggregates of substrate and surfactant aggregate as there is no electrostatic attraction between aggregate and positive oxidant species.