



## REVIEW

### Micellar Catalysis of Chemical Reactions by Mixed Surfactant Systems and Gemini Surfactants

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Micellar catalysis exhibited by mixed surfactant systems and gemini surfactants was reviewed. The review focused on mixed surfactant systems and tried to correlate the changes in the physico-chemical properties of these systems to the variations of their catalytic activities. Mixed surfactant systems are promising as the catalytic efficiency of some single surfactants was significantly enhanced in the presence of other critically selected surfactants. The selection should consider the charge, size, and structures of the head group as well as an appropriate length of hydrocarbon tail. The overall conclusion has arrived the mixed surfactant systems could be a tool by which the reaction rate can be tuned by changing the composition and/or the components' structures. The higher catalytic activity of gemini surfactants compared to conventional ones, their facile synthesis and liability for structure control made them of superior choice for micellar catalysis.

**Keywords:** Micellar catalysis, Mixed surfactant system, Gemini surfactants, Reaction rate control.

## INTRODUCTION

Accumulation of particle catalysts usually leads to declined catalysts activity. However, in the micellar catalyst, an abrupt catalyst activity enhancement upon the accumulation of catalyst particles to form aggregates [1]. These aggregates are called micelles and possess different geometrical structures to range from lamellar, vesicular and spherical structures depending on the abundance of molecules. Apart from the miscellaneous applications of surfactants, the most fascinating and promising is their catalytic action on many chemical reactions.

In a reaction solution, micelle represents a microscopic reaction center in which reactants are packed either in the micellar interface or in the hydrophobic core. As a result of concentrating reactants into a tiny volume, the reaction rate enhanced compared to its rate in the bulk solution. Micellar catalysis was observed 70 years ago and assumed to act *via* a mechanism similar to enzymes [2]. In 1970s, however, a theory

was formulated for micellar catalysis, which is based on the partitioning of the reactant between aqueous solution and micellar aggregates (two phases) and the overall rate will be the sum of the two rates in two phases [3]. Micellar inhibition of chemical reactions was also observed [4,5] and given full theoretical consideration [6].

Mixed surfactant systems were found to exhibit improved physico-chemical properties. These surfactants show synergism due to interactions between the head groups or hydrophobic tails of surfactants. This interaction may cause many of the properties to change non-ideally compared to those of individual surfactants. Synergism can enhance or widen surfactants' applications due to the emergence of unexpected desired properties that are not exhibited by the single surfactant systems. For example, mixed micelles may form at concentrations less than those for individual surfactants (lower CMC) [7-11]. Synergism was also observed with other properties, *e.g.* surface tension, foaming and clouding [12,13]. The experimental and

theoretical aspects for synergetic interaction in mixed surfactant systems were discussed in detail [14-19]. The formation of mixed micelles surges if attractive interaction between the components of the mixed system dominates. Demixing can also occur due to electrostatic repulsion or steric interactions between hydrophilic groups leads to immiscibility [16].

Mixed surfactant systems are expected to form mixed micelles (Fig. 1a) once a critical micelle concentration is reached. However, in addition to the dispersing aggregation number commonly observed in micelles of single surfactants, a diversity in micellar composition was observed with mixed surfactant systems [17]. For example, two breakpoints were observed in the surface tension *versus* concentration plots of 3,6,9-trioxai-cosanoate (TOI)-C<sub>12</sub>E<sub>20</sub> and were attributed to two CMCs of two mixed micelles; one of them is TOI rich and the other is C<sub>12</sub>E<sub>20</sub> rich [18]. Mixed micelles can form in the mixtures of surfactants and non-surfactant forming amphiphilic molecules [19].

The behaviour of micellar catalysis of surfactant mixed systems cannot be anticipated easily as the number of variables that contribute to it is so numerous. Two surfactants of the same type of head groups and hydrocarbon chain lengths but with different counterions (for example, DTAB and DTAC) need not show the same behaviour [20]. In some cases, surfactant, when added to a ligated catalyst that can form mixed micelles, an enhancement of reactivity is observed. Kalsin *et al.* [21] reported the effect of added surfactants (cationic, anionic and zwitterionic) in the catalytic properties of ruthenium surface-active complexes RuL<sup>n</sup> on the transfer hydrogenation of ketones in water [21]. It is observed that careful selection of surfactant may enable control of hydration of mixed micelles and control the reaction rate. In particular, RuL<sup>n</sup>, which is not capable of forming single micelles, its activity was increased substantially when mixed with anionic surfactants.

Gemini or dimeric, surfactants are amphiphiles that possess two heads and two tails. The two parts are linked at or close to the head groups by a relatively shorter chain called a spacer.

These materials were synthesized for the first time by Menger & Littau [22]. Gemini surfactants form micellar aggregates at a specific concentration (CMC) like the conventional aggregates. CMCs of gemini surfactants are usually much lower than those of their corresponding monomers [23,24]. The micelle structure formed by gemini surfactants may adopt varieties of structures that depend on the nature and length of the spacer, nature of head groups and concentration of the surfactant in the solution. Still, the spherical structure is the most common, particularly at low concentrations (Fig. 1b) [25]. The lower viscosity of gemini surfactant solutions and their wide range of hydrophilic-lipophilic balance (HLB) made them of broader applications compared to their conventional counterparts.

In the current review, we report a survey of directions by which micellar catalysis was evolved. Since using a conventional single surfactant system has been reviewed extensively, some examples [26-28], we chose to track the progress in two directions: mixed surfactant systems and gemini surfactants.

Various aspects of mixed surfactant systems and gemini surfactants such as classification, physio-chemical properties and applications were already reviewed in several articles [22-24,29-31]. However, there are no comprehensive reviews found in the literature devoted to the micellar catalysis of chemical reactions by these two types of catalytic systems. This was the motivation for us to undertake this review work and devote it to the micellar catalysis by mixed surfactant systems and gemini surfactants. A critical method is followed, *i.e.*, upon reporting any work in these two fields, its results are presented and discussed with reference to each system's physico-chemical properties which might also be investigated in the same work or others found in the literature.

**Catalysis by mixed surfactant systems:** It is appropriate to disclose the catalytic activity of mixed surfactant systems based on their components' categories. So, the discussion is sub-divided depending on the type of surfactant pair involved in the mixed system.

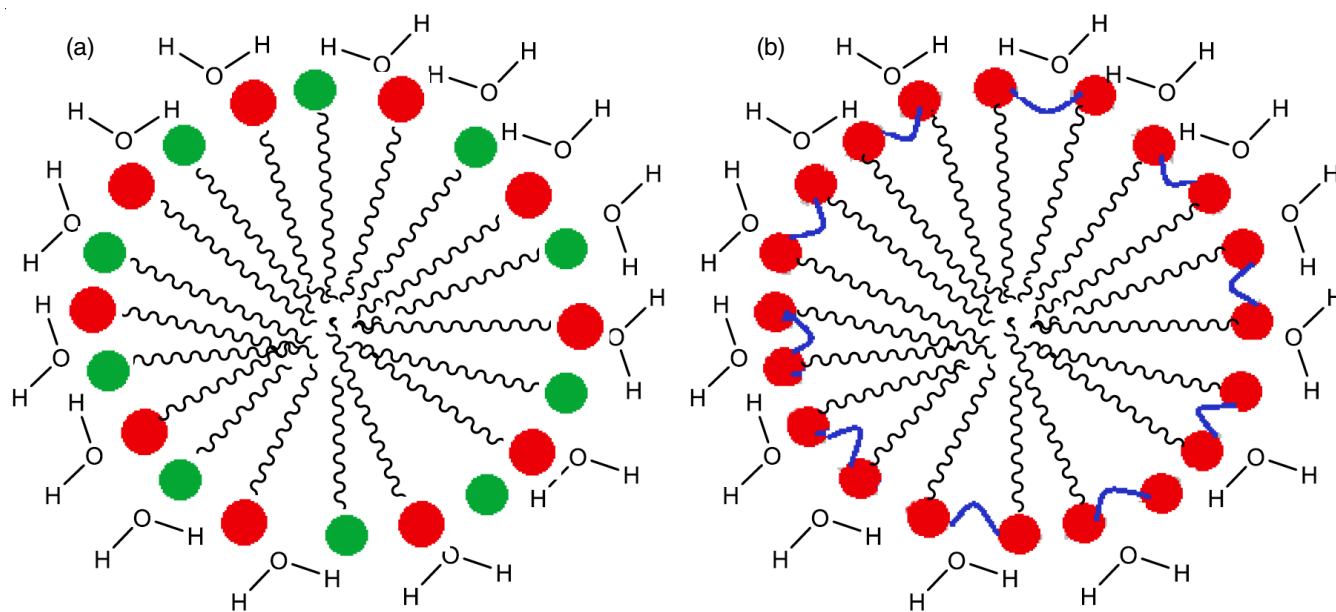


Fig. 1. General micellar structures of mixed surfactant system (a) and gemini surfactant (b)

**(a) Catalysis by anionic-non-ionic mixed systems:** The interaction among molecules of a mixed system is not the same for all types of molecules, so there will be a net interaction and a prevailed departure from ideality. This behaviour reflects itself in the physico-chemical properties of these systems in terms of synergism phenomena. For example, in the mixture of anionic SDS and non-ionic sugar-based dodecylmalonobis-*N*-methylglucamide (DBNMG), the aggregation number measured by time-resolved fluorescence quenching (TRFQ) at 45 °C was found to increase from 48 of pure SDS to 63 with 36 mol% DBNMG and then diminished to 49 for pure DBNMG [32]. This increased aggregation number relative to those of single surfactants is a result of synergetic interaction. Synergism arises due to the non-ideality behaviour of mixed systems. The increased aggregation number is one of several physico-chemical properties that could be improved in the mixed system relative to those of single surfactants. This desired improvement may make mixed systems more efficient to catalyze the chemical reactions. Nevertheless, one should be careful as mixing may lead to antagonism (positive deviation from ideality), resulting in a change of micellar action to a non-desirable direction. Eventually, the critical selection of the components of mixed surfactant systems is essential for obtaining the desired outcome properties.

The presence of an anionic surfactant in the reaction in which one of the reactants is negatively charged results in repulsion between the hydrophilic micellar interface and the reactant, and eventually keeps the latter away from the Stern layer. Therefore, the presence of anionic surfactant inhibits the reaction. The addition of a second neutral molecule can modify the micelle's surface charge, allowing the nucleophile to disclose to the proximity of the Stern layer. An example of this type of catalysis is *N*-methyl-*N*-nitroso-*p*-toluene sulfonamide (MNTS) hydrolysis in a basic medium. The presence of SDS inhibited the reaction rate, but when cyclodextrin was added, the rate increased with increasing SDS concentration, reached a maximum, after which it declined to the normal value with a continuing addition of SDS [33].

Davies & Foggo [34] also reported more interesting results for mixed SDS-Brij-35 catalyzed the nucleophilic substitution reaction of *m*-chloroperbenzoic acid (mCPBA) with iodide [34]. The reaction rate showed ascending behaviour with total surfactant concentration as far as the SDS mole fraction is  $\leq 0.2$  (catalytic effect). For SDS mole fraction  $> 0.2$ , the curve exhibited descending with the total concentration of surfactant (inhibitory effect). The authors calculated the micellar association constants of reactant (mCPBA) and the transition state using a multiple micellar pseudo-phase (MMPP) model to explain the results. The micellar's catalytic effect occurred because the micellar association constant is higher with transition state than that with mCPBA. The inhibitory effect was observed because the micellar association constant with mCPBA is higher than the transition state.

In another work by Muñoz *et al.* [35], the mixed system SDS-Brij-35 did not produce a significant change in the micellar catalytic profile of the hydrolysis of phenyl chloroformate in comparison to those of pure surfactants. In this work, hydroxide

ions were biased by adding very dilute solutions of HCl or HBr to assure the reaction occurs only with water molecules. As a result, a general descending trend of rate constant was observed irrespective of the type of micellar system used. This observation was attributed to depletion of water from the micellar interface and not the surfactant head group's charge kind only. Of course, the charge had its impact, but the dominant factor was the change in dielectric properties within Stern-layer.

In an attempt to study the catalytic properties of a mixed surfactant system on a specific reaction, it is interesting to look at the catalytic profile of the individual components. Torres *et al.* [36] investigated the catalyzed hydrolysis of *p*-nitrophenyl perfluorooctanoate (PNPF) by mixed systems SDS-(perfluorononanoic acid, PFNA and PFNA-Brij-35 at pH 6.0 [36]. The catalytic profiles of the three pure surfactants (SDS, PFNA and Brij-35) had already been reported by the same group [37]. The substrate was reported to show self-aggregation and therefore competes with hydrolysis. Brij-35/PFNA mixed system showed two CMCs corresponding to micellization at lower mole fraction PFNA and a change in micellar morphology at higher PFNA mole fraction [38]. Consequently, the variation in the reaction rate with total surfactant concentration and fixed mole fraction of PFNA mimicked the surface properties of the mixture; it showed diminishing before CMC<sub>1</sub>, rise between CMC<sub>1</sub> and CMC<sub>2</sub>, and finally decreased markedly after CMC<sub>2</sub>. The inhibition effect at low and high total surfactant concentration may be attributed to substrate association with PFNA. Between CMC<sub>1</sub> and CMC<sub>2</sub> PFNA molecules are self-associated in micellar entities, leaving a chance for the substrate to associate with some rich Brij-35 aggregates, resulting in rate enhancement. However, at fixed total surfactant concentration, the rate diminished with increasing the mole fraction of PFNA. The SDS/PFNA mixed system though it had single CMC, the catalytic behaviour was not much different. It showed a decrease in the rate constant with the PFNA mole fraction at fixed total surfactant concentration. Nevertheless, when changing the total surfactant concentration at a fixed PFNA mole ratio, the rate increased to a maximum. It then descended to a value comparable to that of the more abundant component. Demixing of the two surfactants at high PFNA mole fraction was suggested. Torres *et al.* [39] also attempted to study the same mixed systems' effect on the rate of hydrolysis of phenyl trifluoroacetate in a neutral water medium. The reaction was found to be inhibited in the presence of PFNA-Brij-35 when the total surfactant concentration higher than CMC. Below CMC, the rate constant was not affected by the variation of total surfactant concentration. Though the mixed system exhibited two CMCs as indicated above, the rate constant responded only to the higher CMC. In the range of first CMC, the rate constant did not show any significant variation. The two single surfactants were found to inhibit the reactions as well. The explanation given for the inhibition is that the presence of surfactants, particularly in a concentration above CMC, decreased the substrate's abundance in the aqueous medium. The pseudo-phase separation model's indicated a negligible contribution of the associated surfactant-substrate rate to the reaction's overall rate.

Acharjee *et al.* [40] used the mixed system SDS-TX-100 to catalyze the oxidation of isoamyl alcohol by chromic acid. Measurements of rate constants were performed for concentrations above CMCs of the two surfactants. The catalytic behaviours of single surfactants were also investigated for comparison. Surprisingly, SDS was more effective than TX-100, though the CMC of TX-100 is much lower than that of SDS as measured. This unanticipated result was explained by that the active oxidant species is the fully protonated Cr(VI), *i.e.*  $\text{H}_2\text{CrO}_4$  or  $\text{H}_3\text{CrO}_4^+$ . The neutral or positive charge provided an environment that allowed the oxidant to be within the vicinity of the SDS micelle's negative Stern layer and to be closer to the hydroxyl group of the substrate located within the palisade layer. The catalytic activity of mixed micelle showed slightly lesser activity than those of pure surfactants. However, the rate constant was enhanced when the concentration of one of the surfactants was increased with a fixed concentration of other.

Kinetic synergism usually is exhibited profoundly in specific compositions of mixed surfactants. Rose *et al.* [41] studied the two mixed systems SDS-TX-100 and SDS-Tween-20 catalyzed the oxidation reaction of  $[\text{Fe}(\text{NN})_3]^{3+}$  with phenylsulfinylacetic acid (PSSA). The systems that possessed the composition (3:1) showed rate constants higher than those by pure surfactant, whereas other tested compositions showed lower activity than pure SDS.

The SDS-TX-100 system was used to catalyze the reaction between malachite green ( $\text{MG}^+$ ) and nitrite ions [42]. Here, SDS caused an inhibition effect on the rate constant, where the reaction rate regularly declined with the addition of SDS. On the other hand, presence of TX-100 with SDS in the mixed system enhanced the rate constant and the enhancement became more pronounced with increasing TX-100 in the system. SDS micelle's negative charge effectively repelled nitrite ion apart from  $\text{MG}^+$  solubilized in the hydrophobic micelle core.

**(b) Catalysis by cationic-non-ionic mixed systems:** It was reported that the catalytic activity observed during the oxidation of hydrocarbons in the presence of a cationic surfactant to be due to mixed micelle of the surfactant with hydroperoxides ( $\text{ROOH}$ ) formed in the first reaction step [43]. Hydroperoxides behave as non-ionic surfactant molecules [44], associate with the cationic micelles to form mixed micelles that accelerate hydroperoxides' conversion into free radicals required to speed up the overall rate of the reaction. Interestingly, anionic surfactants do not catalyze hemolytic decomposition and are therefore, considered as antioxidants for alkyl aromatic hydrocarbons [45]. It seems that the net charge of the micelle surface is the controlling factor in mixed micellar catalysis of reactions involving free radicals. In agreement with this conclusion, Baglioni *et al.* [46] found that a net positive charge on the mixed micellar surface facilitates the escape of electrons from photogenerated cation radicals of  $N,N,N',N'$ -tetramethylbenzidine. Using electron spin echo modulation (ESEM) and electron spin resonance (ESR), they found that the yield of photogenerated cations was significantly enhanced in the presence of mixed non-ionic-cationic surfactants of DTAC and  $\text{C}_{12}\text{E}_6$  with the increasing mole fraction of cationic surfactant beyond 0.6. Lesser mole fraction of cationic surfactant or negatively charged

mixed micelle of  $\text{SD}/\text{C}_{12}\text{E}_6$ , appeared not to affect the reaction rate.

Variations in the mixed surfactant system composition may result in changing of the reaction phase. This conclusion was reported by Dar *et al.* [47] from their investigation on the effect of the presence of the mixed system CTAB/ $\text{C}_{12}\text{E}_8$  on the rate of the reaction between *t*-butylhydroquinone (TBHQ) with 4-hexadecylbenzenediazonium ( $16\text{-ArN}_2^+$ ). The pseudo-first-order kinetic data of the reaction changed from the mono-exponential and tend to follow the biexponential model with decreasing the mole fraction of  $\text{C}_{12}\text{E}_8$  from 1 to 0. The results were interpreted by the progressive change from the monophasic to the biphasic mechanism with decreasing the mole ratio of  $\text{C}_{12}\text{E}_8$ . The suggested mechanism assumes that the reaction occurs in the interface region, where many factors may contribute to the overall reaction rate. The authors utilized chemical trapping to evaluate the molarities of water molecules, bromide ions and hydrogen ions at the interface region. Sudden change in these quantities occurred close to the  $\text{C}_{12}/\text{E}_8$  mole fraction of 0.6, which agreed with the observed breaks in the reaction rate- $\text{C}_{12}/\text{E}_8$  mole fraction curves. These breaks correspond to the composition at which the major conversion from the monophasic to biphasic mechanism occurred. The presence of the biphasic reaction path was attributed to a complex mechanism of the reaction that involves the formation of diazoether intermediate, which is subjected to either reversible reaction to form the reactants or decomposition to end with the products. The formation constant of the complex was high as far as  $X_{\text{CTAB}} > X_{\text{C}_{12}\text{E}_8}$ , but decreased gradually with increasing the mole fraction of  $\text{C}_{12}\text{E}_6$ .

An interesting idea in employing micellar catalysis is to use the cationic surfactant to catalyze a reaction in which one of the reactants is the surfactant's counter ion. The typical example of this type is the nucleophilic substitution reaction on methyl 4-nitrobenzenesulfonate (MNBS) with chloride ion catalyzed by the cationic surfactant CTAC and the mixed system CTAC/Triton X-100 solution [48]. For mixed CTAC/Triton X-100, CMC decreased with increasing Triton X-100, and the system was found to deviate negatively from ideality. Increasing the mole fraction of Triton X-100 results in slowing down the reaction. This result was justified by the more inclusion of Triton X-100 into the micelle, decreasing the counter ion's abundance (nucleophile) in the micellar interface. Similar observations were found for mixed CTAB- $\text{C}_{10}\text{SO}$  surfactants catalyzed nucleophilic substitution reaction of methyl naphthalene-2-sulfonate with  $\text{Br}^-$  [49]. The CMC profile, however, was different. The increased mole fraction of  $\text{C}_{10}\text{SO}$  in the mixed system raised CMC moderately with smaller  $\text{C}_{10}\text{SO}$  mole fractions and sharply with higher mole ratios. This variation of CMC was attributed to the higher CMC of  $\text{C}_{10}\text{SO}$  than that of CTAB.

A typical example of the competition between the electrostatic and hydrophobic properties in mixed surfactant systems is methyl violet hydrolysis in an alkaline medium catalyzed by CTAB-TX-100 system [50]. The electrophile (methyl violet cation) tends to solubilize better in the more hydrophobic micellar core, whereas hydroxide ion favours more positively

charged micelle. Hence, TX-100 rich micelle will be favourable for the electrophile, while the nucleophile will prefer the CTAB rich micelle. The physico-chemical properties of CTAB-TX-100 mixed system showed synergism with positive deviation from ideality throughout the whole mole fraction range and the formation of mixed micelles was confirmed [51-53]. Singh & Srivastava [50] reported that incorporating TX-100 into the micelles of CTAB resulted in diminishing the maximum rate constant of the reaction. This effect continues with the rising content of TX-100 in the mixture. These observations were justified by the decreased positive charge density of mixed micelle with increasing the fraction of neutral TX-100. However, the authors omitted the strong enhancement in rate constants observed at lower CTAB concentration, which may be attributed to the synergism on the critical micelle concentration. Although the presence of TX-100 lowered the charge density of mixed micelle, it lowered the CMC of the system, which was considered as the concentration at which the rate constant started to rise sharply. The literature reported CMCs of CTAB and TX-100 in aqueous solution are 0.29 mM [54] and 0.9 mM [55]. Due to synergism resulting from the net attraction, the CMC is expected to be very close to the more hydrophobic component. This behaviour manifests itself in the catalytic profile as an earlier enhancement in the rate constant compared to that in the absence of TX-100.

Ghosh *et al.* [56] reported the kinetic catalytic data of the binary cationic-nonionic mixed system CTAB, TTAB, CPC as cationic surfactants, and Brij-35 and TX-100 as non-ionic surfactants. These systems were employed to catalyze the acid hydrolysis of *N*-phenylbenzohydroxamic acid (PBHA), *N*-*p*-tolylbenzohydroxamic acid (*p*-TBHA), acetohydroxamic acid (AHA) and benzohydroxamic acid (BHA) [56]. The CMCs of various mixed systems were measured by conductivity method, but the obtained values were much lower than those reported in other literature sources. The experiments were carried out for a 1:1 mole ratio in each mixed system. The overall result in this study is that the various cationic-non-ionic mixed systems showed an inhibitory effect on the titled reactions. Electrostatic interactions have prevailed in these results since hydrolysis in an acidic medium means that  $H^+$  plays a crucial role in the mechanism. The positively charged  $H^+$  did not favour the positively charged micelle interface, which was acquired from the presence of cationic surfactants. Evidence that supports this explanation is the more powerful inhibition when mixed cationic-cationic (CTAB + CPC) mixed system was used. Further, a catalytic effect on these reactions was observed when a single SDS was used.

For nucleophilic substitution, it is clear that the cationic surfactants are favoured. The rate of the reaction increases with increasing the hydrophobic and charge density of the micellar surface. The nature of the head group does not have a decisive role. Using quantitative structure-property relationship (QSPR) Mozrzymas [57] found that the nature of the head group did not significantly affect the charge of the head group of quaternary ammonium based cation surfactants. However, for product selectivity, the mixed cationic-nonionic surfactant can be used to tune the reaction outcome toward a specific

product. The choice of non-ionic surfactant would also be critical. Zakharova *et al.* [58] studied the catalytic effect of the mixed system CTAB-Brij-97 on the reaction of hydrolysis of ethyl *p*-nitrophenyl chloromethyl phosphonate (EPNCP) in a basic medium. The analysis of the physico-chemical properties of these systems revealed a negative deviation from ideality with an interaction parameter ( $\beta$ ) of -4.6. The resultant mixed micelle was found to be enriched with Brij-97. Single CTAB exhibited a catalytic effect on the reaction, while Brij-97 did not induce any effect on the rate constant. The maximum rate constant of each composition of the mixed system increased with the increased mole fraction of non-ionic surfactant. The absence of a significant effect of the non-ionic surfactant Brij-97 on the reaction rate was impressive.

On the contrary, mixed CTAB-Brij35 was reported to show peculiar catalytic behaviour that ranged from acceleration to inhibition and even led to stop the reaction at high Brij35 mole fractions [59]. The overall impact of nonionic surfactant would depend on the hydrophilic-lipophilic balance (HLP). So, based on this, the choice of the type non-ionic surfactant in the mixed system provides additional contribution for tuning the reaction rate.

Butt *et al.* [60] investigated the catalytic activity of mixed systems composed of cationic 1-dodecyl-3-methyl imidazolium chloride (DDMIMCl) and non-ionic Brij-56 on the rate of reduction degradation of rhodamine B. DDMIMCl-Brij-56 mixed systems showed higher catalytic activity compared to single solutions of DDMIMCl. The results were explained by the alleviation of DDMIMCl head-head groups repulsion, and the exchanged  $\pi$ -positive charge interactions between rhodamine B and mixed micelles. The observed inhibition at post-micellar concentrations with single DDMIMCl was significantly reduced with the mixed system. This behaviour was in agreement with the change in micellar size measured by dynamic light scattering, which indicated a bigger size of mixed micelles. Further, mixed micelles size continued to increase with the increase of Brij-56. It attained its maximum at 0.2 Brij-56 mole fraction, the composition, which corresponds to the mixed system of the highest catalytic activity.

**(c) Catalysis by anionic-cationic mixed systems:** Ochoa-Solano *et al.* [61] reported the catalytic effect of anionic surfactant *N*- $\alpha$ -myristoyl-L-histidine (NMLH), on the hydrolysis of *p*-nitrophenyl acetate. When cetyltrimethylammonium bromide (CTAB) was added, the rate of hydrolysis was enhanced remarkably as well. For the mixed systems of two surfactants, the reaction rate was found to increase with increasing the ratio of CTAB:NMLH. At the ratio of 20:1, the maximum rate constant was attained. CTAB molecules are involved in mixed micelles, decreasing the repulsive interaction between anionic micelle and reactant that inhibits the ester's association within the stern layer. In the mixture of anionic and cationic surfactants, a net attractive interaction dominates and a negative deviation from ideality is expected.

The effect of two types of mixed cationic-anionic systems composed of the cationic surfactants DTAB or DeTAB and the anionic SDS on the rate of complexation reaction between pyridine-2-azo-*p*-dimethylaniline (PADA) and  $Ni^{2+}$  was reported

by Favaro & Reinsborough [62]. In one of their previous work, the authors [63] found that the presence of a single SDS led to an enhancement of reaction rate with the maximum rate observed near CMC. The overall effect of the addition of either DTAB or DeTAB to SDS was to decrease the catalytic activity of SDS. This inactivation was attributed to the incorporation of positively charged surfactant into the anionic micelle, reduced the affinity of  $N^{2+}$  to the micelle surface that accommodates PADA in its core. Also, solubility measurements that were carried out indicated lesser solubility of the substrate (PADA) into the mixed SDS-DTAB or SDS-DeTAB systems. The authors also discussed the mechanism of mixed micelle formation and assumed that free SDS micelles form first, and then molecules of DTAB/DeTAB get incorporated within SDS micelle. This mechanism was recently supported by Cui *et al.* [64] using  $^1H$  NMR. They arrived at a general conclusion that micelles of the surfactant that have lower CMC form first, then mixed micelle was formed by incorporating other surfactant molecules into it. The problem with this mechanism is that no clear evidence can be provoked from the behaviour of bulk physico-chemical properties of mixed surfactant systems.

The effect of two mixed systems *viz.* CPB-SDS (CPB = cetylpyridinium bromide) and CPB-DBS (DBS = dodecylbenzene sulfonate) on the conversion of 1-decene to decanal catalyzed by  $RhCl(CO)(TPPTS)_2(TPPTS:P(m-C_6H_4SO_3Na))$ , presented another example of the effect of synergism on the micellar activity [65]. This reaction had already been reported not to be catalyzed by surfactants other than cationic [66]. However, the addition of SDS or DBS to the cationic CPB boosted the conversion% about 4-fold that with a single CPB in the same reaction conditions. Also, there was a slight improvement in the regioselectivity toward *n*-decanal. However, if additive surfactant's mole ratio exceeds 0.2, the conversion and regioselectivity started to decline gradually. The physico-chemical properties, CMC and solubility of 1-decane in the two mixed systems behaved about the same way.

**(d) Catalysis by anionic-anionic mixed systems:** For mixed systems of the same type of surfactants, the behaviour is expected to be close to ideality. However, the ideal behaviour may be left when the head groups of two-component surfactants are too much different, particularly when one of them is a gemini surfactant. In the latter case, the natures of two surfactants are so different, which may lead to non-ideality. Strong antagonism was observed in the mixture of SDS and sodium salt of *bis*(1-dodecyl succinamic acid) (NaBDS) [67]. The interaction results in CMCs of the mixture being higher than that of the more hydrophilic component. The interaction parameter was calculated and found to be of positive value, confirmed the antagonism type interaction. When the mixed SDS-NaBDS used to catalyze the oxidation of D-fructose by alkaline chloramine-T, the rate was less than the algebraic sum of the rate constants when the same concentrations of the two surfactants used individually.

Connolly & Reinsborough [68] studied the influence of three mixed systems consists of sodium perfluoroheptanoate (SPFH) with each of three hydrocarbon anionic surfactants sodium decylsulfate (SDeS), sodium nonanesulfonate (SNS),

and sodium octanesulfonate (SOS), on the complexation of  $Ni^{2+}$  with pyridine-2-azo-*p*-dimethylaniline (PADA). The reaction rate in the presence of mixed system SDeS-SPFH showed little effect compared to single SDeS. The maximum rate showed a non-regular variation with DPFH mole ratio with the highest efficiency was found for the composition 1:3. The maximum rate constant of 1:1 composition was in between those of two pure surfactants. For SOS-SPFH mixed system, the composition 1:1 system showed a maximum rate *i.e.* 75% of that of pure SPFH but nine times that of SOS. The same composition of SNS-SPFH showed similar results to those of SOS-SPFH. As each binary mixed system's components possess the same charge, synergism was not observed except slightly with some compositions of SDeS-SPFH system. Also, each of the three mixed systems that were investigated in this work showed a unimolecular behaviour regarding the CMC, *i.e.* they showed single CMCs throughout the complete ranges of compositions.

**(e) Catalysis by cationic-cationic mixed systems:** Hervés *et al.* [69] studied the influence of mixed DTAC and OTAC on the rate of hydrolysis *N*-methyl-*N*-nitroso-*p*-toluene sulphonamide in an alkaline medium. The CMCs reported in this work were considered as the concentration corresponds to an initial rise in the rate constant in the curves of observed rate constants *versus* concentration. The CMCs reported were as expected for an ideal mixture and did not show a synergism effect. Hence, the reaction rate as a function of mole fraction of one of the surfactants did not show a remarkable change compared to that of the single surfactants.

The absence of synergism is a characteristic of mixtures of charge-like surfactants. However, synergism can be observed with mixed surfactants of widely different structured head groups despite the charges being identical. Mohareb *et al.* [70] employed mixed surfactant systems of the cationic surfactants alkyltriphenylphosphonium bromide ( $C_n$ TPB,  $n = 14, 16$ ) and cetyltrimmonium bromide (CTAB), hexadecyldiethylethanolammonium bromide (C16DEEA) to investigate the micellar catalysis on the  $SN_2$  reaction between methyl 4-nitrobenzenesulfonate and bromide ion. They observed that mixed systems of similar head groups, namely, C14TPB and C16TPB showed ideal behaviour concerning the observed reaction rate constant. In contrast, mixed systems of different head groups showed a negative deviation in the reaction rate from ideality. The overall observed effect of the mixed system was to make the reaction slower compared to the reaction catalyzed by single surfactants.

**Micellar catalysis by gemini surfactants:** Gemini surfactants contain two hydrophobic tails and two head groups connected with skeletal spacer. Gemini surfactants were included in a separate section, as their catalytic behaviour is more powerful than that of the convenient single surfactant system. However, the mechanism by which the effect becomes more superior somewhat different from that observed with the synergetic effect of mixed surfactant. Here, physico-chemical properties vary with differing spacer structure and length and the kinds of head and hydrocarbon tail. Kumar & Rub [71] studied the catalytic effect of gemini surfactants [16-s-16] on the kinetics of the reaction between histidine and ninhydrin in an aqueous solution of pH = 5.0 and 343 K. The measured CMCs of the

gemini surfactants 16-s-16 ( $s = 4, 5$  and  $6$ ) were found to increase with increasing the spacer length. The catalytic activity, however, showed a reverse order to that of CMCs. This behaviour is contrary to the general observation that surfactants' catalytic efficiency of the same head group increases with decreasing the surfactant CMC. Another peculiar behaviour was observed in this work is the continuing post micellar catalytic enhancement. The rate enhancement typically levels off upon reaching the CMC and after that the rate constants either remains unchanged or start to diminish due to dilution.

The presence of surfactants in the aqueous solution may affect acid-base equilibria and pH of aqueous reaction solutions [72]. Therefore, the micellar catalysis of a reaction with a pH-sensitive reactant should be carried out under controlled pH. One of these reactions is the hydrolysis of *p*-nitrophenyl picolinate (PNP) in micellar gemini surfactant media with different hydrophobic tails (16-2-16, 2Br<sup>-</sup> and 12-2-12, 2Br<sup>-</sup>) [73]. The substrate PNP has different  $pK_a$  values in the two surfactants media and hence its hydrolysis was considered acid-base catalyzed. At controlled constant pH value, the hydrolysis rate showed an enhancement with increasing the concentration of each gemini surfactant. The catalytic efficiency of 16-2-16, 2Br<sup>-</sup> was more powerful than 12-2-12, 2Br<sup>-</sup>. The reason behind this difference was attributed to the stronger solubilization of the substrate in the micelle of the more hydrophobic and longer tail (16-2-16, 2Br<sup>-</sup>) surfactant.

The length of the spacer has a pronounced effect on the micellar activity of gemini surfactant. One investigation provided evidence for this assumption was reported by Azum & Kumar [74]. In this study, three gemini surfactants of the same tail length and different spacer length, namely 16-s-16 ( $s = 4, 5$  and  $6$ ), were used to catalyze the reaction between the dipeptide complex ( $[Zn(II)-Gly-Leu]^+$ ) with ninhydrin in an aqueous solution of pH = 5.0. The CMCs of three surfactants were measured using two techniques, surface tension and electrical conductivity. The CMC was found to increase with the increase in the spacer length. Again, the characteristic catalytic behaviour of gemini surfactant reported above also prevailed in this study; the plots between the rate constant versus surfactant concentration have been divided into three regions; below CMC, near post-CMC and far-post CMC regions. The first two regions resembled the conventional surfactant's general sigmoidal plot but with higher rate constants. However, the substantial enhancement of reaction rate with increasing the surfactant concentration above CMC (third region) was observed only with gemini surfactants. This behaviour was attributed to a change of micelles' morphology with increasing surfactant concentration to a much higher value than CMC. This phenomenon was studied by Brinchi *et al.* [75] using <sup>1</sup>H NMR technique and ascribed to micellar morphology change as evidenced by changes in <sup>1</sup>H NMR line widths. Three regions of micellar catalytic profile of gemini surfactants was observed frequently in similar micellar catalyzed reactions investigations *viz.* decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion and dephosphorylation of 2,4-dinitrophenyl phosphate dianion catalyzed by gemini surfactants pXMo(DDA)<sub>2</sub>, pXMo(MDA)<sub>2</sub>, pXMo-(CDA)<sub>2</sub> and pXDo(TA)<sub>2</sub> [75], cyclization of 2-( $\omega$ -bromo-

alkyloxy)phenoxide ions catalyzed by 16-4-6 surfactants differ in the structure of spacer [76], reaction of ninhydrin with DL-tryptophan catalyzed by 16-s-16 surfactants ( $s = 4, 5, 6$ ) [77], reaction of ninhydrin with the dipeptide (Gly-Leu) in 16-s-16 in surfactants ( $s = 4-6$ ) [78], reaction of ninhydrin with chromium-glycylglycine complex catalyzed by 16-s-16 surfactants ( $s = 4, 5, 6$ ) [79], reaction of ninhydrin with tyrosine catalyzed by 16-s-16 ( $s = 4-6$ ) [80] and reaction of  $[Ni(II)-his]^+$  with ninhydrin catalyzed by 16-s-16 ( $s = 4-6$ ) [81].

The physico-chemical properties, and therefore catalytic activity of gemini surfactants, were affected by spacer length and other factors. The micellar geometry is subjected to conformational and morphological change in varying the structure and spacer length to some extent. Ghosh *et al.* [82] investigated the catalytic behaviour of two types of gemini surfactants; the first is ammonium based (16-s-16, 2Br<sup>-</sup>,  $s = 3, 4, 6, 12$ ), and the second is pyridinium based (12py-n-py12, 2Cl<sup>-</sup>,  $n = 3, 4$ ), on the hydrolysis of *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenyl diphenyl phosphate (PNPDPP) by hydroxamate ions. The reported values of CMCs of each type of surfactant showed an increase with increasing the spacer length with CMCs of pyridinium-based were about 20-fold those of ammonium based ones. The catalytic activity of surfactants toward PNPA hydrolysis by benzohydroxamate ions as a function of spacer length did not show a significant variation until  $n = 6$ . Increasing the spacer length of ammonium based surfactant further (to  $n = 12$ ), imposed a significant rise in the rate constant.

Contrary to expectations deduced from CMCs, pyridinium gemini surfactants exhibited higher catalytic activity than ammonium based. For both types, the hydrolysis rate constant was found to increase with the surfactant concentration, reached a maximum and then slightly decreased with further increase in the concentration. It looks that the authors did not extend their study to much higher surfactant concentration than CMCs to observe the frequently reported marked rise in the rate constant [61-66]. Similarly, the hydrolysis of PNPDPP by different hydroxamate ions in the presence of pyridinium based surfactants showed better performance.

Hydrolysis of PNPA was also studied in an alkaline medium of NaOH in the presence of an ammonium-based Gemini surfactant (12-4-12) in which two amide groups were introduced into its spacer [83]. The surfactant was synthesized in a two-step procedure and possessed a CMC of 1.9110 mmol L<sup>-1</sup>. The surfactant showed a significant enhancement of reaction rate with a linear relationship between the rate and surfactant concentration. Besides, the catalytic activity was superior to that of the monomeric CTAB. The study was completely performed at concentrations above the CMC of the surfactant. Also, the structure of the micelle may allow the formation of a relatively bigger size micelle due to the polar spacer. This described micellar structure may delay the saturation of micellar catalytic activity and allow the linear relationship to be observed in the catalytic profile.

A triazole based cationic gemini surfactant (18-triazole-18, 2C<sup>-</sup>) was used to catalyze the nucleophilic hydrolysis of 2,4-dinitrochlorobenzene (DNCP) in an aqueous alkaline medium [84]. In this type of surfactant, the functional atom is

the same as that in ammonium-based, but its environment was changed. The work was carried out with CTAB as well for comparison. The reaction rate was found to increase with increasing the concentration of 18-triazole-18, 2C<sup>-</sup>, reached a maximum and then showed descending with a further increase in concentration. For CTAB, the behaviour at the low surfactant concentration range showed a similar rise, but the curve did not drop and remained without change with further increase in CTAB concentration. The maximum rate attained was slightly higher with the gemini surfactant than CTAB, which was explained by the higher affinity of nucleophile to the head group of gemini surfactant micelles. This result was in agreement with the results obtained from the pseudo phase ion-exchange (PIE) model, which produced a higher binding constant of nucleophile to the gemini surfactant micelle than with CTAB. Moreover, the onset in the rate rise initiated at a much lower concentration with gemini surfactant than CTAB. This can be explained if the CMCs of two surfactants were compared with the onset concentration for each. The CMC values reported in the same reference were 0.19 mM for 18-triazole-18, 2C<sup>-</sup> and 0.9 mM for CTAB. The ratio is close to 4.7, which is about the two surfactants' ratio of onset concentration values. The descending trend of reaction rate constant at higher concentration was attributed to the substantial increase in gemini surfactant micro-viscosity with a further increase in its concentration.

Similar results were obtained when the two surfactants (16-s-16 MEA 2Br<sup>-</sup>, s = 4 and 6) were used to catalyze the nucleophilic reaction between the phosphodiester *bis*(4-nitrophenyl)phosphate (BNPP) and the  $\alpha$ -nucleophiles hydroperoxide (HOO<sup>-</sup>), acetohydroxamate (AHA<sup>-</sup>) and butane-2,3-dione monoximate ions (BDMO<sup>-</sup>) [85]. In this study, the nucleophile is not hydroxide ion as in the work of Qiu *et al.* [84]. Therefore, the nucleophile is less abundant and the reaction is expected to be more sluggish. Another difference between results of Qiu *et al.* [84] and Kumar *et al.* [85] is that the nucleophile in the later is more hydrophobic, hence drifting water out of micellar interface would be less important in affecting the rate constant and this might be the cause of less steep descending in the plots of rate constant *versus* surfactants concentration.

The affinity of nucleophile to the micellar interface depends on the type of head group of surfactants and the nature of nucleophile. Mirgorodskaya *et al.* [86] investigated the solubilization and catalytic activity of two gemini surfactants hexanediyl- $\alpha,\omega$ -*bis*[(2-hydroxyethyl)methylhexadecylammonium)] bromide (16-6-16(OH)) and hexanediyl- $\alpha,\omega$ -*bis*-(hexadecyldimethylammonium) bromide (16-6-16) on alkaline hydrolysis of *p*-nitrophenyl esters of acetate, caprilate, caprate and laurate. The two surfactants differ in that two *N*-alkyls, in two head groups of Gem 6-16(OH) were hydroxyethylated. Gem 6-16(OH) had CMC about 5-fold lower than that of Gem 6-16 and showed more powerful solubilization. Maximum solubility was observed for *p*-nitrophenylcaprate among other esters in the presence of Gem 6-16(OH). The catalytic activity of Gem 6-16(OH) toward esters hydrolysis was found to be much higher than Gem 6-16. It looks that the more polar head of hydroxyethylated surfactant facilitated micelle formation, leading to lower CMC and increased its solubilization capacity by enabling the formation of

hydrogen bonds. Consequently, these relatively improved the physio-chemical properties made the Gem6-16(OH) more efficient.

Gemini surfactants were also used as integrated catalysts in some reactions. Qiu *et al.* [87] employed a gemini surfactant (12-2-12) Br, in the hydrolysis of PNP catalyzed by Cu ligated by triazole-based ligands. The rate constant was enhanced sharply with increasing the concentration of the surfactants, reached a maximum and then declined with further increase in the concentration of the surfactant. The presence of surfactant enhanced the solubility of both substrate and the ligated catalyst and increased their availability, resulting in a higher reaction rate.

Gemini surfactants integrated with enzyme catalysis were also investigated. Verma *et al.* [88] reported a study on the effect of gemini surfactants of different chain lengths and head groups on the catalytic activity of  $\alpha$ -chymotrypsin toward the hydrolysis of PNPA. However, in such studies, one has to differentiate between the intrinsic micellar catalysis and the micellar and enzyme interactions. Both contributions are influenced by micelle-enzyme interactions. Therefore, the authors fitted their data to Michaelis-Menten equation and calculated both the constants  $K_m$  and  $k_{cat}$ . The first is a measure of the substrate's affinity to the enzyme while second is the catalytic rate constant. The reported values of  $k_{cat}$  and  $K_m$  and the catalytic efficiency  $k_{cat}/K_m$  indicates that incorporation of the gemini surfactant increased  $K_m$ , and thereby the overall catalytic efficiency was decreased. This result is expected since micelles compete with the enzyme for the substrate. Therefore, the outcome results depend on the relative activity of each enzyme and substrate.

The phase transfer catalysis role of gemini surfactants was also studied by Zu & Pan [89]. Herein, the gemini surfactant (12-10-12), in which the spacer contains two ester groups, was utilized to catalyze the nucleophilic substitution reaction between sodium acetate and 4-methylbenzyl chloride in DMF. The micellar structure in the non-polar medium is different from that in the aqueous medium. In the non-polar medium, a reversed micelle is formed. The proposed mechanism included the binding of sodium acetate from the solid phase by a surfactant to form an intermediate complex, which subsequently reacts with 4-methylbenzyl chloride in the liquid phase to form the product. The rate was enhanced significantly and followed a linear relationship with the surfactant concentration. The linear trend of surfactant catalytic profile is unusual since the variations in the surfactant concentration are often accompanied by changes in its physico-chemical properties. Therefore, there will be a non-steady change of molecular interaction. The CMC of the surfactant was not reported in this work. It is assumed that the complete investigation was performed well above the CMC, in which the micellar structure attained a steady configuration.

Öztürk *et al.* [90] synthesized two gemini surfactants (14-6-14) and (16-6-16) that contain a hydrophilic spacer with an oligoxyethylene group in its structure. The CMCs of two surfactants measured by the conductivity method were 0.383 and 0.325 mM. The surfactant (16-6-16) was examined for micellar catalysis of cycloaddition reaction between long alkyl-chained nitrones and *N*-aryl substituted maleimides in benzene, to



produce the [3+2] diastereoselective isoxazolidine. The yield of the specified product was 90% after 1 h in the presence of 2 mmol of surfactant. About the same yield was recovered after 3.5 h in the absence of surfactant. However, the increased surfactant concentration beyond 2 mmol resulted in reducing the yield within the same reaction time. The catalytic effect of the surfactant was explained by that the reactants were concentrated in the Stern layer of the reversed micelle. This is the reaction center where the polar groups of two reactants associate with polar groups in the heads and spacers of surfactant molecules. The hydrophobic parts of the reactants remain in the organic medium. The decline in the rate constant in the presence of a high surfactant concentration, well above the CMC, was attributed mainly to the dilution that results from the increased volume of the micellar phase.

### Conclusion

In the journey of developing micellar catalysts, mixed surfactant systems were one of the promising outcomes. The fascinating advantages of mixed micellar catalysis are the ability to perform some reactions in aqueous media and substitute the harmful and expensive organic solvents with water, the low cost and eco-friendly solvent. The ability to alter the physico-chemical properties of the mixed surfactant system provides a technique to control the reaction's pathways and finally increases the selectivity toward the desired products. The effect of mixed catalyzed systems cannot be judged easily as many factors contribute to it. Among the effects that can be altered with changing the composition of mixed surfactants are hydrophobicity of mixed micelle, dielectric properties, charge density and abundance of water and counterions in the micellar interface. To understand the catalytic effect of mixed surfactant systems on a reaction at certain conditions, the physico-chemical properties must be investigated. The added advantages of gemini surfactants over conventional ones are the ease of their synthesis and attractive physico-chemical properties, which results in higher micellar catalytic efficiency. The possible structural variations in head groups, spacer and tail length made gemini surfactants intriguing. A vast number of gemini surfactants of different physico-chemical properties could be existed and employed in various applications including micellar catalysis.

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### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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