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Reactivity Controlling Influence of Self-Aggregating Amphiphilic Systems: Recent Developments

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Abstract

Surfactants are amphiphiles containing both hydrophobic tails and hydrophilic heads assemble to form organized assemblies referred as micelles. Micelles having multitude of applications are suitable candidates to catalyze processes involving organic transformations in organic solvent free conditions owing to the presence of different regions in and around micellar structure. Its applications spectrum ranges from synthetic organic chemistry, environmental science, pharmaceutical sector and many industrial processes besides academic research. Micellar catalysis poses as an efficient and a versatile methodology for altering the rates of reaction by developing a micro-heterogeneous medium that can mimic very well biological processes and can facilitate inefficient interactions. In recent years, the application of micellar catalysis by academia and industry people have seen a tremendous growth because of its superior catalytic performance in a clean and green manner that addresses environmental concerns. Micelle mediated electron transfer reactions can be performed to imitate various catabolic and metabolic processes and understanding the kinetics and mechanism of such oxidation reactions bears significance and different kinetic models suitably demonstrate the nature of such micelles that would otherwise act as a catalyst. In this review a comprehensive discussion on the nature and applications of surfactants molecules aggregating to micelles have been presented from the recently published literatures.

Keywords: Amphiphiles, Oxidation, Micelles, Catalysis, Kinetics, Critical micelle concentration.

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Introduction

Surfactants, commonly referred to as surface-active agents, are chemicals that greatly reduce surface tension in between two liquids, or between a liquid and a solid making them extremely useful in a variety of applications-from cleaning products to pharmaceuticals. Surfactants have a hydrophilic (water-attracting) head and a hydrophobic (water-repelling) tail; the defining feature of the surfactants. This amphiphilic structure allows them for their interaction with water and oils as well. Four major classes of surfactants have been identified according to the character of the charge on their hydrophilic head, including: anionic surfactants with negative charge bearing head group, cationic surfactants with positive charge bearing head group, non-ionic surfactants with no charge on the head group and zwitterionic surfactants with both positive and negative charges in the same molecule [1-3]. **Figure 1** shows the structure of some representative surfactant molecules. Expectedly, these amphiphiles work by aligning themselves at the interfaces of different phases (e.g., oil and water), where their hydrophobic tail groups remain in contact with oils or non-polar substances, whereas the hydrophilic head groups with water. This lowers the surface or interfacial tension [4-6], thus permitting processes like emulsification, foaming, and detergency. The amphiphilic materials act as stabilizers during the synthesis of nanoparticles by preventing the agglomeration, control the morphology as well as size. Surfactant based drug formulations are employed in drug delivery due to their ability to encapsulate hydrophobic drugs and improve bioavailability. This review presents a detailed analysis of surfactant aggregation besides its applications in the fields of synthetic organic reactions, electron transfer reactions, pharmaceuticals and nanotechnology as well. In all such cases, mediation of the processes through catalysis, solubilizing or stabilizing agent by surfactants in segregated or aggregated form is observed.

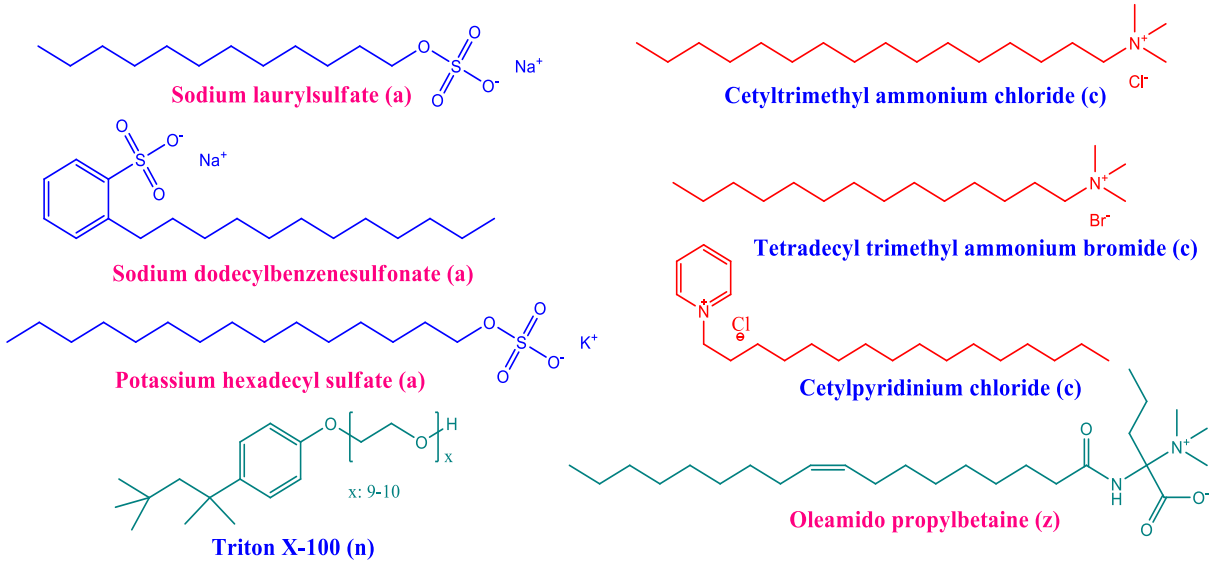


Figure 1 Structure of selected surfactant molecules of common use. a: anionic, c: cationic, n: non-ionic and z: zwitterionic.

Application of surfactants

Surfactants play a critical role in the chemical industry where their specific properties are exploited in a variety of processes and products. They can be used to change surface and interfacial properties or help in improving the formulation of products to facilitate a wide variety of industrial operations.

- Surfactants are used as emulsifiers in paints, coatings, adhesives, and agrochemicals industries to make stable emulsions of liquid mixtures that don't otherwise mix [7-9]. This is quite important to be used in product performance and durability point of view.
- Surfactants as wetting agents are added into the formulation to enhance spreading and penetration of liquids through solid surfaces. This is important especially in industries that require fast and uniform spreading of liquids for processes like coatings, inkjet printing, and metal treatment (cleaning and electroplating) [10-11].
- As wetting agents, surfactants are used for the formulation of tablets and capsules used in the pharmaceutical industries as they improve the solubility of drugs and enhance bioavailability [12-18].
- Surfactants are considered to be quite essential as dispersants as they stabilize suspensions of solid particles in liquids to avoid agglomeration; therefore, this is important for paints [19], ceramics [20], and pharmaceutical applications.
- In oil recovery, foaming surfactants [21-22] improve the displacement of oil from porous rock formations. These amphiphilic agents as foaming agents are used to create a foam blanket that expands over the surface of the fuel to asphyxiate it from oxygen.
- Surfactants can be used as anti-foaming agents in the processes like fermentation, treatment of waters and the production of paper.
- These amphiphilic agents find their use in the field of nanotechnology [23-31] to regulate the size and shapes of nanoparticle synthesized in an economic and inexpensive manner. They stabilize the formation of nanoparticles, preventing them from aggregating and permitting a finite degree of control over the size and structure of the formed nanoparticles.

In emulsion polymerization, surfactants stabilize the particles of polymer, control the particle size of the resulting product, and facilitate the polymerization process. Surfactants are used as corrosion inhibitors [10-11] in industries where metallic surfaces require protection against environmental aggression in the form of moisture, acid or salt by depositing a protective layer on the metallic surfaces. Surfactants have major impacts in biotechnology and pharmaceutical industries in order to enhance the solubility, mode of delivery, and stability of products. Surfactants offer prevention of protein aggregation in formulations by ensuring the stability and efficacy of a biopharmaceuticals. Surfactants improve the poor bioavailability of drugs by forming a micelle that incorporates the drug molecule, which consequently enhances its absorption [32-33]. We have carried out and reported the solubilization studies of 8-hydroxyquiniline [12] and ibuprofen [33] in presence of both SDS and CTAB. In both cases of the study, in the pre-micellar region of concentrations of the amphiphiles, there was initial rise in absorbance with concentration of the

surfactant. The absorbance so also the solubility reached a maximum but around the cmc of the surfactant it fell and rose again. As the surfactant concentration was increased further, the trend of increase of absorbance and so also the solubility beyond cmc has continued with anionic surfactant but in case of cationic surfactant (CTAB) double maximum was observed. The second maximum in the plot of absorbance vs the concentration of CTAB was observed once the [CTAB] crosses the value of cmc. The appearance of a maxima in the pre-cmc region was explained on the basis of a complex formation among drug and surfactant monomers. This probably has resulted in the solubility enhancement. With the increase in the concentration of surfactants, the process of micellization starts and hence surfactant monomers isolate themselves from the drug-surfactant complex thereby decreasing the solubility. In the post-cmc state, the solubility enhancement may attributed to the binding of the drug on to the micellar surface likely due to electrostatic nature of interactions. In pure aqueous medium, it's quite challenging to do synthetic organic reactions because of the poor solubility of organic. Organic reactions most often proceed with the formation of water-sensitive highly unstable intermediates like carbo cations, carbanions, carbenes. Progress of the reaction, efficacy of the processes, yield of the product mostly depends on the formation and stability of these intermediates in the reaction medium. Micelles, acting as a bi-phasic material can protect and stabilize the intermediates formed from the aqueous solvents enabling the desired synthesis and hence are used a reaction medium [34-38]. Micelle mediated organic transformations can be pursued under conditions which are totally free from organic solvents and reduce the carbon footprint. These micelles can have multitude of roles like solvent, catalyst, promoter or ligand [39-42]. In the pharmaceutical industry, solvent waste generated during API (active pharmaceutical ingredient) synthesis is one of the challenging issues as they pose a serious threat to our environment by contributing to contamination of water bodies. With the numerous applications (**Figure 2**) of surfactants, their ability to contribute towards more efficient, sustainable, and advanced chemical processes in a cleaner and greener method keeps progressing.

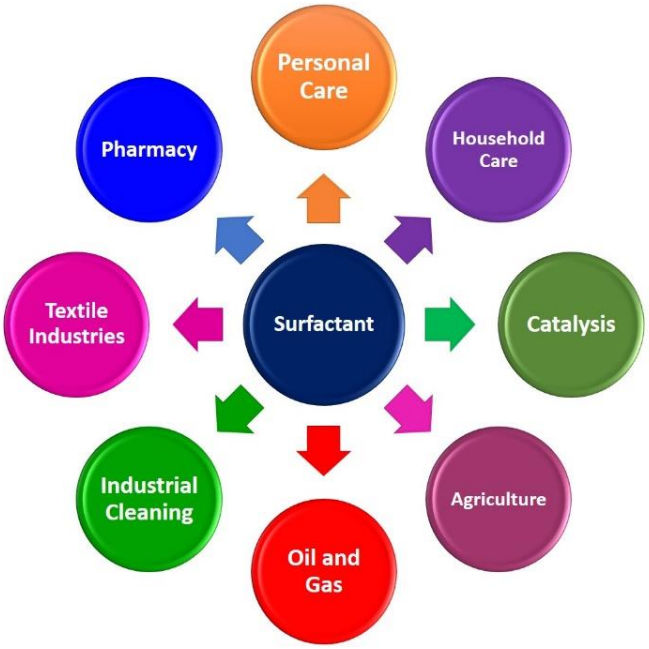


Figure 2 Diversity in the application of surfactants

Surfactant to micelle conversion

The conversion of surfactants to micelles is an important process, taking place at a specific concentration of surfactant molecules regarded as critical micelle concentration (cmc). It is based on the amphiphilic character of the surfactant molecule, which naturally has a part hydrophilic or water-loving and the other hydrophobic or water-hating. The polar or charged part interacts with water, whereas the non-polar, hydrocarbon chain that dislikes water and prefers oils or non-polar substances [43-45]. This results in the aggregation surfactant molecules in a spherical shape in an aqueous solution defined as the micelle. In this configuration, the hydrophilic heads are oriented toward the water, whereas the tails being hydrophobic are oriented to be interior away from water, forming a hydrophobic core. The cmc of some commonly used surfactants [46] is presented in **Table 1**. At relatively low concentrations, the individual surfactant molecules are in solution as monomers where their hydrophilic heads interact with the water, but their hydrophobic tails avoid contact with each other. If more surfactant monomers accumulate at the surface it reduces the surface tension of water due to the hydrophobic tails that extend out from the water and hydrophilic heads that remail in contact with the water. With continued addition of more and more surfactant, the solution eventually saturates. As the concentration of

monomers at the air-water interface and in bulk solution reaches equilibrium, the surfactants spontaneously tend to minimize the unfavorable interaction between their hydrophobic tails and water and form micelles. At the center of the micelle are the hydrophobic tails, while the hydrophilic heads face outward into the aqueous environment. Once micelle formation is underway, any further surfactant added to the solution goes on to associate into more micelles, while the concentration of individual surfactant monomers remains approximately at a saturation value known as cmc. As the concentration of the surfactant is increased beyond the cmc, the size and number of the micelles increase. Longer hydrophobic tails lower the cmc as they increase the driving force for hydrophobic aggregation. On the other hand, bulky or charged head groups may raise the cmc. Sometimes a higher temperature lowers cmc because thermal motion favors micelle formation by enhancing hydrophobic interactions. In the case of ionic surfactants, the addition of salts lowers the cmc by screening the repulsive forces between charged hydrophilic heads. The cmc is lower in highly polar solvents such as water because the hydrophobic effect that favors the micelle formation is stronger [1-3]. A clear understanding of the process of micellization can be made by determining the thermodynamic parameters of micellization viz., ΔG_{mic} (free energy of micellization), ΔH_{mic} (enthalpy of micellization) and ΔS_{mic} (entropy of micellization). The reported data [2] indicate that the negative values of ΔG_{mic} and it is attributed to large positive values of ΔS_{mic}. Very often ΔH_{mic} is found to be positive and even if it is negative, is lesser than that of $T\Delta S_{mic}$. Hence, the process of micellization is governed mainly by the increase in entropy associated with it. The driving force for this entropy change is the affinity of the lyophobic group of the surfactant to move from the solvent atmosphere to the inner layers of the organised assemblies. It is quite evident that the factors affecting the solvent-lyophobic group interactions or any such interactions among the lyophobic groups in the inner layer of the micelles will influence the free energy of micellization and so also the cmc of the surfactant.

Table 1 Critical micelle concentration (cmc) and aggregation number of some representative surfactants measured at 25°C. c: cationic, a: anionic, n: non-ionic, z: zwitterionic

Surfactant Name	cmc (mol dm^{-3})	AN[#]
Dodecylammonium chloride (c)	1.5×10^{-2}	55.5
Decyltrimethylammonium bromide (c)	6.5×10^{-2}	48
Dodecylpyridinium bromide (c)	1.1×10^{-2}	86
Hexadecylpyridinium chloride (c)	9.0×10^{-4}	95
Cetyltrimethylammonium bromide (c)	9.2×10^{-4}	61
Sodium dodecyl sulphate (a)	8.1×10^{-3}	62
Sodium dodecyl sulfonate (a)	9.8×10^{-3}	54
Sodium dodecanoate (a)	2.4×10^{-2}	56
Polyoyethylene (6) octanol (n)	9.9×10^{-3}	32
Polyoyethylene (6) decanol (n)	9.0×10^{-4}	73
Tween 80 (n)	1.3×10^{-3}	60
Brij 35 (n)	6.0×10^{-5}	40
Sodium cholate (z)	10.2×10^{-3}	3-16

[#] Aggregation number (AN) is the average number surfactant molecules per micelle

Reverse micelles get formed in non-aqueous media in which hydrophobic tails come outwards where they interact with a non-polar solvent, whereas the hydrophilic heads stay inside and provide a water-filled core. These structures have useful applications in enzyme catalysis in non-polar solvents. The shapes of micelles vary depending on such factors like surfactant concentration, temperature, and surfactant molecular structure, micelles can also adopt cylindrical (rod-like) or lamellar (disk-like) structures. The conversion of surfactant molecules to organize assemblies is presented in **Figure 3**.

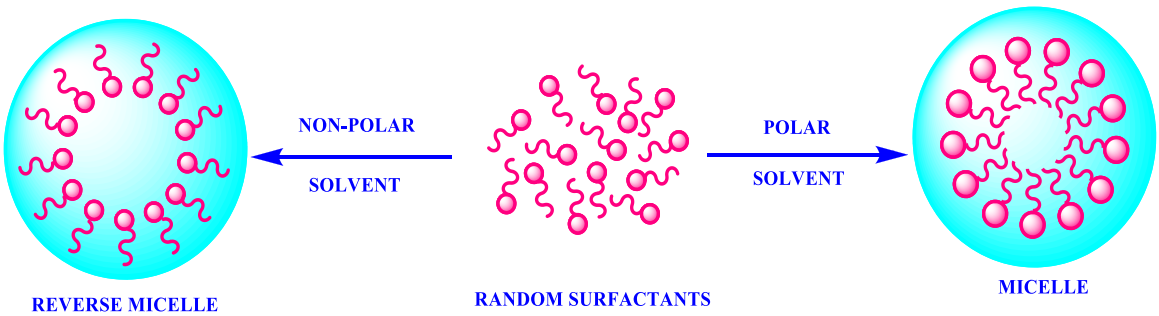


Figure 3 Formation of spherical micelles from surfactant monomers

Micellar layers

These micelles possess layers (**Figure 4**) that vary in character based on their polarity and hydrophobicity of the surfactant molecules from which they origin. It is, thus, essential to study these layers so as to understand their function in processes such as solubilization, micellar catalysis, drug delivery, and so forth. The core of a micelle is the innermost layer. This region is occupied by the hydrophobic (non-polar) tails of the surfactant molecules. This represents the main body of micelles, which primarily comprises the long hydrophobic hydrocarbon chains of the surfactant [1-3]. These tails associate together to avoid contact with water, thus producing a strongly hydrophobic environment within the core of the micelle. The core of the micelle is able to solubilize non-polar substances, such as oils or hydrophobic organic molecules that are otherwise insoluble in water. Such a capability to trap hydrophobic molecules makes micelles useful in applications such as detergency, drug delivery, and catalysis. The palisade layer, also regarded as the interfacial region or the micellar shell, is the intermediate layer between the core and the outer surface of the micelle. This layer contains head groups of the surfactant molecule and some molecules of water which penetrate inside the micelle. It further also comprises partially hydrated hydrophilic groups and partially solvated hydrocarbon chains, close to the surface of the core. Catalytic reactions tend to take place widely in the palisade layer, as it is the interface between the aqueous phase and the hydrophobic core of the micelle [47-50]. This layer is intermediate in polarity, thus stabilizing both hydrophilic and hydrophobic species with respect to their nature and the type of the surfactant used. For an ionic surfactant, charged head groups along with first few members of the carbon chain constitute the palisade layer. These negative charged groups pull the oppositely charged species or counterions from the surrounding aqueous environment in which the micelle is dissolved. These, therefore can affect the properties of the micelle and its reactivity. Many organic molecules are solubilized in this region because of its intermediate polarity and this makes the palisade layer important in processes of solubilization and micellar catalysis as well. The outermost layer of the micelle thus consists of the hydrophilic (polar) head groups of the surfactant molecules. Thus, the surface of the micelle is made up by the hydrophilic head groups oriented outside in the direction of the surrounding aqueous environment. These head groups interact with the surrounding water molecules; hence, the micelle is soluble in water. Depending on the type of surfactant, the surface of the micelle may be negatively charged (anionic surfactants), positively charged (cationic surfactants), or neutral in the non-ionic surfactants, such as Tween or Triton. The Stern layer is a layer close to the surface of the micelle, in which a tightly bound layer of counterions resides. This layer is especially critical for ionic surfactants. In the case of ionic surfactants, counterions from the solution are attracted to the oppositely charged head groups of the surfactant. These counterions form a tightly bound layer near the micelle surface. The diffuse layer, also termed as the Gouy-Chapman layer, envelops the Stern layer. It contains counterions that are more loosely bound to the micelle surface as those in the Stern layer and are free to move around. The concentration of counterions decreases as the distance from the surface of the micelle increases. The diffuse layer along with the Stern layer creates around a micelle. The double electric layer is in charge of stabilizing the micelles, by the balancing of the charges held on the surface of the micelle.

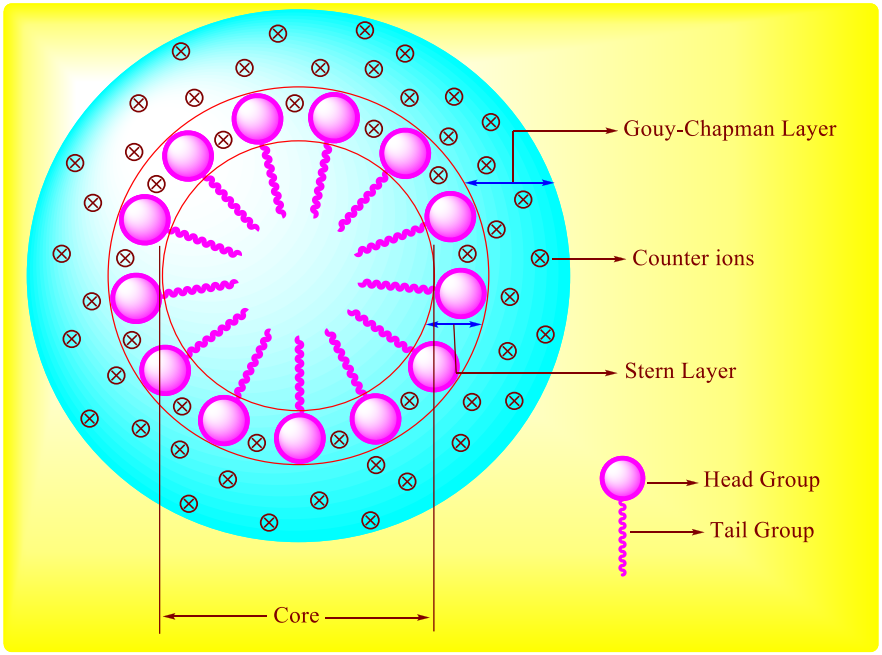


Figure 4 Anatomical view of shrerical micelle in aqueous medium

Methods to determine CMC

There are several experimental techniques to determine the cmc [46] based on changes in physical, chemical, or optical properties of the solution. Perhaps one of the most direct methods of determining cmc is the measurement of electrical conductivity of the solution as a function of surfactant concentration. This technique is applicable for ionic surfactants, which dissociate to ions. Below the cmc, monomers of surfactant in solution contribute to the conductivity of the solution. Above the cmc, micelles form which decrease the number of free ions in the solution and, therefore decrease the rate of increase of conductivity (**Figure 5**). It can be determined by taking the surface tension of the solution again as a function of concentration of surfactant. Surface tension is decreased with the increase in concentration of surfactant because the surfactant molecules line up at the air-water interface. Now, with the enhancement of concentration of surfactant beyond cmc, there is no more decrease in surface tension because extra surfactant molecules form micelles rather than occupying the surface. Light Scattering, Fluorescence Spectroscopy, Osmotic Pressure Measurement, NMR Spectroscopy, Turbidity Measurement are some other techniques through which cmc determination can be carried out.

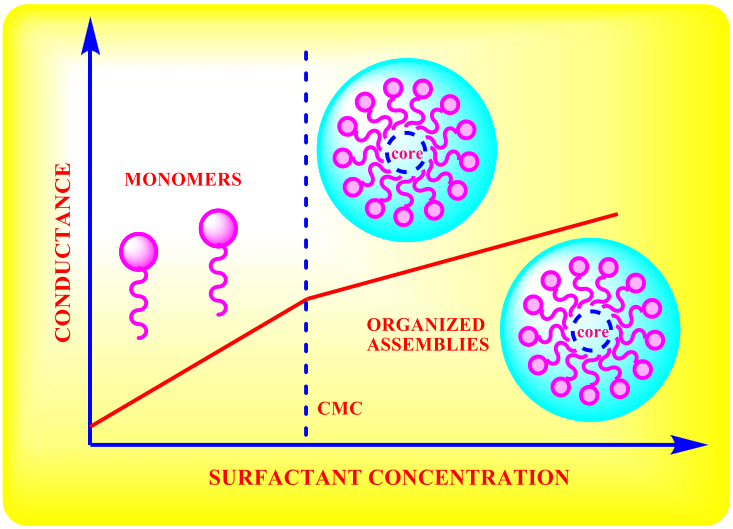


Figure 5 Conductance – [surfactant] profile showing the transformation of random surfactant molecules into micellar aggregates.

Role of micelles in reaction medium

Micelles as catalysts provides a powerful and versatile tool for elevating the reaction rates by creating unique microenvironments which mimic biological systems or facilitate interactions that are otherwise inefficient. Its applications span organic chemistry, environmental science, and drug development, making it an important strategy for both research and industrial processes [51-56]. In the aqueous medium, catalysis by normal micelles and by reversed micelles in the nonpolar solvents is the usual phenomenon. The reaction rate enhancement in normal micelles in an aqueous medium is always, though not always, at the interface of the micelle–aqueous solution. The reactions occur deep in the inner core of the micelle in reversed micelles in a non-aqueous medium. The influential role of micelles of either type on organic reactions may be well explained by the action of electrostatic and hydrophobic interactions. The interaction of electrostatic nature may influence the reaction rate either by virtue of its effect on the transition state of the reaction or by influencing reactant(s) in the proximity of the site reaction. Presence of micelles in the reaction medium can influence the reaction rates through the phenomenon such as (i) enhancing the local concentration of reactant species, thereby making hydrophobic reactants more likely to get partitioned into the hydrophobic core of the micelle and polar or ionic entities tend to associate with the hydrophilic surface. This enhanced local concentration inside or closer to the micellar aggregates increases the chances of collisions among the reactants, thereby speeding up the reaction (ii) altering the microenvironment as a result of which the hydrophobic core provides an organic-like medium in aqueous solution phase that can stabilize transition states or intermediates involved, which are otherwise unstable in water. Also, micelles create non-polar, polar, or ionic domains that can selectively stabilize some reactants or intermediates species formed, thereby lowering the mandatory energy required for some reactions (iii) solubilizing the hydrophobic or water-insoluble participants of the reaction that enables reactive interaction between otherwise immiscible components in aqueous media, such as reactions between organic substrates and water-soluble reactants and hence catalyze the process (iv) by partitioning and orientation or positioning of reactants within the micelle which can lead to selective interactions that facilitates progress of the reaction. The reactants can be "trapped" in a favorable

orientation or close proximity to one another, raising the rate of reaction (v) under the prevailing conditions of pH and ionic strength that may differ appreciably from the bulk solution. **Figure 6** shows the probable locations of the entities in the micellar volume participating during a micelle mediated reaction.

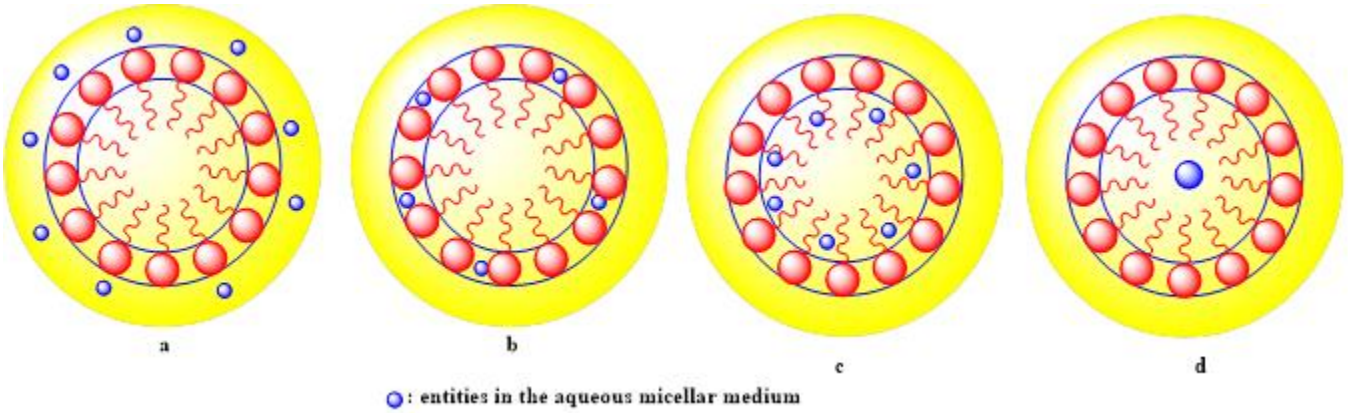
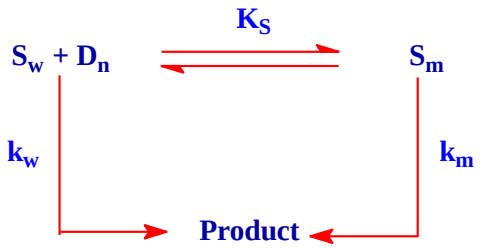


Figure 6 Possible loci of substrates basing on its nature in the micellar structure. a: Gouy-Chapman layer, b: Stern layer, c: Palisade Layer, d: inner core

The profile of rate constant vs [surfactant] very often display a rate maximum at some [surfactant] near about the cmc. Initially, the number of organized assemblies formed increases with rise in the surfactant concentration. When the number of micelles which are needed to dissolve the substrates present gets formed, further increase in the concentration of the surfactant results in dilution of substrate per micelle [58-61]. This explains the fall in the rate constant after the maximum. Moreover, when an ionic surfactant is used in the reaction media, the charged micellar surface is responsible for the enhanced concentration of oppositely charged reactant species at the interface of micelle and bulk aqueous phase through adsorption as well as solubilization into the micelle. Such act of solubilization and/or adsorption of the entities of the reaction will render in reduction of their reactivity in the solution phase. Enhancement of [surfactant] beyond the requirement of solubilization for all reactants is likely to cause the decrease of rate constant, even though rate enhancing activity by such micelles have been observed for reactions under consideration.

Key kinetic models

Several kinetic models have been proposed to explain the process of micellar catalysis based on how surfactants do interact with substrates in the reaction medium and the manner in which these interactions affect reaction mechanisms. The catalysis and solubilization of substrates (S) in aqueous micellar phase may be explained by the pseudo-phase kinetic model developed by Menger and Portnoy [57, 62-66]. According to the model (**Scheme 1**), the substrate is thought to be distributed between the aqueous and micellar phase.



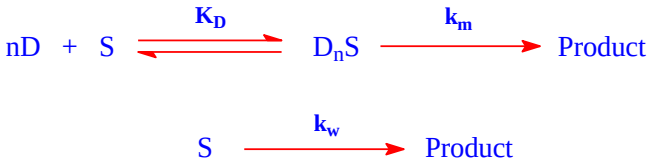
Scheme 1 Menger-Portnoy model of micelle mediated reaction

In Scheme-7, K_S is the binding constant of the substrate with the micelle, D_n represents the micellized surfactant, k_w and k_m are the rate constants in water (w) and micellar (m) phase respectively. The observed rate constant is computed as

$$\frac{1}{k_\psi - k_w} = \frac{1}{k_m - k_w} + \frac{1}{(k_m - k_w)\, K_S\, [D_n]} \qquad (1)$$

Equation-1 predicts that the plot of $(k_\psi - k_w)^{-1}$ vs $[D_n]^{-1}$ (D_n = ([D]-cmc) should be linear and fetches the values of K_S and k_m. Micellar catalysis at lower surfactant concentrations has been well explained by a model developed by

Piszkiewicz [67-71] also regarded as co-operative model (**Scheme 2**). According to this model, substrates (S) aggregates with "n" number of surfactant (D) molecules to form D_nS (critical micelles) which subsequently react to form the product.

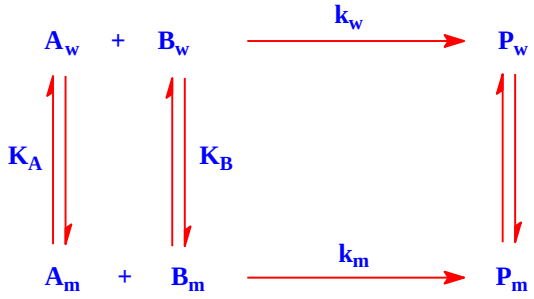


Scheme 2 Piszkiewicz model of micelle mediated reaction

Accordingly, the rate law for the proposed scheme-8 is presented in equation-2.

$$\log\left(\frac{k_\Psi - k_w}{k_m - k_\Psi}\right) = n\log[D] - \log K_D \qquad (2)$$

Here, K_D is the dissociation constant of the micelle back to its free components, k_Ψ is the rate constant in the presence of surfactant, D is the total concentration of surfactant and n is the cooperativity index. For the reactions whose kinetic data fits to this model should give a straight line for the plot of $\log\left(\frac{k_\Psi - k_w}{k_m - k_\Psi}\right)$ vs log D. From the slope and intercept of such plots, values of n and K_D can be determined. For the reactions that show a rate inhibition beyond a certain concentration of surfactant (designated as the kinetic cmc) after initial rate acceleration in the micellar medium so that a maximum is observed in the (rate constant) – [surfactant] profile, Berezin et.al. model [57-60, 72-78] explains all the observed phenomenon. According to this model, a surfactant solution above cmc is considered to be a bi-phasic system so that the chemical reaction is assumed to occur concurrently in two pseudo-phases; the micellar phase and the bulk solvent. The reaction for a model bimolecular reaction between the reactants A and B to form product P is shown in **Scheme 3**.



Scheme 3 Berezin model of micelle mediated reaction

Here, K_A and K_B are the binding constants of the reactants A and B respectively. Based on the Scheme-3, the rate expression is

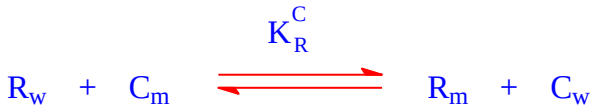
$$k_\Psi = \frac{k_w + \bar{k}_m K_A K_B C}{(1 + K_A C)(1 + K_B C)} \qquad (3)$$

where $\bar{k}_m = k_m / V$, V is the molar volume of the surfactant. C = ([surfactant]-cmc). Equation- 3 can be approximated to

$$\frac{1}{k_\Psi} = \frac{1}{k_w} + \left(\frac{K_A + K_B}{k_w}\right) C \qquad (4)$$

The intercepts (positive) of the plot (a straight line) of $\frac{1}{k_\Psi}$ vs C (from equation-4) fetches k_w and the binding constant ($K_A + K_B$) can be computed from the ratio of slope to intercept. The nature of the k_Ψ – [surfactant] profile showing a maximum can be explained as (i) below the kinetic cmc, k_Ψ increases with [surfactant] due to increased solubilization to reach a limiting state (ii) in the post cmc region, as the number of micelles exceed the requirement (to bind all reactant), dilution of substrate per micelle formed occurs and leads to rate inhibition. The mechanism of micellar catalysis involving charged reactants can suitably be explained by Romsted model [79-83] also referred as Ion exchange model. According to this model, micellar aggregates are viewed as ion exchange resins having the ability to bind and

exchange ions. The reaction rate is altered by the mutual exchange of ions among the micelles and bulk solution, i.e., counter ions bound to micelle and reactive ions (**Scheme 4**).



Scheme 4. Romsted model of micelle mediated reaction.

Here, R: reactive ions, C: counter ions and $K_R^C = \frac{[R_m][C_w]}{[R_w][C_m]}$ is the ion exchange constant.

Influence of cationic surfactant

Cationic surfactants are the obvious candidates of selection for the kind of reaction between organic substrates and anions (of hydrophilic nature) as both of the reactants likely to enter and reside preferentially in the positively charged micelles rather than the mutually interacting only in bulk aqueous solution. Such reactions have probably gathered the maximum attention to demonstrate claims on micellar catalysis by different models. As catalysts, these cationic micelles are normally found to facilitate an alternate route by lowering the energy requirements for the occurrence of a particular process but more or less the mechanism of the reaction remain unaltered even in presence of the amphiphilic molecules. Sijbren Otto and his team [84] have studied the 'Diels-Alder reaction of 3-(para-substituted phenyl)-1-(2-pyridyl)-2-propen-1-ones' (dienophile/substrate), containing neutral, cationic, or anionic substituents, with cyclopentadiene (diene). The reaction is retarded by cationic micelles in absence of transition metal ions. In the situation where the substrates (out of seven dienophiles taken for study) does not prefer to bind to the micelle, the reaction is retarded because of penetration of the diene in the micelles lowers the concentration of the diene in the aqueous phase. The rate retardations are found to be most pronounced when the dienophile binds completely to the micelle. The reaction rate retardation as claimed by the authors is mainly because of the different binding locations of dienophile (prefers the outer regions of the micelle) and diene (residing in the interior). M A Malik and team [85] have carried out the 'Kinetics of MnO_4^- oxidation of succinic acid in aqueous solution of cetyltrimethylammonium bromide'. The catalytic effect of CTAB as stated by the authors was due to the formation of an ion pair between surfactant sub-aggregates and reactants. Besides, an increase in the concentration leading to solubilization of reactants and/or intermediate in the micellar pseudo-phase is responsible for the enhanced reaction rate. A similar explanation was presented by N Ahmad et. al. [86] to explain the micellar catalysis while studying 'effect of cetyltrimethylammonium bromide on the oxidation of phthalic acid'. Ghosh et. al. [87] have studied the 'Propanol to propionaldehyde conversion by chromic acid in sulphuric acid using hetero-aromatic nitrogen bases as promoters (picolinic acid, 2,2'-bipyridine, 1,10-phenanthroline) in aqueous media' and observed the rate inhibition with cationic surfactant N-cetyl pyridinium chloride (CPC). The three heteroaromatic nitrogen base promoters (PA, bipy, phen) undergo chelation with the oxidant (chromic acid) to generate reactive intermediate, a positively charged Cr(VI)–promoter complex. Due to electrostatic repulsion between the cationic micelle and the complex, the reaction rate retardation was observed. Upadhyay et. al. [88] has studied the 'Kinetics of oxidation L-proline and L-methionine by alkaline $KMnO_4$' and observed the rate retardation effect in presence cationic (cetyl ammonium bromide, CTAB). The rate inhibitory effect as explained by the authors is due to the formation/association of an inactive aggregate between the oxidant and surfactant. Forces of attraction/repulsion of electrostatic nature and hydrophobic forces play the pivotal role in the inhibition effect of rate in the presence of surfactants. Saha et. al. [89] have studied the 'Kinetics of cerium(IV) oxidation of some aliphatic alcohols both in presence and absence of surfactants in acidic medium using Ir(III)' as catalyst. Cationic surfactant CPC (N-cetylpyridinium chloride) retards the rate whereas zwitterionic surfactant CHAPS (3-[(3-cholamidopropyl) dimethylammonio]-1-propanesulfonate) shows accelerating effect. The rate retarding influence of CPC micelles accounted for the different locations of alcohol and oxidant in the cationic micelles. They observed that the rate decreased with increase in concentration of CPC. The cationic CPC restricts the positively charged alcohol-oxidant complex in an aqueous phase and hence the neutral substrates accumulated in the Stern layer cannot participate in the reaction. Aniruddha Ghosh et. al. [90] have studied the 'conversion of benzaldehyde to benzoic acid by Cr(VI) using hetero-aromatic nitrogen bases as promoters (picolinic acid, 2,2'-bipyridine, 1,10-phenanthroline) in aqueous media'. The cationic CPC (N-cetyl pyridinium chloride) forms reverse micelle in presence of benzaldehyde due to non-polar nature of benzaldehyde in aqueous media. These reverse micelles have a hydrophilic polar core and a lipophilic non-polar shell. The micelle CPC accelerates the rate of reaction either in presence or absence of promoter. As the positive head groups are directed towards the interior of the reverse micelles, the effective concentration of the substrate in the hydrophobic region increases and results in the rate enhancement. The 'kinetics of phenylalanine oxidation by

permanganate' has been investigated Rafiuddin et.al. [91]. They have observed the pre- and post-micellar catalytic and inhibitory effect of CTAB on the oxidation of phenylalanine by MnO_4^-. The formation of ion-pair among CTAB aggregates and the reactive species of both reactants is responsible for the rate enhancement while the dilution effect in the micellar pseudo phase in the post-micellar state is the cause of inhibitory role of CTAB. 'Oxidation of tyrosine by permanganate in presence of cetyltrimethylammonium bromide' was studied by Zaheer Khan and his co-workers [92]. When concentration of CTAB was less than cmc the rate constants values reduced from 18.5×10^{-4} to 7.2×10^{-4} s^{-1}. But when the CTAB was used at a concentration higher than that of the cmc value, the first order rate constant values jumped from 7.2×10^{-4} to 15.8×10^{-4} s^{-1}. In premicellar condition of CTAB there was a strong inhibition of reaction rate whereas increase in rate constant in the post micellar concentration of CTAB was ascribed to the incorporation of the substrate and MnO_4^- in to the Stern layer of the micelles. Zaheer Khan et. al. has done the 'kinetic study of cationic CTAB micelles-assisted oxidation of isoleucine' [93] and reported the catalytic role of micelles at lower [CTAB] values and stated that the rate enhancement due to the incorporation/solubilization of the substrate and MnO_4^- into the Stern layer as well as palisade layer. At higher concentrations of CTAB the inhibitory effect was observed and it was due to the dilution. Using cetyltrimethylammonium bromide Malik et. al. [94] carried out the 'Kinetics study of oxidation of d-glucose by permanganate in aqueous solution' and reported the mechanism of the micellar influence by considering the association of permanganate with the cationic head group of CTAB. This resulted in k_{obs}–[CTAB] plot showing increase in the rate with CTAB concentration and reach a limiting value. R Tripathi et. al. [95] has studied the 'alkaline $KMnO_4$ oxidation of glucose and fructose in micellar medium' and reported inactive surfactant-MnO_4^- aggregate formation with CTAB which resulted in rate retardation. Bidyut Saha and his team [96] have analyzed the 'Permanganate oxidation of 2-butanol in aqueous medium using CPC surfactant along with picolinic acid (PA) and 2,2-bipyridine (bipy) as promoter'. A100-fold rate enhancements was reported when combination of bipy and CPC was used in the reaction medium. S Patel and team has studied the oxidation of different substrates [97-106] using a lipopathic oxidant by attaching inorganic anionic oxidants (permanganate/dichromate) to a cationic organic carrier, cetyltrimethyl ammonium ion which takes the oxidants into the organic phase. These hydrophobic oxidants exist as tight ion pairs of the cationic carrier CTA^+ and the anionic oxidant counterions in non-polar medium and they have the rate controlling influence. P Subramaniam and N T Selvi [107] has studied the 'Cetyltrimethylammonium bromide mediated phenylsulfinylacetic acid with Cr(VI)' and observed that the rate profile displaying an initial rate increase at a low concentration of CTAB (due to strong binding of SO_4^{2-} on the cationic micellar surface) and a sharp inhibition of rate at higher concentrations (due to partitioning of the substrate and the oxidant in aqueous phase by electrostatic repulsion). Saha et. al. has studied the 'Chromic acid oxidation of L-sorbase' [108], oxidation of glycerol [109], 'Chromic acid oxidations of glycerol to glyceraldehyde' [110] in aqueous media and deeply analyzed the influence of surfactant-promoter combination on the rate of reactions. Cationic, CPC was found to retard the reaction. While studying the 'Effect of cationic micelles of cetyltrimethylammonium bromide on the MnO_4^- oxidation of valine' Zaheer Khan et. al. [111] have observed the catalytic role played by CTAB and explained the observations by arguing that the penetration of non-polar side chain of the reactant into the palisade area of CTAB micelles occurs through hydrophobic interactions which in fact increases effective [substrate] at the site of reaction that in turn increases the rate. Kabir-Ud-Din et. al. has observed the rate enhancing effect of cationic surfactant cetyltrimethylammonium bromide, CTAB while examining the Oxidation of D-Fructose [112], L-sorbase [113] and D-Mannose [114] by cerium(IV) in sulfuric acid medium. In all of these experimental works anionic SDS was found to be non-influential.

Influence of anionic surfactant

Anionic micelles can provide a successful reaction site for positively charged reactants which otherwise do not react to any extent in aqueous solution. Reactions in anionic surfactants media more often takes place in the Stern region of the micelle. The electrostatic and hydrophobic interactions between the reactant and micelles have the key role in the movement of the reactant into the micelle. As mentioned earlier Ghosh et. al. [87] has used anionic surfactant sodium dodecyl sulphate (SDS) also to study the conversions in aqueous media. SDS accelerated the reaction both in presence and absence of promoters. They observed that the rate of oxidation is maximum when bipy was used as promoter catalyzed by SDS. The rate enhancement activity as claimed is because of preferential partitioning of the positively-charged Cr(VI)–bipy (by electrostatic attraction) and neutral substrate in the micellar surface. This happened due to the easy penetration of Cr(VI)–bipy complex with small volume into smaller hydrophobic core of SDS micelle. Kabir-Ud-Din et. al. [115] has explored the 'Role of Mn(II), SDS micelles, and inorganic salts on the kinetics of the redox reaction of l-sorbose and Chromium(VI)'. To justify the kinetic observations, the authors argued that because of the electrostatic interactions between the anionic head groups of SDS micelle and H^+, $[H^+]$ increases in the Stern layer thus the reactants namely, chromic acid and L-sorbose together that is responsible for the rate enhancement. R Tripathi et. al. [95] has studied the 'Alkaline $KMnO_4$ oxidation of glucose and fructose in anionic surfactant medium'. The findings said that

the formation of inactive surfactant-MnO_4^- aggregate was responsible for the inhibitory action of SDS micelle. As already mentioned earlier, Sijbren Otto and his team [84] while studying the 'Diels-Alder reactions has used anionic SDS surfactant' also and observed similar influence. Aniruddha Ghosh et. al. [90] in their study of 'Benzaldehyde to benzoic acid conversion by Cr(VI) using hetero-aromatic nitrogen bases as promoters' (picolinic acid, 2,2'-bipyridine, 1,10-phenanthroline) have used anionic SDS surfactant alongside CTAB. Acceleration of rate was observed when combination of SDS and any of the three hetero-aromatic nitrogen bases (PA, bipy and phen) were used as promoters. Because of the electrostatic attraction the positively charged oxidant-promoter complex can preferably be distributed in the micellar pseudo-phase of the anionic surfactant SDS. The oxidation process thus propagated in both the micellar pseudo-phase and aqueous phase to give the observed rate acceleration. A K Singh and his team [116] have performed the 'Kinetic study of oxidation of paracetamol by water-soluble colloidal MnO_2 in the presence of SDS surfactant' and reported that the Micelles of SDS in aqueous medium accelerated the reaction rate. Executing the reactions in SDS micellar media viz., oxidation of p-anisaldehyde to p-anisic acid [117], 'Ru(III) catalyzed oxidation of 2-propanol by Cr(VI)' [118], Saha and his team has observed the multiple fold rate enhancements. Zoya Zaheer and team [119] have reported the catalytic role of sodium dodecylbenzenesulphonate (SDBS) during the oxidation of tartaric acid by permanganate. Zaheer Khan et. al. [120] have studied the 'Oxidation of citric acid by MnO_4^- with anionic SDS surfactant assisted by biocompatible natural sugar-based surfactant (crocin)' and observed inhibitory effect of SDS alone as well as the combination of crocin and SDS. As mentioned previously, in the kinetic studies of oxidation of L-sorbase [108], glycerol [109], glycerol to glyceraldehyde [110] using Cr(VI) as oxidant in aqueous media by Saha et. al. mediated by anionic SDS surfactant, SDS was found to have a catalytic role in all the cases.

Influence of non-ionic and zwitter ionic surfactant

Non-ionic surfactants forming the micellar aggregates are more likely not have catalytic role on the rate of if the all of the participants of a particular reaction are not charge bearing species. Lack of tendency of electrostatic attraction of ionic reactants towards the non-ionic micelles will lead to little or non-solubilization within the micelle. However, there are instances of rate acceleration when non-ionic surfactants are used in the reaction medium. This rate acceleration is of course selective for the reactants and the environment in which the reaction is carried out. Triton X-100 (TX- 100) accelerated the reaction both in presence and absence of promoters like picolinic acid, 2,2'-bipyridine, 1,10-phenanthroline (phen) for the propanol to propionaldehyde conversion in aqueous media [87]. The enhancement of rate is observed when combination of TX-100 and phen (promoter) was used. It may be due to the allowance of maximum number of neutral substrates into large hydrophobic core of TX-100 micelle. Similar to this, rate acceleration has been noticed when TX-100 micelles in combination with any of the promoters like picolinic acid, 2,2'-bipyridine, 1,10-phenanthroline (phen) are used in the conversion of benzaldehyde to benzoic acid by Cr(VI) [90]. The higher rate enhancement in the combination of TX-100 and phen promoted path is likely due to the larger hydrophobic core of TX-100 that allows maximum number of neutral substrates as well as maximum number of Cr(VI)–phen complex into the TX-100 micellar core to accumulate. 'The Diels-Alder reaction of 3-(para-substituted phenyl)-1-(2-pyridyl)-2-propen-1-ones' having neutral, cationic, or anionic substituents as substrate dienophiles with cyclopentadiene (diene) mediated by a non-ionic dodecyl heptaoxyethylene ether surfactant [84] was retarded when no transition metal ions (Zn^{2+}/Cu^{2+}) were used in the reaction medium. Triton X-100 forms an inactive aggregate with MnO_4^- and retards the oxidation reaction of glucose and fructose by alkaline $KMnO_4$ [95]. 'Kinetics of oxidation of dl-tartaric acid by potassium permanganate in aqueous and aqueous non-ionic micellar media' was studied by Mohammed Hassan et. al. [121]. The presence of TX-100 was found to catalyze the reaction up to a concentration of surfactant and thereafter reached a constant value at high concentration of surfactant. 'Kinetics study of the oxidation of propan-1-ol and propan-2-ol by permanganate in the absence and presence of Tween-20 in perchloric acid medium' was performed by P K Sen et. al. [122]. They reported that the value of rate constant increased initially with increasing [Tween-20] and after passing through a maximum it decreased gradually. The reason behind the observation was explained by stating that in the presence of Tween-20, both the oxidant and the substrate were distributed between the aqueous phase and the micellar pseudo-phase and then react. M Akram et. al. for the oxidative degradation of dipeptide (glycyl–glycine) [123] and glycyl-leucine [124] by water-soluble colloidal manganese dioxide in the aqueous and non-ionic, Triton X-100 micellar media have reported that the pseudo-first-order rate constant increase about two-fold with increase in concentration of the surfactant. A similar influence of Triton X-100 has been reported by A Nasar and Qamruzzaman [125] for the 'Degradation of tricyclazole by colloidal manganese dioxide' and Mohammad Altaf and Deogratius Jaganyi [126] for the 'Oxidation of methionine by colloidal MnO_2 in aqueous media'. Kabir-ud-Din et. al. has examined the 'Reduction of soluble colloidal MnO_2 by DL-malic acid' [127, 128], 'Reduction of water soluble colloidal MnO_2 by glycolic acid' [129] in presence of Triton X-100 and noticed the catalytic role of the surfactant. The association reactants chromic acid and L-sorbose with TX-100 micelles through hydrogen bonding was responsible role catalytic of TX-100 micelles in the redox reaction of l-sorbose and Chromium(VI) [115]. The association of reactants, chromic acid and L-sorbose

with TX-100 micelles through hydrogen bonding was responsible role of TX-100 micelles toward the catalytic activity. Triton X-100 has played a rate accelerating role in the oxidation of L-sorbose [108], glycerol [109], glycerol to glyceraldehyde [110].

Conclusion

A remarkable advancement has been made in the field of micellar catalysis in recent years as confinement of reactants to micelles enhances the efficacy of chemical transformations. The significant change in the property of the surfactants in aqueous solution phase beyond cmc gives the system a superior edge over the conventional catalysts. The existence of polar and non-polar regions with-in the micelles makes the micelles as the nano scale reactor. The reaction paths of electron transfer reactions that are sluggish can be provided with an alternative route through micellar catalysis that are environmentally friendly. Hence, micelles as catalysts will continue to inspire people and have the applicability rather to a greater extent in the future too. If not the conventional surfactants but the designer ones tuned according to the specific need affecting many spheres of chemical processes of human need will have the new futuristic dimensions. This article has presented a broader review of the articles published in the field of surfactant science and its applicability to catalyze process of industrial and academic interest.

References

[1] E. J. Fendler, J. H. Fendler, Catalysis in Micellar and Macromolecular Systems, Academic Press, New York, 1975.
[2] M. J. Rosen, T. J. Kunjappu, Surfactants and Interfacial Phenomena, John Wiley & Sons, Inc., New Jersey, USA, 2012.
[3] Y. Moroi, Micelles, Theoretical and Applied Aspects, Plenum Press, New York, 1992.
[4] R. K. Padhy, S. Sahu, Editors: Z. H. Khan, J. Mark and N. A. Salah, 'Heterogeneous Oxidation of Alcohols Catalyzed by Titania Supported Palladium Nanoparticles in Aqueous Micellar Solution, Springer Proceedings in Materials, 2023, 28(74):517-528.
[5] S. Pandey, S. K. Upadhyay, Effect of cationic micellar aggregates on the kinetics of oxidation of amino alcohols by N-bromosuccinimide in alkaline medium, Journal of Colloidal and Interface Science, 2005, 285:789-794.
[6] G. P. Panigrahy, S. K. Mishra, Micellar-catalysis: Effect of sodium lauryl sulphate in the oxidation of lactic acid by chromic acid, Journal of Molecular Catalysis, 1993, 81:349-362.
[7] Myers Drew, Surfactant Science and Technology, John Wiley & Sons, New Jersey, 2006.
[8] F. E. Friedli, Detergency of Specialty surfactants, Marcel Dekker, USA, 2001.
[9] K. S. Birdi, Hand book of surface and colloid chemistry, 3rd edn., CRC press, NY, 2009.
[10] M. A. Hegazy, M. Abdallah, H. Ahmed, Novel cationic gemini surfactants as corrosion, inhibitors for carbon steel pipelines, Corrosion Science, 2010, 52(9):2897-2904.
[11] L. H. Qiu, Y. Wu, Y. M. Wang, X. Jiang, Synergistic effect between cationic gemini surfactant and chloride ion for the corrosion inhibition of steel in sulphuric acid, Corrosion Science, 2008, 50 (2):576-582.
[12] R. K. Padhy, A. P Padhi, R. Patro, B. Mahapatra, S. Dash, S. Sahu, Interfacial and surface adsorption phenomenon in the dissolution behavior of 8-hydroxy quinoline, Materials Today: Proceedings, 2024, 98:33-39.
[13] C. R. Yagui, A. Pessoa Jr, L. Tavares, Micellar solubilization of drugs, Journal of Pharmacy and Pharmaceutical Sciences, 2005, 8:147-163.
[14] V. P. Torchilin, Micellar nanocarriers: pharmaceutical perspectives, Pharmaceutical Research, 2007, 24:1-16.
[15] Z. Viranov, V. Katev, D. Radeva, S. Tcholakova, N. D. Denkov, Micellar solubilization of poorly water-soluble drugs: effect of surfactant and solubilizate molecular structure, Drug Development and Industrial Pharmacy, 2017, 44(4):677-686.
[16] M. Malmsten, Surfactants and Polymers in Drug Delivery, Marcel Dekker, NY, 2002.
[17] Z. Weiszhar, J. Czucz, C. Revesz, L. Rosivall, J. Szebeni, Z. Rozsnyay, Complement activation by polyethoxylated pharmaceutical surfactants: Cremophor- EL, Tween-80 and Tween-20, European Journal of Pharmaceutical Sciences, 2012, 45(4):492-498.
[18] K. Bouchemal, S. Briancon, E. Perrier, H. Fessi, Nano-emulsion formulation using spontaneous emulsification: solvent, oil and surfactant optimisation, International Journal of Pharmaceutics, 2004, 280(1):241-251.
[19] E. W. S. Hagan, M. N. Charalambides, C. R. T. Young, T. J. S. Learner, S. Hackney, Viscoelastic properties of latex paint films in tension: Infleunce of the inorganic phase and surfactants, Progress in Organic Coatings, 2010, 69 (1):73-81.
[20] P. Perumal, A. Hasnain, T. Luukkonen, P. Kinnunen, M. Illikainen, Role of surfactants on the synthesis of impure kaolin-based alkali-activated, low-temperature porous ceramics, Open Ceramics, 2021, 6:100097.

[21] O. Massarweh, A.S. Abushaikha, The use of surfactants in enhanced oil recovery: A Review of recent advances, Energy reports, 2020, 6:3150-3178.
[22] A. Rahman, F. Torabi, E. Shriff, Surfactant and nanoparticle synergy: Toward improved foam stability, Petroleum, 2023, 9(2):255-264.
[23] S. M. Shaban, J. Kang, D. H. Kim, Surfactants: Recent advances and their applications, Composite communications, 2020, 22:100537.
[24] B. Huang, C. Huang, J. Chen, X. Sun, Size-controlled synthesis and morphology evolution of Nd2O3 nano-powders using ionic liquid surfactant templates, Journal of Alloys and Compounds, 2017, 712:164-171.
[25] Z. Khan, S. A. Al-Zaharani, Q. A. Al-Sulami, S. A. Al-Thabaiti, W. S. Al-Arjan, Effects of shape-controlling cationic and anionic surfactants on the morphology and surface resonance plasmon intensity of silver@copper bimetallic nanoparticles, Journal of Molecular Liquids, 2019, 275:354-363.
[26] D. Li, F. Wenjun, F. Yimin, G. Qijin, S. Mingjun, Stability properties of water-based gold and silver nanofluids stabilized by cationic gemini surfactants, Journal of the Taiwan Institute of Chemical Engineers, 2019, 97:458-465.
[27] X. Li, M. Yoneda, Y. Shimada, Y. Matsui, Effect of surfactants on the aggregation and stability of TiO2 nanomaterial in environmental aqueous matrices, Science of The Total Environment, 2017, 574:176-182.
[28] R. D. Chekuri, S. R. Tirukkovalluri, Synthesis of cobalt doped titania nano material assisted by gemini surfactant: Characterization and application in degradation of Acid Red under visible light irradiation, South African Journal of Chemical Engineering, 2017, 24:183-195.
[29] F. Ordonez, F. Chejne, E. Pabon, K. Cacua, Synthesis of ZrO2 nanoparticles and effect of surfactant on dispersion and stability, Ceramics International, 2020, 46(8, B):11970-11977.
[30] M. Hasheminejad and A. Nezamzadeh-Ejhieh, A novel citrate selective electrode based on surfactant modified nano-clinoptilolite, Food Chemistry, 2015, 172:794-801.
[31] J. Yuenyongsuwan, N. Nithiyakorn, P. Sabkird, E. A. O. Rear, T. Pongprayoon, Surfactant effect on phase-controlled synthesis and photocatalyst property of TiO2 nanoparticles, Materials Chemistry and Physics, 2018, 214:330-336.
[32] S. D. Bhattamishra, R. K. Padhy, Estimation of Ibuprofen Solubilization in Cationic and Anionic Surfactant Media: Application of Micelle Binding Model, Indian Journal of Chemical Technology, 2009, 16:426-430.
[33] Z. Vinarov, V. Katev, D. Radeva, S. Tcholakova, N. D. Denkov, Micellar solubilization of poorly water-soluble drugs: effect of surfactant and solubilizate molecular structure, Drug Development and Industrial Pharmacy, 2018, 44 (4):677-686.
[34] T. N. Ansari, S. Sharma, S. Hazra, F. Hicks, D. K Leahy, S. Handa, Trichloromethyl Carbanion in Aqueous Micelles:Mechanistic Insights and Access to Carboxylic Acids from (Hetero) Aryl Halides, ACS Catalysis, 2022, 12:15686-15695.
[35] C. Ceriani, F. Pallini, L. Mezzomo, M. Sassi, S. Mattiello, L. Beverina, Micellar Catalysis beyond the Hydrophobic Effect: Efficient Palladium Catalyzed Suzuki-Miyaura Coupling of Water and Organic Solvent Insoluble Pigments with Food Grade Surfactants, Journal of Organometallic Chemistry, 2022, 962:122267-
[36] H. A. Stanway-Gordon, J. A Odger, M. J. Waring, Development of a Micellar-Promoted Heck Reaction for the Synthesis of DNA-Encoded Libraries, Bioconjugate Chemistry, 2023, 34:756-763.
[37] H. Pang, Y. Hu, J. Yu, F. Gallou, B. H. Lipshutz, Water-Sculpting of a Heterogeneous Nanoparticle Precatalyst for Mizoroki-Heck Couplings under Aqueous Micellar Catalysis Conditions, Journal of American Chemical Society, 2021, 143:3373-3382.
[38] S. R. Yetra, T. Rogge, S. Warratz, J. Struwe, W. Peng, P Vana, L. Ackermann, Micellar Catalysis for Ruthenium(II)-Catalyzed CH Arylation: Weak-Coordination-Enabled C-H Activation in H2O, Angewandte Chemie International Edition, 2019, 58:7490-7494.
[39] S. Handa, B. Jin, P. P. Bora, Y. Wang, X. Zhang, F. Gallou, J. Reilly, B. H. Lipshutz, Sonogashira Couplings Catalyzed by Fe Nanoparticles Containing Ppm Levels of Reusable Pd, under Mild Aqueous Micellar Conditions, ACS Catalysis, 2019, 9:2423-2431.
[40] J. S. Graham, H. A. Stanway-Gordon, Micelle-Mediated Sonogashira Coupling for DNA-Encoded Library Synthesis, M. J. Waring, Chemistry-A European Journal, 2023, 29:e202300603.
[41] P. Klumphu, C. Desfeux, Y. Zhang, S. Handa, F. Gallou, B. H. Lipshutz, Micellar Catalysis-Enabled Sustainable Ppm Au- Catalyzed Reactions in Water at Room Temperature, Chemical Science, 2017, 8:6354-6358.
[42] A. Ranaudo, C. Greco, G. Moro, A. Zucchi, S. Mattiello, L. Beverina, U. Cosentino, Partition of the Reactive Species of the Suzuki-Miyaura Reaction between Aqueous and Micellar Environments, Journal of Physical Chemistry B, 2022, 126:9408-9416.
[43] K. L. Mittal, B. Lindman, Surfactants in Solution, Ed: M. A. Boston, Springer US, 1984.

[44] C. A. Bunton, L. S. Romsted, C. Thamavit, The pseudophase model of micellar catalysis. Addition of cyanide ion to N-alkylpyridinium ions, Journal of American Chemical Society, 1980, 102(11):900-3903.
[45] C. A. Bunton, L. S. Romsted, Reactive Counterion Surfactants in Solution Behavior of Surfactants, Ed. M. A. Boston, Springer US, 1982.
[46] P. Mukerjee, K. J. Mysels, Critical micelle concentrations of aqueous surfactant systems, NSRDC-NBS-36, Washington, DC, 1971.
[47] K. Ravi, B. D. Bankar, S. Jindani, A. V. Biradar, Surfactant-Assisted Selective Oxidation of Aromatic Amines to Nitro Compounds by in Situ-Formed Performic Acid, ACS Omega 2019, 4:9453-9457.
[48] M. Bu, G. Lu, J. Jiang, C. Cai, 'erging Visible-light Photoredox and Micellar catalysis: Arylation Reactions with Anilines Nitrosated in Situ, Catalysis Science and Technology, 2018, 8:3728-3732.
[49] Y. Suzaki, Y. Kobayashi, Y. Tsuchido, K. Osakada, Pd-catalyzed Sonogashira coupling in aqueous media. Observation of micelles that contain substrates and catalyst, Molecular Catalysis, 2019, 466:106-111.
[50] Y.S. Reddy, T. Rogge, S. Warratz, J. Struwe, W. Peng, P. Vana, L. Ackermann, Micellar Catalysis for Ruthenium(II)-Catalyzed C−H Arylation: Weak-Coordination-Enabled C−H Activation in H2O, Angewandte Chemie International Edition, 2019, 58(22):7490-7494.
[51] A. V. Solomonov, Y. S. Marfin, E. V. Rumyantsev, E. Ragozin, T. S. Zahavi, G. Gellerman, A. B. Tesler, F. Muench, A. Kumagai, A. Miyawaki, Self-assembled micellar clusters based on Triton-X-family surfactants for enhanced solubilization, encapsulation, proteins permeability control, and anticancer drug delivery, Materials Science and Engineering C, 2019, 99:794-804.
[52] T. Kitanosono, K. Masuda, P. Xu, S. Kobayashi, Catalytic Organic Reactions in Water toward Sustainable Society, Chemical Review, 2018, 118 (2):679-746.
[53] F. Trentin, A. M. Chapman, A. Scarso, P. Sgarbossa, R. A. Michelin, G. Strukul, D. F. Wass, Platinum(II) Diphosphin-amine Complexes for the Efficient Hydration of Alkynes in Micellar Media, Advanced Synthesis and Catalysis, 2012, 354:1095-1104.
[54] T. Kitanosono, M. Miyo, S. Kobayashi, Catalytic Organic Reactions in Water toward Sustainable Society, Tetrahedron, 2015, 71:7739-7744.
[55] T. Kitanosono, M. Miyo, S. Kobayashi, Surfactant-Aided Chiral Palladium(II) Catalysis Exerted Exclusively in Water for the C−H Functionalization of Indoles, ACS Sustainable Chemical Engineering, 2016, 4:6101-6106.
[56] B. S. Kitawat, M. Singh and R. K. Kale, Robust Cationic Quaternary Ammonium Surfactant-Catalyzed Condensation Reaction for (E)-3-Aryl-1-(3-Alkyl-2-Pyrazinyl)-2-Propenone Synthesis in Water at Room Temperature, ACS Sustainable Chemical Engineering, 2013, 1:1040-1044.
[57] R. K. Padhy, S. D. Bhattamisra, Surfactant Catalyzed Oxidation of Ethanolamines by Ce(IV), Asian Journal of Chemistry, 2021, 33(1):21-25.
[58] R. K. Padhy, S. Sahu, Oxidation of Iminodiethanol by Ce (IV) in microheterogeneous system: A comprehensive kinetic analysis, Journal of Dispersion Science and Technology, 2023, 44 (9):1584-1594.
[59] S. Sahu, R. K. Padhy, S. P. Nanda, Surfactant Catalyzed Electron Transfer Mechanism in the Oxidation of Racemic Tartaric Acid by Ce(IV), Materials Today: Proceedings, 2023, 78:786-791.
[60] S. Sahu, R. K. Padhy, S. P. Nanda, Interfacial catalytic influence of sodium lauryl sulphate in the oxidation of cyclic alcohols by Cr(VI), Materials Today: Proceedings, 2024, 102:341-348.
[61] R. Swain and G. P. Panigrahi, Kinetics and mechanism of oxidation of hydroxylaminehydrochloride by vanadium (V) in the presence of sodium lauryl sulphate, Indian Journal of Chemistry, 2001, 40(11):1191-1195.
[62] F. M. Menger, C. E. Portnoy, Chemistry of reactions proceeding inside molecular aggregates, Journal of American Chemical Society, 1967, 89:4698-4703.
[63] N. Chhetria, S. A. Bhoitea, A. K. Singh, B. Jain, Effect of micelles of di-2,3-dichloroaniline phosphate, Indian Journal of Chemistry, 2020, 59A:551-562.
[64] D. Kumar, M. A. Rub, Kinetic and mechanistic investigations of [Zn (II)-Trp]+ and ninhydrin in aqueous and cationic CTAB surfactant, Journal of Physical Organic Chemistry, 2019, 32 (11):e3997.
[65] N. I. Ugbaga, I. S. Ola, I. Abdulkadir, O. A. David, Oxidation of aspartic acid with molybdenumoxime-ligand framework in acidified-aqua and interfacial active media: Menger-Portnoy kinetic model, Inorganic. Chemistry Communication, 2024, 161:111979.
[66] H. A. Ewais, A. S. Basaleh, Y. M. Al Angari, Kinetic studies on the persulfate oxidation of methylene blue in the absence and presence of silver(I) as a catalyst in aqueous and micellar media, International Journal of. Chemical Kinetics, 2023, 55(6):271-280.
[67] D. Piszkiewicz, Positive cooperativity in micelle catalyzed reactions, Journal of American Chemical Society, 1977, 99(5):1550-1557.
[68] M. M. Velazquez, I. Garcia-Mateos, M. A. Herraez, L. J. Rodriguez, Pseudo-phase ion-exchange model for

micellar catalysis in the acid hydrolysis of vinyl ethers, International Journal of. Chemical Kinetics, 1984, 16(3):269-276.
[69] A. N. Laguta, S. V. Eltsov, Micellar effects in kinetics of interaction of malachite green and brilliant green with water, Kharkov University Bulletin Chemical Series, 2017, 28(51):96-103.
[70] K. A. Singh, N. Sen, K. S. Chatterjee, M. A. B. H. Susan, Kinetic study of oxidation of paracetamol by water-soluble colloidal MnO2 in the presence of an anionic surfactant, Colloid and Polymer Science, 2016, 94(10):1611-1622.
[71] I. U. Nkole, S. O. Idris, I. Abdulkadir, A. D. Onu, Application of Piszkiewicz model on the electron transfer reaction of dithionite ion and bis-(2-pyridinealdoximato)dioxomolybdate(IV) complex, Science Reporter, 2022, 12(1):22125.
[72] I.V. Berezin, K. Martineck, A.K. Yatsimirskii, Physicochemical Foundations of Micellar Catalysis, Russian Chemical Review, 1973, 42:787-802.
[73] A. N. Laguta, S. V. Eltsov, N. O. M. Petrossyan, Micellar rate effects on the kinetics of nitrophenol violet anion reaction with HO– ion: Comparing Piszkiewicz's, Berezin's, and Pseudophase Ion-Exchange models, Journal of Molecular Liquids, 2019, 277:70-77.
[74] N. Chhetri, S.A. Bhoite, A. K. Singh, B. Jain, Effect of micelles on hydrolysis of di-2,3-dichloroaniline phosphate, Indian Journal of Chemistry, 2020, 59A:551-562.
[75] I. U. Nkole, S. O. Idris, A. D. Onu, I. Abdulkadir, The study of Piszkiewicz's and Berezin's models on the redox reaction of allylthiourea and bis-(2-pyridinealdoximato)dioxomolybdate(IV) complex in an aqueous acidic medium, Beni-Suef University Journal of Basic and Applied Science, 2022, 11:68
[76] M. K. Turovskaya, I. A. Belousova, N. G. Razumova, T. S. Gaidash, T. M. Prokop'eva, A. A. Kotenko, V. A. Mikhailov, Reactivity of Inorganic α-Nucleophiles in Acyl Transfer in Aqueous and Micellar Media: IV. Peroxyhydrolysis of Acyl Derivatives in Organized Microheterogeneous Systems1, Russian Journal of Organic Chemistry, 2024, 60(2):252-258.
[77] A. N. Laguta, Quantitative analysis of micellar effect on the reaction rate of cationic triphenylmethane dyes with water according to Berezin's model, Kharkov University Bulletin Chemical Series, 2020, 35(58):37-44.
[78] A. N. Laguta, S. V. Eltsov, N. O. Mchedlov-Petrossyan, Kinetics of alkaline fading of methyl violet in micellar solutions of surfactants: Comparing Piszkiewicz's, Berezin's, and pseudophase ionexchange models, International Journal of Chemical Kinetics, 2019, 51(2):83-94.
[79] L. S. Romsted, A General Kinetic Theory of Rate Enhancements for Reactions between Organic Substrates and Hydrophilic Ions in Micellar Systems. in Micellization, Solubilization, and Microemulsions, Ed. M. A. Boston, Springer US, 1977.
[80] L. S. Romsted, Micellization, solubilization and microemulsions, Ed: K. L. Mittal, Plenum Press, NY, 1997.
[81] B. Samley, A. R. Toosi, Study of Malachite Green Fading in the Presence of TX-100, DTAB and SDS, Bulletin of Korean Chemical Society, 2009, 30(9):2051-2056.
[82] A. Mohr, V. T. Pozo, H. Korth, H. Rehage, R. Sustmann, Hydrophobic N -Diazeniumdiolates and the Aqueous Interface of Sodium Dodecyl Sulfate (SDS) Micelles, Chem Phys Chem, 2008, 9(16):2397-2405.
[83] C. Armstrong, W. Gotham, P. Jennings, J. Nikles, L. S. Romsted, M. Versace, Acid Catalyzed Hydrolysis of Hydrophobic Ketals in Aqueous Cationic Micelles: Partial Failure of The Pseudophase Ion Exchange Model. In: Surfactants in Solution, Ed. M. A. Boston, Springer US, 1989.
[84] S. Otto, J. B. F. N. Engberts, J. C. T. Kwak, Million-Fold Acceleration of a Diels-Alder Reaction due to Combined Lewis Acid and Micellar Catalysis in Water, Journal of American Chemical Society, 1998, 120:9517-9525.
[85] M. A. Malik, F. M. Al-Nowaiser, N. Ahmad, Z. Khan, Kinetics of MnO4- Oxidation of Succinic Acid in Aqueous Solution of Cetyltrimethyl-ammonium Bromide, International Journal of Chemical Kinetics, 2010, 42:704-712.
[86] N. Ahmad, M. A. Malik, S. A. Al-Thabaiti, A. Y. Obaid, Z. Khan, Effect of Cetyltrimethylammonium Bromide on the Oxidation of Phthalic Acid by in Aqueous Medium, Journal of Dispersion Science and Technology, 2011, 32:35-40.
[87] A. Ghosh, R. Saha, B. Saha, Suitable combination of promoter and micellar catalyst for kilo fold rate acceleration on propanol to propionaldehyde conversion in aqueous media, Journal of Industrial and Engineering Chemistry, 2014, 20:345-355.
[88] R. Tripathi, S. K. Upadhyay, Inhibitory Effect of {Surfactant-MnO4-} Aggregation in KMnO4 Oxidation of Proline and Methionine: A Kinetic Study, Journal of Korean Chemical Society, 2014, 58:351-358.
[89] A. Ghosh, R. Saha, B. Saha, Effect of CHAPS and CPC micelles on Ir(III) catalyzed Ce(IV) oxidation of aliphatic alcohols at room temperature and pressure, Journal of Molecular Liquids, 2014, 196:223-227.
[90] A. Ghosh, R. Saha, S. K. Ghosh, K. Mukherjee, B. Saha, Suitable combination of promoter and micellar catalyst

for kilo fold rate acceleration on benzaldehyde to benzoic acid conversion in aqueous media at room temperature: A kinetic approach, Spectrochimca Acta Part A, 2013, 109:55-67.
[91] Z. Zaheer, Rafiuddin, Sub- and post-micellar catalytic and inhibitory effects of cetlytrimethylammonium bromide in the permanganate bromide in the permanganate, Colloids and Surfaces B, 2009, 69:251-256.
[92] M. A. Malik, S. N. Basahel, A. Y. Obaid, Z. Khan, Oxidation of tyrosine by permanganate in presence of cetyltrimethylammonium bromide, Colloids and Surfaces B, 2010, 76:346-353.
[93] M. A. Malik, R. A. Sheikh, S. A. Al-Thabaiti, A. Y. Obaid, Z. Khan, Micelles-Assisted Oxidation of Isoleucine: A Kinetic Study, Journal of Dispersion Science and Technology, 2011, 32:1173-1178.
[94] M. A. Malik, S. A. Al-Thabaiti, Z. Khan, Kinetics of oxidation of d-glucose by permanganate in aqueous solution of cetyltrimethylammonium bromide, Journal of Colloid and Interface Science, 2009, 337:9-14.
[95] R. Tripathi, N. Kambo, S. K. Upadhyay, Premicellar/Micellar Inhibition in Alkaline $KMnO_4$ Oxidation of Reducing Sugars: A Kinetic Study, Journal of Dispersion Science and Technology, 2012, 33:1393-1400.
[96] A. Ghosh, K. Sengupta, R. Saha, B. Saha, Effect of CPC micelle on N-hetero-aromatic base promoted room temperature permanganate oxidation of 2-butanol in aqueous medium, Journal of Molecular Liquids, 198:369-380.
[97] S. Sahu, P. R. Sahoo, S. Patel, B. K. Mishra, Oxidation of Arylthiourea by Cetyltrimethylammonium Dichromate, Synthetic Communications, 2010, 40:3268-3273.
[98] S. Garnayak, S. Patel, Oxidation of Oxidation of Lipopathic Mn(VII), Cetyltrimethylammonium Permanganate: A Mechanistic Study, International Journal of Chemical Kinetics, 2015, 47:429-438.
[99] P. R. Sahoo, S. Patel, B. K. Mishra, Oxidation Kinetics of Oxidation Kinetics of Cetyltrimethylammonium Dichromate, International Journal of Chemical Kinetics, 2013, 45:236-242.
[100] S. Garnayak, S. Patel, Oxidative Cleavage of Acetaminophen by Cetyltrimethylammonium Dichromate: A Mechanistic Study, Industrial and Engineering Chemistry Research, 2013, 52:13645-13653.
[101] S. Patel, B. K. Mishra, Oxidation of Cholesterol by a Biomimetic Oxidant, Cetyltrimethylammonium Dichromate, Journal of Organic Chemistry, 2006, 71:3522-3526.
[102] S. Garnayak, S. Patel, Oxidative degradation of norfloxacin by a lipophilic oxidant, cetyltrimethylammonium permanganate in water–acetonitrile medium: A kinetic and mechanistic study, Journal of Molecular Liquids, 2015, 209:327-335.
[103] S. Patel, B. K. Mishra, A Novel Lipopathic Cr(VI) Oxidant for Organic Substrates: Kinetic Study of Oxidation of Benzyl Alcohol, International Journal of Chemical Kinetics, 2006, 38:651-656.
[104] S. Garnayak and S. Patel, Oxidation of Epinephrine to Adrenochrome by Cetyltrimethylammonium Dichromate: A Mechanistic Study, Industrial and Engineering Chemistry Research, 2014, 53:12249-12256.
[105] S. Sahu, S. Patel, B. K. Mishra, Deoximation by Cetyltrimethylammonium Dichromate: A Kinetic Study, International Journal of Chemical Kinetics, 2011, 43:482-488.
[106] S. Garnayak, S. Patel, Oxidation of Antitubercular Drug Isoniazid by a Lippathic Oxidant, Cetyltrimethylammonium Dichromate: A Mechanistic Study, International Journal of Chemical Kinetics, 2016, 48:32-44.
[107] P. Subramaniam, N. T. Selvi, Dynamics of cetyltrimethylammonium bromide-mediated reaction of phenylsulfinylacetic acid with Cr(VI): Treatment of pseudo-phase models, Journal of Serbian Chemical Society, 2015, 80:1019-1034.
[108] K. Mukherjee, R. Saha, A. Ghosh, S. K. Ghosh, B. Saha, Combination of best promoter and catalyst for hypervalent chromium oxidation of L-sorbose to lactone of C5 aldonic acid in aqueous media at room temperature, Journal of Molecular Liquids, 2013, 179:1-6
[109] S. K. Ghosh, A. Basu, R. Saha, A. Ghosh, K. Mukherjee, B. Saha, Micellar catalysis on picolinic acid promoted hexavalent chromium oxidation of glycerol, Journal of Coordination Chemistry, 2012, 65:1158-1177.
[110] A. Ghosh, R. Saha, K. Mukherjee, S. K. Ghosh, P. Sar, S. Malik, B. Saha, Choice of suitable micellar catalyst for 2,2'-bipyridine-promoted chromic acid oxidation of glycerol to glyceraldehyde in aqueous media at room temperature, Research on Chemical Intermediates, 2013, 41:3057-3078.
[111] R. A. Sheikh, F. M. Al-Nowaiser, M. A. Malik, A. O. Al-Youbi, Z. Khan, Effect of cationic micelles of cetyltrimethylammonium bromide on the MnO4- oxidation of valine, Colloids Surf A, 2010, 366:129-134.
[112] Kabir-Ud Din, M. S. Ali, Z. Khan, Effect of Surfactant Micelles on the Kinetics of Oxidation of D-Fructose by Cerium (IV) in Sulfuric Acid Medium, International Journal of Chemical Kinetics, 2006, 38:18-25.
[113] Kabir-Ud Din, M. S. Ali, Z. Khan, Micelle-assisted cerium(IV) oxidation of L-sorbose in aqueous sulfuric acid, Colloid and Polymer Science, 2007, 285:745-752.
[114] Kabir-Ud Din, M. S. Ali, Z. Khan, Micelle Catalyzed Oxidation of D-Mannose by Cerium (IV) in Sulfuric Acid, Acta Physico-Chimica Sinica, 2008, 24:810-816.

[115] Kabir-Ud Din, A. M. A. Morshed, Z. Khan, Role of Manganese (II), Micelles and Inorganic Salts on the Kinetics of the Redox Reaction of L-Sorbase and Chromium(VI), International Journal of Chemical Kinetics, 2003, 35:543-554.
[116] A. K. Singh, N. Sen, S. K. Chatterjee, M. A. B. H. Susan, Kinetic study of oxidation of paracetamol by water-soluble colloidal MnO2 in the presence of an anionic surfactant, Colloid and Polymer Science, 2016, 294:1611-1622.
[117] R. Saha, A. Ghosh, B. Saha, Kinetics of micellar catalysis on oxidation of p-anisaldehyde to p-anisic acid in aqueous medium at room temperature, Chemical Engineering Science, 2013, 99:23-27.
[118] S. Chowdhury, A. Rakshit, A. Acharjee, A. Ghosh, K. Mahali, Ru(III) catalysed oxidation of 2-propanol by Cr(VI) in micellar media, B. Saha, Journal of Molecular Liquids, 2019, 290:111247.
[119] Z. Zaheer, E. S. Aazam, Anionic-micelles assisted oxidation of tartaric acid by permanganate: A kinetic and mechanistic approach, Journal of Molecular Liquids, 2017, 229:436-442.
[120] Z. Khan, S. A. Al-Thabaiti and M. A. Malik, Biocompatible natural sugar-based surfactant assisted oxidation of citric acid by MnO4- in absence and presence of SDS, RSC Advances, 2016, 6:45993-46001.
[121] M. Hassan, N. A. Alhemiary, A. Albadani, Kinetics of Oxidation of dl-Tartaric Acid by Potassium Permanganate in Aqueous and Aqueous Micellar Media, Arabian Journal for Science and Engineering, 2012, 37:1263-1270.
[122] P. K. Sen, P. R Samaddar, K. Das, Kinetics and mechanism of the oxidation of propan-1-ol and propan-2-ol by permanganate in the absence and presence of Tween-20 in perchloric acid medium, Transition Metal Chemistry, 2005, 30:907-914.
[123] M. Akram, M Altaf, Kabir-Ud Din, Oxidative degradation of dipeptide (glycil-glycine) by water-soluble colloidal manganese dioxide in the aqueous and micellar media, Colloids and Surfaces B, 2011, 82:217-223.
[124] M. Akram, M. Altaf, Kabir-Ud Din, S. A. Al-Thabaiti, Kinetics and mechanism of the reduction of colloidal MnO2 by glucyl-leucine in the absence and presence of surfactants, Journal of Saudi Chemical Society, 2012, 16:217-225.
[125] Qamruzzaman, A. Nasar, Degradation of tricyclazole by colloidal manganese dioxide in the absence and presence of surfactants, Journal of Industrial and Engineering Chemistry, 2014, 20:897-902.
[126] M. Altaf, D. Jaganyi, Oxidation of Methionine by Colloidal MnO2 in Aqueous and Micellar Media: A Kinetic Study, Journal of Dispersion Science and Technology, 2013, 34:1481-1487.
[127] Kabir-Ud Din, S. M. S Iqubal, Kinetics of Reduction of Water Soluble Colloidal MnO2 by Mandelic Acid in the Absence and Presence of Non-Ionic Surfactant Triton X-100, Colloid Journal, 2010, 72:195-204.
[128] Kabir-Ud Din, S. M. S Iqubal, Z. Khan, Reduction of soluble colloidal MnO2 by DL-malic acid in the absence and presence of nonionic TritonX-100, Colloid and Polymer Science, 2005, 283:504-511
[129] Kabir-Ud Din, S. M. S. Iqubal, Z. Khan, Effect of ionic and non-ionic surfactants on the reduction of water soluble colloidal MnO2 by glycolic acid, Colloid and Polymer Science, 2005, 284:276-283.

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