Journal of the Turkish Chemical Society Section: A Chemistry
TURKISH CHEMICAL SOCIETY

Surfactant Micelles as Catalysts: Kinetic Modelling and Key Models

Karri Lavanya[1], **R S S Srikanth Vemuri**[1*], **Shyamala Pulipaka**[2], **Venkata Nagalakshmi Kilana**[3], **Ravi Vital Kandisa**[4]

[1]Department of Basic Sciences and Humanities, Vignan's Institute of Engineering for Women (Autonomous), Visakhapatnam, Andhra Pradesh, India–530049.
[2]Department of Chemistry, Andhra University, Visakhapatnam, Andhra Pradesh, India-53003.
[3]Department of Chemistry, Gayatri Vidya parishad College of Engineering (Autonomous), Madhurawada, Visakhapatnam, Andhra Pradesh, India–530048.
[4]Kalam Institute of Technology - WHO Collaborating Centre, Visakhapatnam, India-530031.

Abstract: Surfactant molecules possess both hydrophilic and hydrophobic properties, featuring a hydrophilic head and a hydrophobic tail. When surfactants reach a critical micellar concentration, they assemble into stable molecular aggregates called micelles. These micelles serve as effective catalysts for a range of chemical reactions. To elucidate and make sense of experimental data related to micelle-catalyzed reactions, researchers often employ kinetic modeling as a valuable tool. Several kinetic models have been introduced to describe the reaction rates within micellar environments. In this discussion, we will provide a concise overview of four widely utilized models: The Berezin model, the pseudophase model, the ion exchange model, and the Piskiewicz model.

Keywords: Micellar catalysis, Kinetic modeling, Berezin model, Pseudophase model, Ion exchange model, Piskiewicz model.

Submitted: December 3, 2023. **Accepted:** June 24, 2024.

Cite this: Lavanya K, Vemuri RSSS, Pulipaka S, Kilana VN, Kandisa RV. Surfactant Micelles as Catalysts: Kinetic Modelling and Key Models. JOTCSA. 2024;11(3): 1165-80.

DOI: https://doi.org/10.18596/jotcsa.1399457

***Corresponding author's E-mail:** vrsssrikanth@gmail.com

1. INTRODUCTION

Surfactant molecules exhibit amphiphilic properties, with a hydrophilic head and a hydrophobic tail, making them soluble in both aqueous and non-aqueous oil phases (1,2). Below the Critical Micellar Concentration (CMC), surfactant molecules are generally believed to exist as individual molecules in the solution. However, as the concentration surpasses the CMC, these surfactant molecules start to aggregate, forming structures known as micelles (1,2). These micelles play a crucial role in altering the rates of chemical reactions. The arrangement of reactants and products within the micellar environment significantly influences the transition states of reactions, thereby impacting their reaction rates (3-24). To gain a deeper understanding of the underlying mechanisms of these catalyzed reactions within micelles, it is most effective to employ appropriate kinetic models.

In the early 1980s, significant efforts were made to establish this field of chemistry as a distinct discipline, with researchers like Berezin (25-27), Romsted, and Bunton (28-32) contributing to its development. Mittal and Lindman's Surfactants in Solution explores the formation of micelles and the impact of surfactants on reaction kinetics. Mittal's Solution Chemistry of Surfactants delves into the chemical and physical interactions of surfactants in various environments (33,34). Bunton and Romsted's contribution in Solution Behavior of Surfactants, edited by Mittal and Fendler, focuses on the role of reactive counter ions in surfactant systems, examining their interactions and catalytic effects. These works collectively offer valuable knowledge for understanding micellar catalysis and the underlying mechanisms of surfactant behavior in solutions (35).

The most widely accepted models for explaining the effects of micelles on reaction rates include the pseudophase model (29,30), the Berezin model (25), the Piskiewicz model (36,37), and the pseudophase ion exchange model (38). These models aid in providing a better understanding of the intricate processes involved in reactions occurring within micellar environments.

The purpose of this review article on kinetic models for micellar-catalyzed reactions is to consolidate and critically evaluate the various theoretical frameworks that explain how micelles impact the kinetics of response. By examining models such as the pseudophase, Berezin, Piskiewicz, and pseudophase ion exchange models, we aim to clarify the mechanistic pathways and provide a comparative analysis to guide researchers in selecting appropriate models for various catalytic systems. Ultimately, this comprehensive analysis will advance our understanding and utilization of micellar systems in chemical reactions.

2. MICELLAR CATALYSIS

Micelles, the organized assemblies of surfactant molecules, serve as remarkable catalysts for specific chemical reactions by creating an ideal microenvironment (39). The application of the Gouy-Chapman model assists in comprehending the electrical double layer formed around charged surfactant molecules. When surfactant molecules possess charged groups, such as ionic head groups or ionized hydrophilic regions, an electric double layer takes shape around each micelle. In this model, the electric double layer comprises two distinct areas: the Stern layer, which is the innermost layer characterized by a compact arrangement of ions strongly associated with the charged surface, and the diffuse layer, extending outward from the Stern layer, where ions exhibit a more diffuse distribution and a weaker association with the surface. Within the confines of the micelle, the concentration of reactant molecules exceeds that in the surrounding bulk solution. This localized increase in concentration significantly elevates the likelihood of reactant molecules colliding and initiating chemical reactions, resulting in an accelerated reaction rate. Furthermore, micelles have a unique capability to solubilize hydrophobic reactant molecules within their hydrophobic core. By solubilizing these reactants, micelles effectively elevate their effective concentration, rendering them more accessible to other reactant molecules, thus enhancing their participation in the reaction.

Micelles also excel in stabilizing reaction intermediates or transition states that are energetically unfavorable or unstable. By encapsulating these species within their structure, micelles create a favorable environment for the response to advance, reducing activation energy and boosting reaction rates. The well-defined surface of micelles further contributes to their catalytic activity. Reactant molecules can interact with the micelle’s surface, promoting adsorption and subsequent reactions at the interface. This surface reaction mechanism significantly augments the overall reaction rate.

Essentially, micellar catalysis employs a multifaceted approach to accelerate reaction rates by concentrating reactants, dissolving hydrophobic compounds, stabilizing intermediates, and providing a structured surface for interactions. These qualities make micelles an indispensable tool for numerous chemical processes.

Micellar catalysis, with its ability to catalyze reactions by creating a favorable environment, has sparked interest among researchers eager to explore its potential. To delve deeper into the mechanisms driving these catalyzed reactions within micelles, scientists have embraced kinetic modeling. This approach offers a systematic framework for describing and predicting the behavior of reactions in this distinctive setting. Several kinetic models have been proposed to elucidate the intricate details of micellar catalysis. These models, such as the Berezin model and the pseudophase model, the ion exchange model, and the Piskiewicz model, offer valuable insights into how micelles influence reaction rates, providing researchers with the tools to interpret and predict the outcomes of reactions catalyzed by these molecular assemblies. By combining kinetic models with micellar catalysis, scientists are effectively advancing their understanding of these systems and their practical applications in diverse fields such as medicine and wastewater treatment.

3. KINETIC MODELS

The majority of kinetic data have been analyzed using the following kinetic models, providing a quantitative or semi-quantitative discussion.

3.1. Pseudophase Model

The pseudophase model, first formulated by Menger and Portnoy (29,30), provides a structured approach for rationalizing kinetic data in micellar systems. According to this model, chemical reactions can occur in one or both two pseudophases found in the micellar system, namely the aqueous pseudophase and the micellar pseudophase. It postulates that reactants partition between the bulk solution and the micellar phase, with the actual reaction exclusively taking place within the micelles. The concentration of reactants within the micellar phase is treated as a pseudo concentration, giving the model a distinctive name.

A widely accepted scheme for an unimolecular, micellar-catalyzed reaction is as follows (Figure 1)

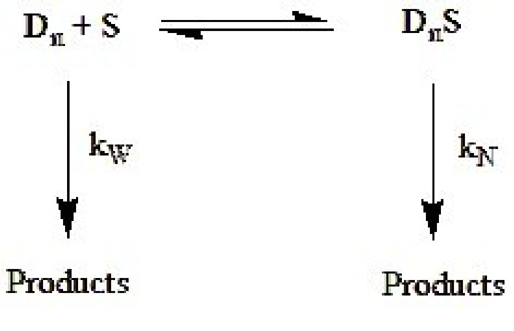


Figure 1: Scheme for an unimolecular micellar–catalyzed reaction.

Where K is the micelle-substrate binding constant, k_W and k_M are rate constants for the water and micellar phases, respectively, and S is a neutral substrate. K_ψ is the observed rate constant. The formula for micelle concentration $[D_n]$ is $[D_n] = ([C]\text{-}CMC)/N$. Where CMC stands for the critical micellar concentration, N is the aggregation number, and C is the surfactant's stoichiometric concentration. Model outputs the rate-law

$$k_\psi = \frac{k_W + k_M K[D_n]}{(1+K[D_n])} \tag{1}$$

This rate law adjusts to

$$\frac{1}{k_W - k_\psi} = \frac{1}{k_W - k_M} + \frac{1}{k_W - k_M}\left(\frac{N}{K([C]\text{-CMC})}\right) \tag{2}$$

The relationship between reaction rates and micellar effects can be effectively studied by analyzing the slope and intercept of a plot, where $1/(K_W\text{-}K_M)$ is plotted against 1/([C]-CMC). These calculations yield the rate constants k_M and K.

The pseudophase model has proven to be a successful tool for explaining how micelles influence rates of various reactions, as summarized in Table 1. However, there are instances, such as the acid hydrolysis of p-nitrobenzaldehyde acetals and p-nitrophenyl diphenyl phosphate with fluoride ion in cetyltrimethylammonium fluoride (CTAF) (31), where the model falls shot. In these cases, where the only counterions present are OH^- or F^-, it is postulated that the reaction occurs not only in the aqueous and micellar pseudo phases but also at the interface where the micelle meets the surrounding water.

Table 1: Reactions in micellar medium interpreted by Pseudophase model.

Reaction	**Micellar medium**	**Remarks**	**Ref**
P – Nitrophenyl Acetate with Benzo hydroxamate ion	Alkyl dimethyl and diethyl ethanol ammonium bromides.	The pseudophase model provided the quantitative explanation of the kinetic micellar effect for this reaction.	40
1,3- dipolar cycloadditions of benzonitrile oxide with a series of N-substituted maleimides	SDS CTAB Alkyl poly (ethylene oxide) surfactants	Micellar accelerations have been observed, and the kinetic data obtained has been analyzed using the pseudophase model for bimolecular reactions.	41
Ninhydrin with Chromium – glycylglycine Complex.	16-s-16 gemini	The quantitative analysis of reaction rate variations in the presence of gemini surfactants was conducted successfully using the pseudophase model.	42
Ninhydrin with Glycine-Leucine dipeptide.	16-s-16 gemini	In gemini surfactants, the reaction exhibits a greater acceleration. The catalytic effects and rate increment brought about by gemini surfactants have been quantitatively explained by a pseudophase model of the micellar solution.	43
Ninhydrin with Chromium (III) amino acid in acetate buffer.	Dimeric gemini	The study utilized the pseudophase model of micellar catalysis to investigate the impact of gemini on the rate constant.	44
Ninhydrin with Zn (II)-Gly-Leu Complex.	CTAB	The relationship between the rate constant (k_ψ) and the concentration of CTAB was thoroughly discussed and described. The kinetic data were analyzed based on the pseudophase model of surfactant micelles. Various parameters, including thermodynamic and binding constants, were also calculated.	45
Ninhydrin with (Cr (III) - Gly-Tyr) 2+ Complex.	CTAB, gemini	The results obtained in the micellar medium were interpreted using the pseudophase model of micelles. Furthermore, the micellar binding constants KS for the $[Cr(III)\text{-}Gly\text{-}Tyr]^{2+}$ complex and K_N for ninhydrin were determined using the kinetic data.	46
Ninhydrin with Copper (II) – Glycl phenyl alanine complex.	CTAB	The pseudophase model interpreted the effect of CTAB on reaction rate.	47
Ninhydrin with (Cu (II) - Gly-L-Ala) + complex.	TTABr	The reaction follows first- and fractional-order kinetics with respect to $[Cu(II)\text{–}Gly\text{-}L\text{-}Ala]T^+$ and [ninhydrin]T in aqueous and TTABr micelles. The applied pseudophase model successfully	48
Ninhydrin with Glycine in Sodium acetate- Acetic Buffer.	gemini	The pseudophase model was utilized to analyze the experimental data of the rate constant (k_ψ) for [gemini]. The observed catalytic effect is ascribed to the combined influence of hydrophobic and electrostatic interactions between gemini surfactant molecules and the reactive species.	49
Ninhydrin with Glycyl phenylalanine (Dipeptide).	CTAB gemini	It was found that the surfactants had a catalytic effect on the reaction. Similar to conventional gemini surfactants, they exhibited the usual pattern of increasing and then stabilizing rate constants.	50

Reaction	Micellar medium	Remarks	Ref
Ninhydrin with Methionine Amino Acids.	gemini	The ninhydrin-methionine reaction exhibited a characteristic influence commonly associated with surfactants, which was elucidated through the application of a pseudophase model of micelles. Furthermore, additional factors, such as reaction rates and binding constants, were determined through calculations.	51
Reaction between dyes and mixed Surfactants in aqueous medium.	DTAB SDS	The quantitative analysis of reaction rate variations in the presence of DTAB and SDS surfactants was conducted successfully using the pseudophase model.	52
Ninhydrin with Tyrosine Aminoacid.	gemini	A detailed analysis of the relationship between the rate constant (k_ψ) and surfactant concentration was conducted using the pseudophase model. Through this quantitative approach, the micellar binding parameters and thermodynamic parameters were calculated.	53
Ninhydrin with Arginine Amino acid	gemini	A detailed analysis of the relationship between the rate constant (k_ψ) and surfactant concentration was conducted using the pseudophase model.	54
Hydrolysis of phenyl chloroformate	SDS, Brj35 , TTAB	A simple pseudophase model was applied. The trend of the reaction is SDS < Brj_{35}< TTAB < SB3 – 14	55
Kinetic study in water-ethylene glycol cationic, zwitterionic, nonionic, and anionic micellar solutions	TDAB, SDS	The researchers observed that the effects of the micellar medium could be explained by considering various factors, such as charge-charge interactions, polarity, ionic strength, and water content in the micellar interfacial region.	56
The reaction between$[Ru(NH_3)_5pz]^{2+}$ + $S_2O_8^{2-}$	CTACl AOT	The results are interpreted by taking the pseudophase model, modified in some cases, as a general basis in order to take into account the specificity of the reaction medium.	57
Picolinic acid promoted hexavalent chromium oxidation of glycerol	SDS CPC	Reaction inhibits in CPC, whereas it accelerates in SDS.	58
Oxidation of methyl blue by Ce(IV)	TX-100	The rate decreases when there is an increase in TX-10 concentration.	59
Oxidation of aspartic acid with molybdenum-oxime-ligand	SDS	The interfacial active species proves useful in catalyzing aspartic acid oxidation.	60
Persulfate oxidation of methylene blue	SDS TX-100	The rate of reaction decreases with respect to the increase in [SDS] and is not affected by TX-100.	61

The pseudophase model offers a simplified representation of complex systems, making it more accessible for understanding and analysis. It enables researchers to make predictions about how the system behaves under various conditions, which is crucial for exploring and optimizing its properties.

However, the model has limitations. It assumes that reactions exclusively occur within the micellar phase, overlooking the possibility of alternative reaction pathways. In certain situations, reactions may take place at the interface between the micelle and the solvent or involve species not integrated into the micelles. These scenarios are not adequately addressed by the pseudophase model, highlighting the need for alternative models to account for these complexities.

3.2. Piszkiewicz Model

Combining elements from both the Berezin and pseudophase models, the Piszkiewicz model introduces a fresh perspective on micellar catalysis (36,37). This model says that the reaction primarily takes place within a distinct reaction layer situated at the surface of the micelle. The rate of the response is governed by the concentration of reactants within this reaction layer, which acts as a critical zone for the reaction to occur. Importantly, the Piszkiewicz model takes into account the distribution of reactants between the bulk solution and the micellar surface, recognizing the dynamic interplay between these two regions.

Visualizing the Piszkiewicz model (Figure 2), one can envision a scenario where the micelle's surface plays a pivotal role in mediating the reaction. It is within this reaction layer that reactants interact and transform, guided by their proximity to the micellar surface. This unique model bridges the gap between the traditional Berezin and pseudophase models, offering a more comprehensive insight into the micellar catalysis process. It provides insights into the crucial role of the micellar surface and the interplay between the bulk solution and the micellar environment in catalyzing chemical reactions.

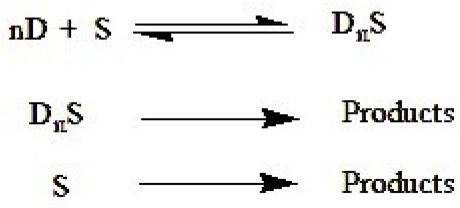


Figure 2: Visualization of the Piszkiewicz model.

Here, the rate constants for the reaction in the micelle and water, respectively, are k_M and k_W. K_D is the dissociation constant of the micelle-substrate complex. The equation yields the rate law.

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

The equation (3) can also be modified to adopt the following form:

$$\log\left\{\frac{k_{obs} - k_W}{k_M - k_{obs}}\right\} = n \log[D] - \log K_D \quad (4)$$

Hence, a graphical representation of log[D] against log $[k_{obs} - k_W] / [K_M - K_{obs}]$ should yield a linear relationship. The slope of this plot corresponds to the value of ‘n,’ often referred to as the cooperativity index, which characterizes the system’s behavior. When log $[k_{obs} - k_W] / [K_M - K_{obs}]$ equals zero, the value of n log[D] becomes equivalent to log K_D.

The Piszkiewicz model offers a quantitative framework to understand the enhanced rates observed in micellar-catalyzed reactions (as summarized in Table 2). It equips researchers with the mathematical tools to calculate rate constants and predict reaction rates under varying conditions. This model takes into consideration how reactants are organized within micelles, the role played by micellar interfaces, and the influence of micellar properties on reaction rates. This knowledge is instrumental in the design and optimization of catalytic systems.

Table 2: Reactions in micellar medium interpreted by Piszkiewicz model.

Reaction	Micellar medium	Remarks	Ref
Picolinic acid promoted hexavalent chromium oxidation of glycerol	SDS CPC	Reaction inhibits in CPC, whereas it accelerates in SDS.	58
Oxidation of L-leucine by N-bromo napthalimide	CTAB	The results were elucidated by utilizing the models developed by Piszkiewicz, Raghavan, and Srinivasan.	62
Alkaline fading of malachite green	DTAB TX-100 SDS	The researchers utilized both Piszkiewicz’s pseudophase ion exchange model and traditional/classical models in their study.	63
Reaction of dithionite ion and bis-(2-pyridinealdoximato) di oxomolybdate (IV) complex	SDS	The quantitative analysis of the impact of anionic surfactants on the reaction medium was determined using the Piszkiewicz model, which describes the intricate sequence of complex interactions	64
Oxidation of L-lysine by permanganate ion in perchloric acid medium	SLS and PEG	The reaction has been found to possess positive activation entropy, indicating the dissociative nature of the transition state and outer-sphere electron transfer mechanism.	65
Interaction of malachite green and brilliant green with water	Brij 35, sodium dodecyl sulfate, cetyltrimethylammonium bromide, and 3- (dimethyl dodecyl ammonium)-propane sulfonate	Spectrophotometric measurements were utilized to establish the relationship between the concentration of different surfactants, and the rate constants governing the interaction of malachite green (MG) and brilliant green (BG) dyes with water. The medium effect and the concentration effect characterized the impact of surfactant micelles on the rate constants of the reactions.	66
Oxidation of paracetamol by water-soluble colloidal MnO_2 in the presence of an anionic surfactant	SDS	The influence of SDS as a catalyst in water-based solutions has been extensively studied using Piszkiewicz. Several important parameters have been determined, including the binding constant (7.59×10^{-2} mol^{-1} dm^3), dissociation constant potential reaction mechanism, and rate law have been proposed.	67
Oxidative degradation of acridine orange by acidic chlorite	CTAB	The results were elucidated by utilizing the models developed by Piszkiewicz, Raghavan, and Srinivasan.	68
Oxidation of hydroxylamine hydrochloride by Vanadium (V)	SDS	The results were elucidated by utilizing the models developed by Piszikiewicz, Raghavan, and Srinivasan.	69
Hydrolysis of di-2-methoxy-4-nitroaniline phosphate	SDS Brij-35	The binding constants between the reactants and surfactants evaluated from the Piszkiewicz model.	70
Thioglycolic acid oxidation by N,N’-phenylene	SDS CTAB	SDS and CTAB catalyzed the reaction.	71

Reaction	Micellar medium	Remarks	Ref
bis(salicylideneiminato) manganese(III)			
Redox reaction of bis-(2-pyridinealdoximato)dioxomolybdate(IV) complex with thiosulphate	CTAB	A slow rate characterizes the aqueous acidic medium compared with the surfactant (CTAB) medium and with the second order rate constant of 0.1299 ± 0.004 and 0.294 ± 0.02 $dm^3\ mol^{-1}\ 1s^{-1}$, respectively.	72
Oxidation of glutamic acid by bis-(2-pyridinealdoximato)dioxomolybdate(IV) complex	CTAB	Cetyltrimethylammonium bromide in the system increased the oxidation rate of the GTA due to the high impact of hydrophobic and ion interaction between the micelle and substrates.	73

Numerous experimental studies have validated the Piszkiewicz model. By comparing predicted rate constants and reaction rates with actual experimental data, a strong agreement has been observed in many instances.

However, it's important to note that the Piszkeiwicz model relies on simplifying assumptions. For instance, it assumes the existence of a single reactive species within micelles and disregards interactions between micelles. While these simplifications make the model mathematically manageable, they may oversimplify the complexities of real systems. Consequently, there can be deviations between model predictions and experimental observations in certain cases, underscoring the necessity for a detailed comprehension of the system's complexity.

3.3. Ion Exchange Model

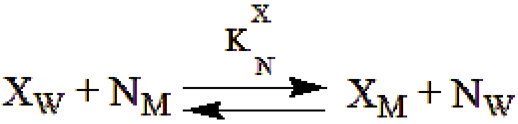
The ion exchange model, focused on reactions involving charged reactants (38), provides a unique perspective on micellar catalysis. It views micellar aggregates as similar to ion exchange resins, possessing the capability to bind and exchange ions. The essence of the model lies in the concept that the rate of the reaction is profoundly influenced by the exchange of ions between these micellar aggregates and the surrounding bulk solution.

The Ion-Exchange Model provides a detailed understanding of how charged reactants and catalysts interact within micellar catalysis. It emphasizes the significance of ion exchange equilibrium, which plays a crucial role in determining the reaction rate. This model is particularly useful for reactions involving ionic reactants or catalysts, where the exchange of ions between the micelles and the bulk solution significantly impacts the catalytic process.

To work effectively, the model makes two key assumptions:

1. The micellar surface is either saturated with counterions, or the binding constant (ß) remains constant.
2. The selectivity of the surface for various counterions can be expressed through a straightforward ion exchange constant.

The value of ß, typically falling in the range of 0.6 to 0.9 (74), is independent of surfactant concentration in the presence of counterions. This model allows researchers to predict the effects of various parameters, such as surfactant concentration, temperature, and pH, on the reaction rate. By understanding the factors influencing the ion exchange equilibrium, reaction conditions can be strategically manipulated to enhance catalytic performance. The exchange between the micelle (M) and the aqueous phase (W) is described by the ion–exchange constant. K_N^X.



$$X_W + N_M \overset{K_N^X}{\rightleftharpoons} X_M + N_W$$

Figure 3: Ion–Exchange model.

$$K_N^X = \frac{[N_W][X_M]}{[X_W][N_M]} \quad (5)$$

N is the reactive ion, and X is the counterion of the surfactant.

$M_N^S = [N_M]/[D_N]$, $M_X^S = [X_M]/[D_N]$ and $M^S{}_N + M^S{}_X = ß$

According to Romsted (10) $M^S{}_N$ represents the concentration of the reactive ion in moles per liter of Stern layer volume.

$[D_N]$ = [C-CMC], where C is the concentration of surfactant. S is the neutral substrate bound along with X.

However, directly validating this model experimentally poses challenges. The small scales involved in observing and measuring the ion exchange process within micelles make it complex. Consequently, some assumptions and predictions of the model may require further experimental validation.

While the ion exchange model provides a comprehensive understanding of the interaction between reactants and catalysts within micellar catalysis, it is essential to recognize its limitations. One significant limitation is the difficulty in direct experimental validation due to the small scales involved in observing and measuring the ion exchange process within micelles. This can lead to discrepancies between theoretical predictions and experimental observations. Furthermore, the model assumes a constant level of counterion binding (β) and a straightforward ion exchange constant, which might oversimplify the actual complexities of micellar systems. The model's accuracy is primarily contingent upon these assumptions holding under various experimental conditions. Consequently, some aspects of the model's predictions may require further experimental scrutiny to ensure reliability. Additionally, the ion exchange model is particularly suited for reactions involving ionic reactants or catalysts. For reactions involving non-ionic species or those predominantly occurring at the micellar interface, alternative models might offer more precise representations. Addressing these limitations is crucial for refining the model and enhancing its applicability to a broader range of catalytic processes.

The ion exchange model is particularly suitable for reactions involving ionic micelles. In this model, the micellar surface acts similarly to an ion-exchange resin, selectively binding and exchanging ions. This model considers the micelle as a charged entity with counterions bound to its surface. The rate of reaction is influenced by the exchange of reactive ions with the micellar-bound counterions, described by the ion-exchange constant. K_N^X (equation 5).

For ionic micelles, the ion exchange model is suitable, whereas the pseudophase model is more fitting for non-ionic micelles. The first-order rate constants exhibit an increasing trend with rising surfactant concentration, reaching stability when the substrate is fully micellar-bound. This pattern is particularly observed when the reactive ion serves as the sole counterion in the solution, aligning with the ion-exchange pseudophase model of micellar catalysis in aqueous systems (35). This behavior has been noted in reactions like nucleophilic addition or substitution by cyanide or bromide ions and in acetal hydrolysis within micellized alkane sulfonic acids.

The practical interpretation of the equilibria (PIE) model extends its utility beyond measuring the intrinsic pK and surface pH of micelles. It can also be effectively employed to determine the surface pH in microemulsions, vesicles, and biological membranes. Furthermore, Romsted and Zanetted have demonstrated that the model remains applicable to micellar solutions containing buffers, even in the presence of added counterions, provided that the exchangeable counterion amounts in the aqueous pseudophase are expressed as activities. The buffer is hydrophilic and carries the same charge as the micelle surface, remaining exclusively in the aqueous phase (75).

The ion exchange model delivers a comprehensive mechanistic understanding of how reactants and catalysts interact within micellar catalysis. It elucidates the transport of reactants into micelles, their interaction with catalysts, and their subsequent exit from the micelles. This comprehension proves invaluable for optimizing reaction conditions and designing more efficient catalytic systems.

By understanding the factors influencing the ion exchange equilibrium, researchers can strategically manipulate reaction conditions to enhance catalytic performance. However, directly observing and measuring the ion exchange process within micelles can be complex due to the small length scales involved, necessitating further experimental validation of some model assumptions and predictions (as summarized in Table 3).

Table 3: Reactions in micellar medium interpreted by ionic exchange model.

REACTION	Micellar medium	Remarks	Ref
Acid hydrolysis of vinyl ethers	SDS CTAB Brij35	In the cases of cationic and non-ionic micelles, minimal effects on rate were observed. However, anionic micelles exhibited an increase in the reaction velocity, and the rate constants reached their maximum values as the concentration of SDS (sodium dodecyl sulfate) increased.	38
Picolinic acid promoted hexavalent chromium oxidation of glycerol	SDS CPC	Reaction inhibits in CPC, whereas it accelerates in SDS.	58
Alkaline fading of malachite green (MG^+)	DTAB TX-100 SDS	Piszkiewicz’s pseudophase ion exchange model and classical models were used.	63
Hydrophobic n-diazeniumdiolates and the aqueous interface of sodium dodecyl sulfate (SDS) micelles.	SDS	The quantitative analysis of the reaction is achieved successfully through the utilization of the ion exchange model.	76
Application of the pseudophase ion exchange model to a micellar-catalyzed reaction in water−glycerol solutions	CTAB	The hydrolysis of p-nitrophenyl diphenyl phosphate (NPDPP) in the presence of sodium hydroxide (NaOH), micelles of CTAB, and aqueous solutions of glycerol was studied experimentally. The findings were interpreted using the pseudophase ion exchange model (PPIE). The effect of glycerol on micelle formation and its influence on the reaction medium were investigated. The obtained results suggest that the PPIE model can effectively describe micellar catalysis in water-glycerol solutions.	77
Acid-catalyzed hydrolysis of hydrophobic ketals in aqueous cationic micelles: partial failure of the pseudophase ion exchange model	CTAB CTACl	The objective of the study was to investigate the effects of aqueous CTAX, with and without added salt (NaX), on the rate of acid hydrolysis of two hydrophobic micellar-bound ketals. The experiments were conducted at temperatures of 30°C and 40°C. The main purpose was to assess the accuracy of the Pseudophase Ion Exchange (PIE) model in predicting the reactions of neutral organic substrates with co-ions.	78
Reaction between malachite green and	CBDAC HTAAB	The cationic surfactants show catalytic effect, whereas anionic surfactants show inhibitory effect.	79

REACTION	Micellar medium	Remarks	Ref
sodium hydroxide	SDS		
Reduction of ketones by sodium borohydride	CTAB CTAC	Micellar inhibition. A pseudophase ionic exchange model was applied for kinetic analysis.	80
Oxidation of propane-2-ol to acetone by pentavalent vanadium	CPC SDS TX-100	Inhibits in CPC and accelerates in SDS & TX-100.	81
Oxidation of D-Sorbitol by pentavalent vanadium ion	CPC SDS TX-100	SDS and TX-00 can be used as catalysts for obtaining D-glucose from oxidation D-sorbitol.	82

Despite its wide acceptance, experimental verification of the ion exchange model can present challenges. Directly observing and measuring the ion exchange process within micelles can be complex due to the small length scales involved. Consequently, some aspects of the model's assumptions and predictions may necessitate further experimental validation.

It's important to note that the ion exchange model finds its most suitable application in reactions involving charged reactants or catalysts, where the ion exchange equilibrium plays a significant role. For reactions primarily involving non-ionic species or those occurring predominantly at the micellar interface, alternative models or frameworks may offer a more accurate representation of the catalytic process.

3.4. Berezin Model

The Berezin model (25) operates on the premise that the reaction predominantly unfolds within the aqueous core of the micelle. In this model, the reactants are considered to exist in an equilibrium state with the micellar surface, and the surface concentration of these reactants significantly influences the rate of the reaction.

A key assumption of the Berezin model is the existence of a swift equilibrium between the reactants within the bulk solution and those that have been adsorbed onto the micellar surface. This equilibrium signifies that reactants readily interact with the micelle, and this interaction plays a crucial role in governing the overall reaction rate. The Berezin model provides a simplified yet insightful representation of micellar catalysis, shedding light on the interplay between reactants and the micellar environment in these catalytic processes.

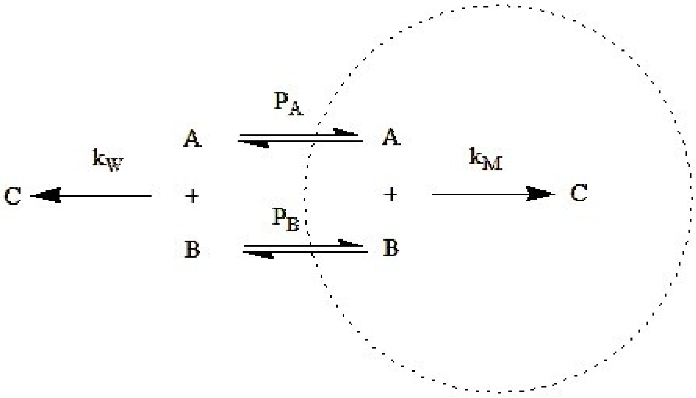


Figure 4: Berezin model.

When examining a surfactant solution above the critical micelle concentration (CMC), we can view it as a two-phase system. In this scenario, we can describe the observed reaction velocity, denoted as V, as an average over the entire system's volume. This means we take into account the contributions from both the micellar phase (V_M) and the aqueous phase (V_W) to calculate the overall reaction rate. This approach allows us to consider how reactions occur within both phases, with their respective reaction velocities, to understand the system's behavior better. In essence, it provides a comprehensive view of the reaction dynamics in surfactant solutions above the CMC.

$$V = V_M C\overline{V} + V_W\left(1 - C\overline{V}\right) = k_{exp}[A]_0[B]_0 \quad (7)$$

$\overline{V}$Represents the molar volume of the surfactant, while C denotes the surfactant concentration (expressed in molarity) that is below the critical micelle concentration (CMC). Under the assumption that the situation adheres to the law of mass action, we derive the following...

$$V_M = k_M[A]_M[B]_M \text{ and } V_w = k_W[A]_W[B]_W \quad (8)$$

Equations are employed to establish concentration between the initial total concentrations of reactants, denoted as $[A]_0$ and $[B]_0$, and their actual concentrations within their respective phases.

$$\frac{[A]_M}{[A]_W} = p_A \quad \text{(Partition coefficient)} \quad (9)$$

$$[A]_0 = [A]_M C\overline{V} + [A]_W\left(1 - C\overline{V}\right) \quad (10)$$

Equations 5, 6, and 7 collectively lead to the following conclusion:

$$k_{exp} = \frac{k_M p_A p_B C\overline{V} + k_W(1\text{-}C\overline{V})}{(1+K_A C)(1+K_B C)} \quad (11)$$

In the given context, the equation $K_A = (P_A - 1)\overline{V}$ Defines the parameters K_A and K_B. Here, k_W and k_M represent the rate constants for the water and micellar phases, respectively, while keep signifies the experimentally determined effective reaction rate constant.

Now, as a limiting scenario, if the measured reaction velocity encompasses not only the rates occurring in the micellar and aqueous phases but also the rate of a reaction involving solubilized and unsolubilized reactants, we can express it in the following manner:

$$V = k_M[A]_M[B]_M C\overline{V} + k'_M[A]_M[B]_W C\overline{V} + k''_M[A \quad (12)$$

In this scenario, various rate constants apply to different phases. For the water and micellar phases, the rate constants are represented as k_W and k_M, respectively. Additionally, there are rate constants k'_M and k''_M for the solubilized and insolubilized phases.

Within the micellar phases, $[A]_W$ and $[B]_W$ are used.

The terms $\overline{V}$And (1-C. $\overline{V}$) Correspond to the volume fractions of the micellar and aqueous phases, respectively.

Combining all these factors, the resulting equation captures the complex interplay of reactions in different places of the system.

$$k_{exp} = ¿¿ \quad (13)$$

The Berezin model offers a successful framework for understanding how micelles impact the rates of bimolecular reactions and provides a means to determine binding constants, as summarized in Table 4. This model simplifies the complex micellar environment, making it more accessible for analysis and comprehension of reaction kinetics with the micelle.

In the Berezin model, the micelle is treated as an effective medium with distinctive properties, such as different dielectric constant solvation characteristics compared to surrounding bulk solvents. This unique perspective enables the model to make quantitative predictions about reaction rates and other kinetic parameters within the micellar system. These predictions can then be compared with experimental data, enhancing our ability to understand and predict reaction behavior in micelles.

Table 4: Reactions in micellar medium interpreted by Berezin model.

REACTION	**Micellar medium**	**Remarks**	**Ref**
Oxidation of dextrose by *N*-bromo phthalimide	SDS Triton X – 100	In SDS, the rate decreases, and in TX-100, the rate increases. Mechanism explains with Berezin's model.	83
Oxidation of tris (2,2'-bipyridyl) cobalt (iii) by parabenzoquinone	SDS	SDS accelerates the reaction and kinetic analysis carried out by using Berezin's model.	84
Hydrolysis of mono-n-ethyl-*o*-toluidine phosphate	CTAB	The rate of hydrolysis by micelles was examined using the Menger-Portnoy, Piszkiewicz, and Berezin kinetic models. Various thermodynamic parameters were assessed. The rate (surfactant) profile allowed for the determination of kinetic parameters, namely the micellar phase (k_Ψ) and binding constant (K_S).	85
Hydrophobic n-diazeniumdiolates and the aqueous interface of sodium dodecyl sulfate (SDS) micelles	SDS	The rate of NO release from micellar-bound diazeniumdiolates is determined by the surface charge of the micelles.	86
Kinetics of nitrophenol violet anion reaction with OH^- ion:	CTAB, CTAOH	Compared to Piszkiewicz's, Terezin's, and pseudophase ion-exchange models.	87
Kinetics of alkaline fading of methyl violet in micellar solutions of surfactants: comparing	Brij 35, 3-(dimethyldodecylammonio)-propane sulfonate SDS	Each of the kinetic models used for the treatment of experimental data has certain inner assumptions and consequently gives results that are somewhat different in their physical meaning. The comparison of the applicability of the models can be made on the basis of values of standard deviations of model parameters calculated as unknown during the fitting. In this respect, Berezin's and PIE models give better results than application of Piszkiewicz's model	88
Reaction rate of cationic triphenylmethane dyes with water according to Berezin's model	non-ionic cationic anionic zwitterionic	Berezin's model performed well when applied to the description of the micellar effect on the reaction of dye with the hydroxide ion. However, it was revealed that this model does not take into account the change in the local concentration of the HO^- ions due to a compression of the double electric layer upon the addition of reacting ions to the system, as well as the constant of association of the HO^- ions with cationic head groups of surfactant.	89

REACTION	Micellar medium	Remarks	Ref
Oxidation of lactic acid by chromic acid	SDS	Catalysis by SDS. Berezin's model and Piszkiewiez's model were applied.	90
The redox reaction of allylthiourea and bis-(2-pyridinealdoximato)dioxomolybdate(iv) complex in an aqueous acidic medium	CTAB, SDS	Piszkiewicz and Berezin models are utilized to analyze and interpret the redox properties of allylthiourea when interacting with a Mo(IV) complex in the presence of surfactants. These models' parameters are employed to explain the observed behavior.	91
Analysis of kinetic data for ionic micellar mediated semi-ionic bimolecular reaction	CTAB	The least-squares values obtained from both models show a similar fit to the observed data; the reliability of the calculated K_S values from the Berezin model appears to be higher than those from the Ion Exchange model. This conclusion is drawn from the fact that the K_S values obtained from the BPP model closely match the corresponding K_S values determined through spectrophotometric methods.	92
Oxidation of methanol to formaldehyde	SDS	Rate enhanced by 324-fold times in the presence of SDS.	93
Oxidation of dextrose by N-Bromosuccinimide	SDS TX-100	The catalytic ability is greater for TX-100 than for SDS.	94
Base catalyzed hydrolysis of 4-nitrophenyl esters of phosphoric, phosphoric, and toluene sulfonic acids	Dicationic and mono-cationic surfactants	In micellar pseudophase, the α-effect of the hydroperoxide ion in the peroxyhydrolysis reaction is retained and reaches 100 times.	95
Catalytic oxidation of benzyl alcohol (BA), p-chlorobenzyl alcohol (p-ClBA), and p-anisyl alcohol (p-OMeBA)	Cetylpyridium chloride (CPCl) Dodecylpyridinium chloride (DPCl)	12-fold catalytic enhancement for the oxidation of p-anisyl alcohol in the CPCl micellar environment	96
Reaction of cyanide and picrate ions	TX-100	The reaction mixture was found to enhance the e rate of the reaction at the CMC below TX-100.	97
Oxidation of racemic tartaric acid by Ce(IV)	SDS	Plots of pseudo-first-order rate constants in the presence of surfactant (sodium dodecyl sulfate, SDS) against the [SDS] abruptly rise in the concentration range below CMC (critical micelle concentration), after which the rate exponentially falls.	98

However, it's important to reorganize the limitations of the Berezin model. This model assumes a uniform and homogeneous micellar structure, which simplifies the real-world complexity and heterogeneity of micelles. Consequently, the Berezin model is most suitable for reactions that occur within the micelle's core or at the micelle-solvent interface. It may not be well-suited for reactions involving reactants that do not strongly interact with the micellar environment, where more intricate models might be necessary for a precise representation of the catalytic process.

4. CONCLUSION

In conclusion, the exploration of micellar catalysis and kinetic modeling offers invaluable insights into the intricate world of chemical reactions within micelles. Through our examination of various kinetic models, including the Berezin, Piszkiewicz, ion exchange, and pseudophase models, we have gained a deeper understanding of the mechanisms governing these reactions and the influence of micelles on their rates. While each model presents its advantages and limitations, their collective contribution has significantly enhanced our comprehension of micellar catalysis. Moving forward, continued research in this field holds great potential for unlocking new avenues for sustainable chemical synthesis and industrial applications. By refining existing models and developing innovative approaches, we can further elucidate the complex interplay between reactants, catalysts, and micellar environments, paving the way for enhanced efficiency and selectivity in catalytic processes.

4.1. Future Aspects

Future research in micellar catalysis and kinetic modeling holds significant promise for advancing our understanding of complex chemical reactions in heterogeneous environments. By integrating cutting-edge computational techniques with experimental data, researchers can elucidate sophisticated reaction mechanisms and design more efficient catalysts. Additionally, exploring the influence of various parameters such as temperature, pH, and surfactant concentration on reaction kinetics will provide valuable insights for optimizing catalytic processes. Moreover, the development of predictive models capable of accurately simulating micellar systems will facilitate the design of novel catalytic materials with tailored properties. Continued exploration of micellar catalysis and kinetic modeling is poised to unlock new avenues for sustainable chemical synthesis and industrial applications, driving innovation in diverse fields ranging from pharmaceuticals to renewable energy.

5. CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

6. REFERENCES

1. Kaatze U. Kinetics of Micelle Formation and Concentration Fluctuations in Solutions of Short-Chain Surfactants. J Phys Chem B [Internet]. 2011 Sep 8;115(35):10470–7. Available from: <URL>.

2. Perinelli DR, Cespi M, Lorusso N, Palmieri GF, Bonacucina G, Blasi P. Surfactant Self-Assembling and Critical Micelle Concentration: One Approach Fits All? Langmuir [Internet]. 2020 Jun 2;36(21):5745–53. Available from: <URL>.

3. Ghosh KK, Sinha D, Satnami ML, Dubey DK, Rodriguez-Dafonte P, Mundhara GL. Nucleophilic Dephosphorylation of p -Nitrophenyl Diphenyl Phosphate in Cationic Micellar Media. Langmuir [Internet]. 2005 Sep 1;21(19):8664–9. Available from: <URL>.

4. Kolay S, Ghosh KK, MacDonald A, Moulins J, Palepu RM. Micellization of Alkyltriphenylphosphonium Bromides in Ethylene Glycol and Diethylene Glycol + Water Mixtures: Thermodynamic and Kinetic Investigation. J Solution Chem [Internet]. 2008 Jan 29;37(1):59–72. Available from: <URL>.

5. Ghosh KK, Verma SK. Kinetics of α-chymotrypsin catalyzed hydrolysis of 4-nitrophenyl acetate in ethanolamine surfactants. Indian J Biochem Biophys [Internet]. 2008;45(5):350–3. Available from: <URL>.

6. Ghosh KK, Verma SK. Effects of head group of cationic surfactants on the hydrolysis of p - nitrophenyl acetate catalyzed by α-chymotrypsin. Int J Chem Kinet [Internet]. 2009 Jun 25;41(6):377–81. Available from: <URL>.

7. Ghosh KK, Sinha D, Satnami ML, Dubey DK, Shrivastava A, Palepu RM, et al. Enhanced nucleophilic reactivity of hydroxamate ions in some novel micellar systems for the cleavage of Parathion. J Colloid Interface Sci [Internet]. 2006 Sep;301(2):564–8. Available from: <URL>.

8. Saha R, Ghosh A, Saha B. Kinetics of micellar catalysis on oxidation of p-anisaldehyde to p-anisic acid in aqueous medium at room temperature. Chem Eng Sci [Internet]. 2013 Aug;99:23–7. Available from: <URL>.

9. Saha R, Ghosh A, Saha B. Micellar catalysis on 1,10-phenanthroline promoted hexavalent chromium oxidation of ethanol. J Coord Chem [Internet]. 2011 Nov 10;64(21):3729–39. Available from: <URL>.

10. Ghosh A, Saha R, Saha B. Suitable combination of promoter and micellar catalyst for kilo fold rate acceleration on propanol to propionaldehyde conversion in aqueous media. J Ind Eng Chem [Internet]. 2014 Jan;20(1):345–55. Available from: <URL>.

11. Saha R, Ghosh A, Sar P, Saha I, Ghosh SK, Mukherjee K, et al. Combination of best promoter and micellar catalyst for more than kilo-fold rate acceleration in favor of chromic acid oxidation of d-galactose to d-galactonic acid in aqueous media at room temperature. Spectrochim Acta Part A Mol Biomol Spectrosc [Internet]. 2013 Dec;116:524–31. Available from: <URL>.

12. Acharjee A, Rakshit A, Chowdhury S, Malik S, Barman MK, Ali MA, et al. Micellar catalysed and heteroaromatic base promoted rate enhancement of oxidation of an alicyclic alcohol in aqueous medium. J Mol Liq [Internet]. 2019 Mar;277:360–71. Available from: <URL>.

13. Ghosh A, Saha R, Mukhejee K, Ghosh SK, Bhattacharyya SS, Laskar S, et al. Selection of Suitable Combination of Nonfunctional Micellar Catalyst and Heteroaromatic Nitrogen Base as Promoter for Chromic Acid Oxidation of Ethanol to Acetaldehyde in Aqueous Medium at Room Temperature. Int J Chem Kinet [Internet]. 2013 Mar 22;45(3):175–86. Available from: <URL>.

14. Chowdhury KM, Mandal J, Saha B. Micellar catalysis of chromium(VI) oxidation of ethane-1,2-diol in the presence and absence of 2,2′-bipyridine in aqueous acid media. J Coord Chem [Internet]. 2009 Jun 1;62(11):1871–8. Available from: <URL>.

15. Mukherjee K, Ghosh A, Saha R, Sar P, Malik S, Saha B. Best combination of promoter and micellar catalyst for the rapid conversion of sorbitol to glucose. Spectrochim Acta Part A Mol Biomol Spectrosc [Internet]. 2014 Mar;122:204–8. Available from: <URL>.

16. Acharjee A, Rakshit A, Chowdhury S, Ali MA, Singh B, Saha B. Mixed anionic-nonionic micelle catalysed oxidation of aliphatic alcohol in aqueous medium. J Mol Liq [Internet]. 2020 Apr;303:112655. Available from: <URL>.

17. Saha R, Ghosh A, Saha B. Combination of best promoter and micellar catalyst for chromic acid oxidation of 1-butanol to 1-butanal in aqueous media at room temperature. Spectrochim Acta Part A Mol Biomol Spectrosc [Internet]. 2014 Apr;124:130–7. Available from: <URL>.

18. Ghosh SK, Saha R, Mukherjee K, Ghosh A, Bhattacharyya SS, Saha B. Micellar Catalysis on 1,10-Phenanthroline Promoted Chromic Acid Oxidation of Propanol in Aqueous Media. J Korean Chem Soc [Internet]. 2012 Feb 20;56(1):164–8. Available from: <URL>.

19. Ghosh SK, Ghosh A, Saha R, Saha B. Suitable combination of promoter and micellar catalyst for chromic acid oxidation of formaldehyde to formic acid in aqueous acid media at room temperature. Phys Chem Liq [Internet]. 2015 Jan 2;53(1):146–61. Available from: <URL>.

20. Chowdhury S, Rakshit A, Acharjee A, Mahali K, Saha B. Surface phenomenon in micellar media: An excellent controlling factor for oxidation of fatty aldehyde in aqueous medium. J Mol Liq [Internet]. 2020 Jul;310:113224. Available from: <URL>.

21. Chowdhury S, Rakshit A, Acharjee A, Kumar D, Saha B. Anionic micelles and their ideal binary mixture: Worth media for sustainable oxidation of hydrophobic alcohol. J Mol Liq [Internet]. 2022 Jan;346:117118. Available from: <URL>.

22. Ansari TN, Xu G, Preston A, Gao P. Recent Highlights in Micellar Catalysis: An Industrial Outlook. Org Process Res Dev [Internet]. 2024 Apr 19;28(4):816–30. Available from: <URL>.

23. Senchukova AS, Fetin PA, Perevyazko I, Lezov AA, Fetina VI, Vaitusionak AA, et al. Water-Soluble Copolymers of Styrene and a Surfactant Monomer in Micellar Catalysis. J Polym Res [Internet]. 2024 Mar 27;31(3):80. Available from: <URL>.

24. Acharjee A, Rakshit A, Chowdhury S, Saha B. Micelle catalysed conversion of ‘on water’ reactions into ‘in water’ one. J Mol Liq [Internet]. 2021 Jan;321:114897. Available from: <URL>.

25. Berezin I V, Martinek K, Yatsimirskii AK. Physicochemical Foundations of Micellar Catalysis. Russ Chem Rev [Internet]. 1973 Oct 31;42(10):787–802. Available from: <URL>.

26. Osipov AP, Martinek K, Yatsimirskii AK, Berezin I V. Micellar effects in the acylation of N-substituted imidazoles by p-nitrophenyl esters of carboxylic acids. Bull Acad Sci USSR Div Chem Sci [Internet]. 1974 Sep;23(9):1905–9. Available from: <URL>.

27. Martinek K, Osipov AP, Yatsimirski AK, Berezin IV. Mechanism of micellar effects in imidazole catalysis. Tetrahedron [Internet]. 1975 Jan;31(7):709–18. Available from: <URL>.

28. Bunton CA, Romsted LS, Smith HJ. Quantitative treatment of micellar catalysis of reactions involving hydrogen ions. J Org Chem [Internet]. 1978 Oct 1;43(22):4299–303. Available from: <URL>.

29. Bunton CA, Romsted LS, Savelli G. Tests of the pseudophase model of micellar catalysis: its partial failure. J Am Chem Soc [Internet]. 1979 Feb 1;101(5):1253–9. Available from: <URL>.

30. Bunton CA, Romsted LS, Thamavit C. The pseudophase model of micellar catalysis. Addition of cyanide ion to N-alkylpyridinium ions. J Am Chem Soc [Internet]. 1980 May 1;102(11):3900–3. Available from: <URL>.

31. Bunton CA, Frankson J, Romsted LS. Reaction of p-nitrophenyldiphenyl phosphate in cetyltrimethylammonium fluoride. J Phys Chem [Internet]. 1980 Oct 1;84(20):2607–11. Available from: <URL>.

32. Romsted LS. A General Kinetic Theory of Rate Enhancements for Reactions between Organic Substrates and Hydrophilic Ions in Micellar Systems. In: Micellization, Solubilization, and Microemulsions [Internet]. Boston, MA: Springer US; 1977. p. 509–30. Available from: <URL>.

33. Mittal KL, Lindman B. Surfactants in Solution [Internet]. Mittal KL, Lindman B, editors. Boston, MA: Springer US; 1984. Available from: <URL>.

34. Mittal KL. Solution Chemistry of Surfactants [Internet]. Mittal KL, editor. Boston, MA: Springer New York; 1979. Available from: <URL>.

35. Bunton CA, Romsted LS. Reactive Counterion Surfactants. In: Solution Behavior of Surfactants [Internet]. Boston, MA: Springer US; 1982. p. 975–91. Available from: <URL>.

36. Piszkiewicz D. Micelle catalyzed reactions are models of enzyme catalyzed reactions which show positive homotropic interactions. J Am Chem Soc [Internet]. 1976 May 1;98(10):3053–5. Available from: <URL>.

37. Piszkiewicz D. Positive cooperativity in micelle-catalyzed reactions. J Am Chem Soc [Internet]. 1977 Mar 1;99(5):1550–7. Available from: <URL>.

38. Velázquez MM, García-Mateos I, Herraez MA, Rodriguez LJ. Pseudo-phase ion-exchange model for micellar catalysis in the acid hydrolysis of vinyl ethers. Int J Chem Kinet [Internet]. 1984 Mar 19;16(3):269–76. Available from: <URL>.

39. Menger FM, Portnoy CE. Chemistry of reactions proceeding inside molecular aggregates. J Am Chem Soc [Internet]. 1967 Aug 1;89(18):4698–703. Available from: <URL>.

40. Bal S, Satnami ML, Kolay S, Palepu RM, Dafonte PR, Ghosh KK. Kinetic Studies of Micelle - Assisted Reaction of p-Nitrophenyl Acetate with Benzo-Hydroxamate Ion in Water-Ethylene Glycol Mixtures. J Surf Sci Technol [Internet]. 2007;23(1–2):33–48. Available from: <URL>.

41. Rispens T, Engberts JBFN. A Kinetic Study of 1,3-Dipolar Cycloadditions in Micellar Media. J Org Chem [Internet]. 2003 Oct 1;68(22):8520–8. Available from: <URL>.

42. Kumar D, Rub MA. Interaction of ninhydrin with chromium-glycylglycine complex in the presence of dimeric gemini surfactants. J Mol Liq [Internet]. 2018 Jan;250:329–34. Available from: <URL>.

43. Kumar D, Rub MA. Studies of interaction between ninhydrin and Gly-Leu dipeptide: Influence of cationic surfactants (m-s-m type Gemini). J Mol Liq [Internet]. 2018 Nov;269:1–7. Available from: <URL>.

44. Kumar D, Rub MA. Study of the interaction between ninhydrin and chromium(III)-amino acid in an aqueous-micellar system: Influence of gemini surfactant micelles. J Mol Liq [Internet]. 2020 Mar;301:112373. Available from: <URL>.

45. Kumar D, Rub MA. Role of cetyltrimethylammonium bromide (CTAB) surfactant micelles on kinetics of $[Zn(II)\text{-}Gly\text{-}Leu]^{+}$ and ninhydrin. J Mol Liq [Internet]. 2019 Jan;274:639–45. Available from: <URL>.

46. Akram M, Kumar D, Kabir-ud-Din. Influence of cationic gemini and conventional CTAB on the interaction of $[Cr(III)\text{-}Gly\text{-}Tyr]^{2+}$ complex with ninhydrin. Colloids Surfaces A Physicochem Eng Asp [Internet]. 2013 Jul;428:92–9. Available from: <URL>.

47. Kumar D, Neo KE, Rub MA, Tan ZL, Beh WL, Wong HL. Study of copper(II)–glycylphenylalanine complex with ninhydrin in aqueous and cationic CTAB micellar media: A kinetic and mechanistic approach. J Mol Liq [Internet]. 2015 Mar;203:204–9. Available from: <URL>.

48. Akram M, Saeed AAM, Kabir-ud-Din. Micellar, salt, and organic solvent effects on the rate of $[Cu(II)–Gly-l-Ala]^+$ complex–ninhydrin reaction. J Mol Liq [Internet]. 2015 Sep;209:367–73. Available from: <URL>.

49. Bhattarai A, Abdul Rub M, Posa M, Saha B, Kumar D. Catalytic impacts of cationic twin headed and tailed gemini surfactants toward study of glycine and ninhydrin in sodium acetate-acetic acid buffer system. J Mol Liq [Internet]. 2022 Aug;360:119442. Available from: <URL>.

50. Kumar D, Rub MA, Akram M, Kabir-ud-Din. Interaction between dipeptide (glycyl-phenylalanine) and ninhydrin: Role of CTAB and gemini (16-s-16, s=4, 5, 6) surfactant micelles. J Colloid Interface Sci [Internet]. 2014 Mar;418:324–9. Available from: <URL>.

51. Alghamdi YG, Rub MA, Kumar D. Influence of twin-headed gemini micellar system on the study of methionine amino acid with ninhydrin in buffer solution. R Soc Open Sci [Internet]. 2023 Feb 15;10(2):221229. Available from: <URL>.

52. Sachin KM, Karpe SA, Singh M, Bhattarai A. Study on surface properties of sodiumdodecyl sulfate and dodecyltrimethylammonium bromide mixed surfactants and their interaction with dyes. Heliyon [Internet]. 2019 Apr;5(4):e01510. Available from: <URL>.

53. Kumar D, Rub MA. Study of the reaction of ninhydrin with tyrosine in gemini micellar media. RSC Adv [Internet]. 2019;9(38):22129–36. Available from: <URL>.

54. Rub MA, Bhattarai A, Saha B, Jaffari ZH, Thu HT, Kumar D, et al. Effect of dicationic gemini surfactants on the rate of reaction between ninhydrin and arginine. Chem Pap [Internet]. 2022 May 20;76(5):2865–74. Available from: <URL>.

55. Muñoz M, Rodríguez A, Del Mar Graciani M, Luisa Moyá M. Micellar medium effects on the hydrolysis of phenyl chloroformate in ionic, zwitterionic, nonionic, and mixed micellar solutions. Int J Chem Kinet [Internet]. 2002 Jan 28;34(7):445–51. Available from: <URL>.

56. Rodríguez A, Muñoz M, Graciani M del M, Fernández Chacón S, Moyá ML. Kinetic Study in Water−Ethylene Glycol Cationic, Zwitterionic, Nonionic, and Anionic Micellar Solutions. Langmuir [Internet]. 2004 Nov 1;20(23):9945–52. Available from: <URL>.

57. López-Cornejo P, Pérez P, García F, de la Vega R, Sánchez F. Use of the Pseudophase Model in the Interpretation of Reactivity under Restricted Geometry Conditions. An Application to the Study of the $[Ru(NH_3)_5pz]^{2+}+S_2O_8^{2-}$ Electron-Transfer Reaction in Different Microheterogeneous Systems. J Am Chem Soc [Internet]. 2002 May 1;124(18):5154–64. Available from: <URL>.

58. Ghosh SK, Basu A, Saha R, Ghosh A, Mukherjee K, Saha B. Micellar catalysis on picolinic acid promoted hexavalent chromium oxidation of glycerol. J Coord Chem [Internet]. 2012 Apr 10;65(7):1158–77. Available from: <URL>.

59. Hassan M, AlAhmadi MD, Mosaid M. Micellar effect on the kinetics of oxidation of methyl blue by Ce(IV) in sulfuric acid medium. Arab J Chem [Internet]. 2015 Jan;8(1):72–7. Available from: <URL>.

60. Ugbaga Nkole I, Ola Idris S, Abdulkadir I, David Onu A. Oxidation of aspartic acid with molybdenum-oxime-ligand framework in acidified-aqua and interfacial active media: Menger-Portnoy kinetic model. Inorg Chem Commun [Internet]. 2024 Mar;161:111979. Available from: <URL>.

61. Ewais HA, Basaleh AS, Al Angari YM. 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. Int J Chem Kinet [Internet]. 2023 Jun 20;55(6):271–80. Available from: <URL>.

62. Katre Y, Goyal N, Singh AK. Effect of CTAB Micelle on the Oxidation of L-Leucine by N-Bromophthalimide: a Kinetic Study. Zeitschrift für Phys Chemie [Internet]. 2011 Jan 1;225(1):107–24. Available from: <URL>.

63. Samley B, Toosi AR. Kinetics Study of Malachite Green Fading in the Presence of TX-100, DTAB and SDS. Bull Korean Chem Soc [Internet]. 2009 Sep 20;30(9):2051–6. Available from: <URL>.

64. Nkole IU, Idris SO, Abdulkadir I, Onu AD. Application of Piszkiewicz model on the electron transfer reaction of dithionite ion and bis-(2-pyridinealdoximato)dioxomolybdate(IV) complex. Sci Rep [Internet]. 2022 Dec 22;12(1):22125. Available from: <URL>.

65. Hassan M, Al-Dhoun M, Batineh Y, Najjar AA, Dahadha A, Ibrahim QA. Micellar and Polymer Catalysis in the Kinetics of Oxidation of L-lysine by Permanganate Ion in Perchloric Acid Medium. South African J Chem [Internet]. 2021;75:73–9. Available from: <URL>.

66. Laguta AN, Eltsov SV. Micellar effects in kinetics of interaction of malachite green and brilliant green with water. Kharkov Univ Bull Chem Ser [Internet]. 2017;28(51):96–103. Available from: <URL>.

67. Kumar Singh A, Sen N, Kumar Chatterjee S, Susan MABH. Kinetic study of oxidation of paracetamol by water-soluble colloidal MnO_2 in the presence of an anionic surfactant. Colloid Polym Sci [Internet]. 2016 Oct 28;294(10):1611–22. Available from: <URL>.

68. Pare B, Vijay R, Bhagwat VW, Fogliani C. Catalytic effect of pre-micellar aggregates on oxidative degradation of acridine orange by acidic chlorite. J Indian Chem Soc [Internet]. 2007;85:443–7. Available from: <URL>.

69. Swain R, Panigrahi GP. Kinetics and mechanism of oxidation of hydroxylaminehydrochloride by vanadium (V) in the presence of sodium lauryl sulphate. Indian J Chem [Internet]. 2001;40(11):1191–5. Available from: <URL>.

70. Yadav H, Bhoite SA, Singh AK. Kinetic and mechanistic study of micellar effect of hydrolytic reaction of Di-2-methoxy-4-nitroaniline phosphate. J Dispers Sci Technol [Internet]. 2017 Jan 2;38(1):121–31. Available from: <URL>.

71. Ibrahim I, Idris SO, Abdulkadir I, Onu DA. Thioglycolic acid oxidation by N, N′-phenylenebis(salicylideneiminato)manganese(III) in DMSO/H_2O: Effects of sodium dodecylsulfate and cetyltrimethylammonium bromide. Results Chem [Internet]. 2022 Jan;4:100541. Available from: <URL>.

72. Nkole IU, Idris SO, Abdulkadir I, Onu AD. Redox reaction of bis-(2-pyridinealdoximato)dioxomolybdate(IV) complex with thiosulphate ion in aqueous acidic and surfactant media. Inorg Chem Commun [Internet]. 2022 Jun;140:109468. Available from: <URL>.

73. Nkole IU, Idris SO, Abdulkadir I, Onu AD. Cationic Surfactant-Based Catalysis on the Oxidation of Glutamic Acid by Bis-(2-pyridinealdoximato)dioxomolydate(IV) Complex. Catal Letters [Internet]. 2023 Dec 17;153(12):3581–90. Available from: <URL>.

74. Bunton CA. Reaction Kinetics in Aqueous Surfactant Solutions. Catal Rev [Internet]. 1979 Jan 5;20(1):1–56. Available from: <URL>.

75. Romsted LS, Zanette D. Quantitative treatment of indicator equilibria in micellar solutions of sodium decyl phosphate and sodium lauryl sulfate. J Phys Chem [Internet]. 1988 Aug 1;92(16):4690–8. Available from: <URL>.

76. Mohr A, Pozo Vila T, Korth H, Rehage H, Sustmann R. Hydrophobic N -Diazeniumdiolates and the Aqueous Interface of Sodium Dodecyl Sulfate (SDS) Micelles. ChemPhysChem [Internet]. 2008 Nov 10;9(16):2397–405. Available from: <URL>.

77. Ionescu LG, Trindade VL, de Souza EF. Application of the Pseudophase Ion Exchange Model to a Micellar Catalyzed Reaction in Water−Glycerol Solutions. Langmuir [Internet]. 2000 Feb 1;16(3):988–92. Available from: <URL>.

78. Armstrong C, Gotham W, Jennings P, Nikles J, Romsted LS, Versace M, et al. Acid Catalyzed Hydrolysis of Hydrophobic Ketals in Aqueous Cationic Micelles: Partial Failure of The Pseudophase Ion Exchange Model. In: Surfactants in Solution [Internet]. Boston, MA: Springer US; 1989. p. 197–209. Available from: <URL>.

79. Raducan A, Olteanu A, Puiu M, Oancea D. Influence of surfactants on the fading of malachite green. Open Chem [Internet]. 2008 Mar 1;6(1):89–92. Available from: <URL>.

80. Cerichelli G, Coreno M, Mancini G. Reduction of Ketones by Sodium Borohydride in the Presence of Cationic Surfactants. J Colloid Interface Sci [Internet]. 1993 Jun;158(1):33–9. Available from: <URL>.

81. Ghosh SK, Basu A, Paul KK, Saha B. Micelle catalyzed oxidation of propan-2-ol to acetone by penta-valent vanadium in aqueous acid media. Mol Phys [Internet]. 2009 Apr 10;107(7):615–9. Available from: <URL>.

82. Saha B, Chowdhury KM, Mandal J. Micellar Catalysis on Pentavalent Vanadium Ion Oxidation of D-Sorbitol in Aqueous Acid Media: A Kinetic Study. J Solution Chem [Internet]. 2008 Sep 10;37(9):1321–8. Available from: <URL>.

83. Singh M. Mechanistic aspects of oxidation of dextrose by N-bromophthalimide in acidic medium: a micellar kinetic study. Res Chem Intermed [Internet]. 2013 Feb;39(2):469–84. Available from: <URL>.

84. Subba Rao P V., Krishna GS., Ramakrishna K. Kinetics and mechanism of oxidation of tris(2,2’-bipyridyll-cobalttll) by p-benzoquinone-Micellar effect of sodium dodecyl sulphate. Indian J Chem [Internet]. 1991;30A:136–9. Available from: <URL>.

85. Yadav H, Boite SA. Hydrolysis of mono-n-ethyl-o-toluidine phosphate. Chem Rev Lett [Internet]. 2014;3(11):628–35. Available from: <URL>.

86. Mohr PC, Mohr A, Vila TP, Korth HG. Localization of Hydrophobic N -Diazeniumdiolates in Aqueous Micellar Solution. Langmuir [Internet]. 2010 Aug 3;26(15):12785–93. Available from: <URL>.

87. Laguta AN, Eltsov S V., Mchedlov-Petrossyan NO. Micellar rate effects on the kinetics of nitrophenol violet anion reaction with HO– ion: Comparing Piszkiewicz’s, Berezin’s, and Pseudophase Ion-Exchange models. J Mol Liq [Internet]. 2019 Mar;277:70–7. Available from: <URL>.

88. Laguta AN, Eltsov S V., Mchedlov-Petrossyan NO. Kinetics of alkaline fading of methyl violet in micellar solutions of surfactants: Comparing Piszkiewicz’s, Berezin’s, and pseudophase ion-exchange models. Int J Chem Kinet [Internet]. 2019 Feb 14;51(2):83–94. Available from: <URL>.

89. Laguta A. Quantitative analysis of micellar effect on the reaction rate of cationic triphenylmethine dyes with water according to Berezin’s model. Kharkov Univ Bull Chem Ser [Internet]. 2020;35(58):37–44. Available from: <URL>.

90. Panigrahi GP, Mishra SK. Micellar-catalysis: Effect of sodium lauryl sulphate in the oxidation of lactic acid by chromic acid. J Mol Catal [Internet]. 1993 May;81(3):349–62. Available from: <URL>.

91. Nkole IU, Idris SO, Onu AD, Abdulkadir I. 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 Univ J Basic Appl Sci [Internet]. 2022 Dec 16;11(1):68. Available from: <URL>.

92. Cheong MY, Ariffin A, Niyaz Khan M. A Comparative Analysis of Pseudophase Ion-Exchange (PIE) Model and Berezin Pseudophase (BPP) Model: Analysis of Kinetic Data for Ionic Micellar-mediated Semi-ionic Bimolecular Reaction. Bull Korean Chem Soc [Internet]. 2007 Jul 20;28(7):1135–40. Available from: <URL>.

93. Sar P, Ghosh A, Ghosh D, Saha B. Micellar catalysis of quinquivalent vanadium oxidation of methanol to formaldehyde in aqueous medium. Res Chem Intermed [Internet]. 2015 Aug 5;41(8):5565–86. Available from: <URL>.

94. Singh M. Kinetics and Mechanism of Micellar Catalyzed Oxidation of Dextrose by N-Bromosuccinimide in H_2SO_4 Medium. Int J Carbohydr Chem [Internet]. 2014 Dec 1;2014:783521. Available from: <URL>.

95. Turovskaya MK, Belousova IA, Razumova NG, Gaidash TS, Prokop'eva TM, Kotenko AA, et al. Reactivity of Inorganic α-Nucleophiles in Acyl Transfer in Aqueous and Micellar Media: IV. Peroxyhydrolysis of Acyl Derivatives in Organized Microheterogeneous Systems1. Russ J Org Chem [Internet]. 2024 Feb 29;60(2):252–8. Available from: <URL>.

96. Layek M, Karmakar P, Pal P, Rahaman SM, Kundu S, Mitra M, et al. Influence of Chain Length and Concentration-Dependent Morphological Switching on Oxidation of Aromatic Alcohols in a Micellar Environment. Ind Eng Chem Res [Internet]. 2024 Jan 24;63(3):1334–48. Available from: <URL>.

97. Albadani A, Hassan M, Obayed FA. Kinetic study of factor affecting the reaction of cyanide and picrate ions in the presence of micellar catalyst. Chem Int [Internet]. 2022;8(4):136–43. Available from: <URL>.

98. Sahu S, Kumar Padhy R, Prasad Nanda S. Surfactant catalyzed electron transfer mechanism in the oxidation of racemic tartaric acid by Ce(IV). Mater Today Proc [Internet]. 2023;78:786–91. Available from: <URL>.