

Micelle-catalysed redox reaction

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The reduction of methylene blue (MB) by SnCl₂ has been studied in three different micelles. Micellar catalysis in the cationic and non-ionic micelles has been observed to occur because of the binding of the substrates onto the micellar surface by hydrophobic and/or electrostatic interaction. This binding increases the encounter probability, leading to an accelerated rate of reaction. Investigation with various salting-out and salting-in agents revealed that hydrophobic effect supersedes Coulombic interaction for the observed micellar catalysis. Under the same experimental condition the calculated first-order rate constant in water, cationic and non-ionic micelles is 0.086, 0.303 and 0.167 min⁻¹ respectively. The activation energy for the reaction in water and non-ionic micelles is found to be 40.32 and 21.42 kJ/mol, respectively.

AN enzyme catalyses a redox reaction in two different ways. First, it possesses a redox centre, which is involved in the electron-transfer process and thus reduces the activation barrier^{1,2}. Second, an enzyme can increase the encounter probability by concentrating substrates at its binding sites³. The former is essentially a chemical factor and the latter is a 'concentration effect', but essentially a physical one. The physical factor for catalytic efficiency of an enzyme is that the reaction occurs in a diffusion space³ of the dimension, $d < 3$. This happens through binding of at least one of the reactants to the enzyme-binding site, and thus it becomes easier for another diffusing reactant to approach a fixed target more quickly. This physical factor has been the basis of explanations for the increase in the rate of reaction in many cases⁴. This has a resemblance with a catalyst supported on a solid material. Micelles, microemulsions and organized media have been treated in the light of fractal geometry. The organized assembly is assumed to contain two domains of fractal dimensions, one hydrophobic and the other hydrophilic. Thus, reaction kinetics can be studied in terms of fractal dimensions of the reaction medium^{5,6}. Micelles are known membrane mimetic systems⁷⁻⁹ which function in many ways. They lead to the enhancement of the solubility of organic compounds in water owing to the incorporation of organic compounds in the micelle¹⁰, they catalyse many reactions¹¹ due to the 'concentration effect' in the micellar pseudo-phase, and they may also alter reaction pathways¹². Evidences show³⁻⁶ that inherent fractal dimension and hydrophobic effect, not the charge compensation,

play the deterministic role in micelle-catalysed reactions. With these concepts in mind, the study of the reduction of methylene blue (MB) by SnCl₂ catalysed by organized media such as micelles is presented here to understand the enhanced rate of reaction.

MB (SD Fine Chemicals, India) was purified by repeated recrystallization from ethanol. Cetyl trimethylammonium bromide (CTAB; Aldrich) and sodium dodecylsulphate (SDS; Aldrich) were purified by recrystallization from methanol. Poly (oxyethylene) *iso*-octylphenyl ether, TX-100 (Aldrich) and urea (Loba Chemie) were used as received. Acridine orange (AO), guanidium hydrochloride (GdmCl), NaBH₄, NaCl, LiCl, LiClO₄, KBr were obtained from Aldrich and used as received. All salts used were AR grade. The solvents *n*-heptane, *n*-hexane, methanol and ethanol were freshly distilled for their use. Doubly-distilled conductivity water was used to prepare all the aqueous solutions. Stannous chloride (Glaxo Labs) was used without further purification. Freshly prepared solution of SnCl₂ in 0.1 mol dm⁻³ HCl was used as reducing agent. AOT (sodium salt of dioctylsulphosuccinate, Fluka) was purified following the standard procedure¹³. Prior to the experiment, AOT was vacuum-dried. The microemulsions were prepared as follows. To 0.2 M AOT in *n*-heptane, microlitre amounts of an aqueous solution of MB was added. The resulting mixture was shaken well so as to get a clear solution. To the resulting solution, microlitre amounts of an aqueous solution of SnCl₂ were added. The total amount of water added (i.e., MB solution + SnCl₂ solution) was controlled so as to get the desired w_0 (i.e. ratio of the number of molecules of water to that of AOT).

UV-visible absorption spectra were measured in a Shimadzu UV-160 digital spectrophotometer (Kyoto, Japan) with 1-cm quartz cuvettes. Light-scattering experiments were done using a Coulter counter uc C (N₄) (USA) instrument.

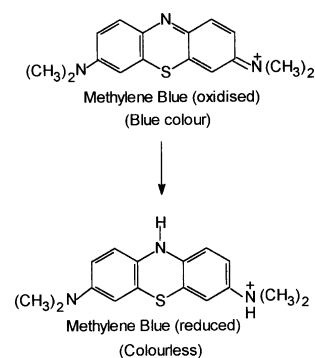
SnCl₂ is a celebrated reducing agent and widely used in solution involving active Sn (II) ion (Sn⁴⁺ + 2e = Sn²⁺; E⁰ = + 0.172 V) for reduction purpose. However, with the increase in HCl concentration, SnCl₂ essentially becomes SnCl₃⁻ (SnCl₂ + HCl ⇌ HSnCl₃) or SnCl₄²⁻ (SnCl₂ + 2HCl ⇌ H₂SnCl₄) ion¹⁴. The appropriate half-reaction may be SnCl₆²⁻ + 2e = SnCl₃⁻ + 3Cl⁻ (1 M HCl and 4 M Cl⁻). Higher concentration of HCl makes SnCl₂ a stronger reducing agent. It has been observed that the Sn (II) ion in the presence of higher concentration of HCl enhances the reduction rate of MB in CTAB as well as in TX-100. This may be due to the enhancement of reducing property of the Sn (II) ion after the formation and then incorporation of anionic Sn (II) species, SC in micelle. The ion association of the complex species SC with CTAB, i.e. with the cationic micelle, was further verified by the solvent extraction. Non-polar *n*-hexane quantitatively extracts the ion associate SC (II)-CTAB from aqueous micellar medium. After the extraction of SC-CTAB species in *n*-hexane, a

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very low reduction rate of MB was observed in aqueous solution. It may be questioned that aqueous HCl alone might influence the observed slow reduction reaction. If the SC-CTAB species is extracted out earlier in *n*-hexane, addition of HCl to the aqueous medium did not cause the enhancement of the rate of MB reduction. So the selective extraction of HCl in *n*-hexane was ruled out. The non-polar *n*-hexane effectively extracts the ion-associate, i.e. SC-CTAB complex species from the reaction mixture. The quantitative extraction of the ion-associate in *n*-hexane took place in 5 mol dm^{-3} HCl. Once the extraction was complete, practically no reduction was observed. The presence of the extracted SC-CTAB ion-associate in *n*-hexane was further confirmed by stripping the *n*-hexane layer with water.

Micelle surface binds many organic/inorganic compounds by electrostatic and/or hydrophobic interaction¹⁵. A favourable binding of the cationic substrate MB in micelle through hydrophobic interaction leads to a higher encounter probability (lowering of $d < 3$) with an incoming species (SnCl_2). MB is highly soluble in common polar solvents ($\lambda_{\text{max}} = 665 \text{ nm}$). Incorporation of MB in CTAB/TX-100 or a change of pH of the solution containing MB does not shift the λ_{max} value. Fluorescence study could not substantiate the binding/incorporation of MB in a micelle, as the dye MB is non-fluorescent. To have a logical but indirect explanation about the incorporation of MB in micelle, AO, a fluorescent cationic dye was introduced into CTAB/TX-100 micelle. Fluorescence quenching (FQ) of AO was observed with Br^- , while AO is incorporated in both the micelles ($d < 3$). On the other hand, simple Br^- did not show any FQ of AO in water ($d = 3$) in the absence of micelle. This fact can readily be explained through the consideration of the fractal model of the micellar surface, which facilitates the binding of AO in micelle^{5,6} and hence the FQ was observed for micelle-bound dye in the presence of Br^- .

MB is a cationic dye and chloro complex of Sn (II). SC is an oppositely charged species. The electrostatic attraction between them for an effective reaction in aqueous medium is probable, but is not observed, presumably because of solvation effect. Even though the reaction is thermodynamically favourable, a kinetic barrier, i.e. solvation effect imposes a barrier for an effective encounter. The extent of solvation is reduced through the use of a suitable micellar environment. The complete reduction of MB occurs leaving a colourless solution (Scheme 1), while the concentration of micelle, [micelle] is three times higher than the dye concentration, [MB], i.e. [micelle]:[MB] > 3. This ratio has been found to be optimal for the quantitative incorporation of the dye, MB in the cationic micelle, which is a prime condition for quantitative bleaching of MB (Figure 1) by SC. Use of a higher amount of MB, more than the prescribed [MB] leaves some unbound MB in the bulk aqueous phase, and for that unincorporated amount of MB no bleaching takes place,



Scheme 1. Oxidized and reduced form of methylene blue.

i.e. no micellar catalysis is observed for the free and unbound MB. So micelle can readily remove the kinetic barrier for the MB-SC reduction reaction.

In the present situation MB binds with CTAB, a cationic micelle, through hydrophobic interaction. SC being a negatively charged species, can penetrate into the Stern layer of CTAB. Figure 2 a explains qualitatively the reduction of MB, where both the substrates are incorporated in the Stern layer of CTAB. The rate of reduction of $0.5 \times 10^{-3} \text{ mol dm}^{-3}$ MB with $0.13 \times 10^{-2} \text{ mol dm}^{-3}$ SnCl_4^{2-} in presence of $10^{-2} \text{ mol dm}^{-3}$ CTAB has been observed to be very fast. However, the rate of reduction of MB becomes slower if the concentration of CTAB falls below its cmc (Table 1). Under these conditions the surfactant does not form any micelle, indicating the importance of micelle formation for catalysis.

The rate of reduction of MB by $0.13 \times 10^{-2} \text{ mol dm}^{-3}$ SC species in the presence of a neutral micelle, TX-100 ($10^{-2} \text{ mol dm}^{-3}$), is considerably slower (Table 2) than CTAB-catalysed reduction. This can easily be explained considering the hydrophobic interaction between MB and TX-100, but weak interaction between the TX-100 micelle and SC species (Figure 2 b). In the latter case there is no electrostatic interaction as in CTAB.

In the absence of micelle, MB and SC cannot come to a closer proximity due to the solvation effect ($d = 3$). So the

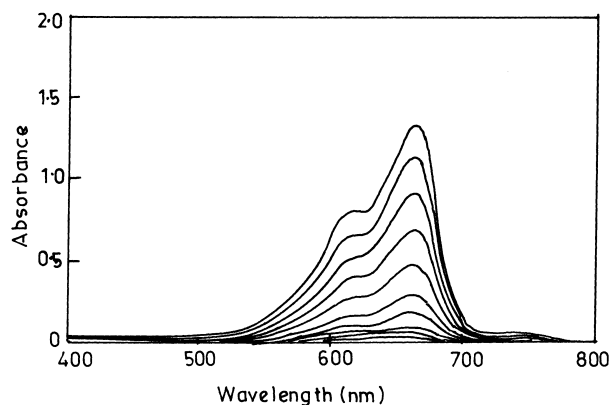


Figure 1. Successive reduction of methylene blue in CTAB by SC.

rate of the reduction becomes slower (Table 2) due to low encounter probability. For SDS, an anionic micelle, the charge repulsion effect removes SC even from the micellar surface (Figure 2 *c*). Hence no reduction of the dye takes place in the experimental time scale.

Thus, the observed rate of reduction has been seen to follow the order: CTAB > TX-100 > water. It has been verified from the simple kinetic plot that the redox reactions followed the first-order kinetics. The rate of reaction has been observed to be independent of MB concentration, but dependent on SC concentration.

Using the same concentration of MB (1×10^{-5} mol dm $^{-3}$) the reduction was studied with the stronger reducing agent NaBH $_4$. A comparison between the fraction of dye reduced in CTAB using equal concentration (2.5×10^{-4} mol dm $^{-3}$) of NaBH $_4$ and SC indicates that the rate is faster in case of SC. This is explained by once again invoking the extent of hydrophobicity of the complex ion of Sn (II) moiety, i.e. SC in moderately high HCl medium. The BH $_4^-$ ion having no hydrophobic character is more diffusing and so less accessible for micelle-bound MB. It can only bind in the CTAB surface by electrostatic force, while for SC in the experimental HCl condition, the hydrophobic force favours its approach towards CTAB. However, lower concentration of HCl retards the micelle-bound MB bleaching.

The micellar catalysis is often rationalized in terms of bringing together of reactants on the Stern layer of the micelle. It is easy to suppose that the surface of the micelle has a fractal dimension ($d < 3$) where the sub-

strates MB and complex SC are accumulated and hence the encounter probability is enhanced compared to a homogeneous solution (CH $_3$ OH or H $_2$ O where the dimension is exactly 3). The reaction rate in CH $_3$ OH is found to be faster than that in water, but slower than that in aqueous CTAB solution. Earlier works have also invoked fractal models of micelles to explain rate enhancement of the reactions 3,16,17 .

Light-scattering (90°) experiments in solution reveal a ~12-fold reduction in diameter of the CTAB micelles from 2000 nm upon the addition of dil. HCl. The CTAB micelle in acidic medium increases its diameter from 170 to 260 nm after incorporation of MB. Like the Cl $^-$ ion, the SC ion too leads to a decrease in the size of the CTAB micelles, presumably due to the electrostatic attraction. Acid addition increases the micellar surface charge upon the adsorption of Cl $^-$ onto CTAB surface. The complex SC ion with more hydrophobic character than Cl $^-$ adsorbs more strongly on the CTAB surface and thus further reduces the micellar size. On the other hand, MB being a cationic dye with hydrophobicity partially neutralizes the adsorbed Cl $^-$ at the micellar surface and thus increases the size of the micelle. The small size of the CTAB–SC moiety in the acidic solution presumably hinders the incorporation of MB, and so catalysis is not observed if the SC complex anion is added to the system before the addition of MB. In all cases, it has been observed that the presence of the cationic micelle is responsible for the effective colour bleaching of the cationic dye, MB in the experimental time scale.

The water–hydrocarbon interactions are modified in the presence of additives. It is widely known that urea and big ions (guanidinium, Gdm $^-$; ClO $_4^-$) disrupt hydrophobic aggregation. Since these compounds lead to increased solubility of organic molecules in an aqueous medium, they are called ‘salting-in-agents’. Small ions (Li $^+$, Na $^+$, Cl $^-$, etc.) reduce the solubility of organic compounds in water and hence are called ‘salting-out-agents’. The latter facilitate hydrophobic binding.

In the present study, to strengthen the contention that hydrophobic effect is an important factor affecting the rate of reduction of MB (0.5×10^{-3} mol dm $^{-3}$) by SC (0.13×10^{-2} mol dm $^{-3}$) in CTAB (10^{-2} mol dm $^{-3}$) and TX-100 (10^{-2} mol dm $^{-3}$), the effect of various salts have been examined.

Experimentally it was found that the rate of complete reduction of MB by SC in CTAB led to delay when

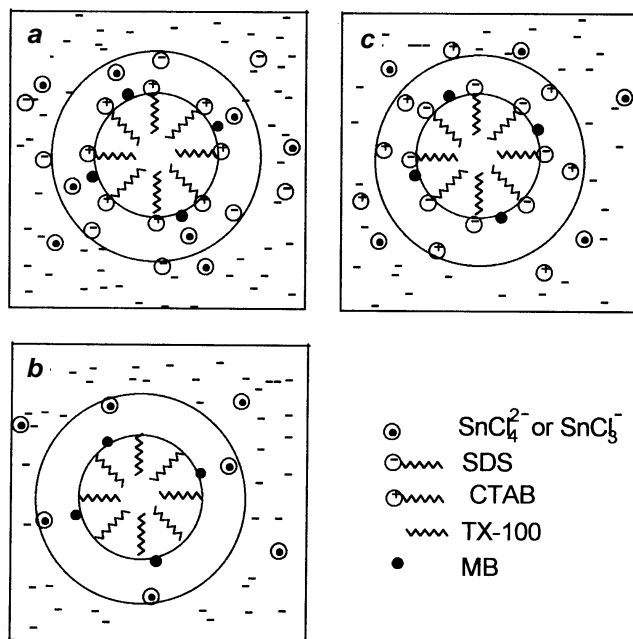


Figure 2. Incorporation of MB in micelle and interaction with the chloro complex of Sn (II) ion, SC. *a*, CTAB; *b*, SDS; and *c*, TX-100 micellar medium. Conditions: MB (0.5×10^{-3} mol dm $^{-3}$), SC (0.13×10^{-2} mol dm $^{-3}$), CTAB (10^{-2} mol dm $^{-3}$), SDS (10^{-2} mol dm $^{-3}$) and TX-100 (10^{-2} mol dm $^{-3}$).

Table 1. Rate constant values for the reduction of MB in different micellar concentration of CTAB

[MB] (mol dm $^{-3}$)	[CTAB] (mol dm $^{-3}$)	[SnCl $_4^{2-}$] (mol dm $^{-3}$)	Calculated rate constant (min $^{-1}$)
0.5×10^{-3}	1.0×10^{-2}	1.3×10^{-3}	0.303
0.5×10^{-3}	2.0×10^{-4}	1.3×10^{-3}	0.062
0.5×10^{-3}	1.0×10^{-3}	1.3×10^{-3}	0.112

0.1 mol dm⁻³ urea and 1.0 mol dm⁻³ guanidinium hydrochloride were added. In the presence of 0.1 mol dm⁻³ LiCl, the reduction of MB has been observed to accelerate. This proves the importance of salting out action of LiCl in the reaction. A similar effect was observed when TX-100 was used as surfactant in place of CTAB. It was found that at the same dye concentration the rate of reduction by SC slowed down when 0.1 mol dm⁻³ urea, 1.0 mol dm⁻³ guanidinium hydrochloride and 0.2 mol dm⁻³ LiClO₄ were added. In the presence of 0.1 mol dm⁻³ LiCl, the reduction in TX-100 showed the usual acceleration in rate (Table 3).

Micellar catalysis can be due to environmental changes decreasing the free energy differences between initial and final transition states and also due to increase in the encounter probability, as a consequence of the close association of the reactants at the micellar interface. So the activation energy might play a role in the micellar catalysis. In TX-100 and in water the activation energy is experimentally determined. The activation energies in water and TX-100 for the reduction of MB (0.5×10^{-3} mol dm⁻³) by SC (0.13×10^{-2} mol dm⁻³) complex species under similar conditions were found to be 40.32 kJ/mol and 21.42 kJ/mol, respectively, while the reaction was studied at six different temperatures between 10° and 40°C. These data clearly speak for the mechanism of rate enhancement. The enhanced rate of reduction thus accounts for the lowered activation barrier as well as increased encounter probability. In CTAB micelle, the reaction becomes very fast at higher temperature (> 35°C) and at a lower temperature (< 25°C) due to the separation of CTAB-SC ion associate from the aqueous medium restrict the determination of activation energy in CTAB.

Reverse micelles are surfactant aggregates formed in an apolar solvent¹⁸. They are basically nanometer-sized water droplets surrounded by a layer of surfactant molecules such as AOT, with the non-polar solvent acting

in the dispersion medium¹⁸. The alkanes, *iso*-octane or *n*-heptane are generally used, since they permit maximum solubilization of water at room temperature. AOT reverse micelle contains 23 molecules per aggregate, forming a rounded cylinder¹⁹. Increasing the concentration of surfactant-entrapped water results in the formation of water-in-oil micro-emulsions. In micro-emulsions, a significant fraction of the water in the pool is perturbed by the polar head-group and counter ions of the surfactant. This effect is emphasized in small water pools (i.e. low w_0). It is found that in small water pools, a fraction of the water molecules solvated Na⁺. These water molecules are considered to be 'bound'¹⁹. For $w_0 \leq 12$, in addition to these bound water molecules, interfacial water molecules are present which are held to the sulphonate or carboxyl groups of AOT by ion-dipole or hydrogen bond. For $w_0 > 12$, water in excess of bound and interfacial molecules forms the central water pool which has a comparatively higher mobility. The immobilized water pools provide a medium for very large and highly specific rate enhancement and thus they resemble the hydrophilic pockets of enzyme.

The interesting results obtained with reverse micelles in earlier experiments provide an inspiration to probe the anomalous nature of the water present in the core of these reverse micelles. For this, the reverse micelles formed by AOT in *n*-heptane were used to study the redox reaction of MB. To ensure complete solubilization of 1.2×10^{-5} mol dm⁻³ MB in the non-polar medium, a relatively high concentration of AOT (0.2 mol dm⁻³) was used.

On the basis of experiments, it was found that the rate of the reduction could be directly correlated to the size of the water pool (i.e. w_0) since, for AOT in *n*-heptane, the radius of the water pool (r_w in Å) is close to $2 w_0$. Under the same reaction conditions and within the same time

Table 2. Rate constant values for the reduction of MB in the presence and absence of micelles at 30°C

Type of solution	[MB] (mol dm ⁻³)	[SnCl ₄ ²⁻] (mol dm ⁻³)	Calculated rate constant (min ⁻¹)
CTAB (1.0×10^{-2} mol dm ⁻³)	0.5×10^{-3}	1.3×10^{-3}	0.303
TX-100 (1.0×10^{-2} mol dm ⁻³)	0.5×10^{-3}	1.3×10^{-3}	0.167
Water	0.5×10^{-3}	1.3×10^{-3}	0.086

Table 3. Rate constant values for the reduction of MB in CTAB and TX-100 micelles with the addition of 20 µl of different compounds

Type of salt	Salt concentration (mol dm ⁻³)	Calculated rate constant (min ⁻¹)	
		CTAB	TX-100
Urea	0.1	0.297	0.156
Guanidinium hydrochloride	1.0	0.288	0.149
Lithium chloride	0.1	0.310	0.172
Lithium perchlorate	0.2	0.295	0.159

span (6 min) it was found that the absorbance decreases to 1/8 of its original value for $w_0 = 8$ and to 1/4 of its original value for $w_0 = 16$. The results obtained may be explained on the basis of the 'free' and 'bound' water molecules present in the reverse micelle. When $w_0 = 8$, most of the water molecules present in the reverse micelle are bound (i.e. a fraction solvates the Na^+ ions, while the remaining fraction is present as interfacial water). Now, MB being relatively hydrophobic gets attached to the surfactant chains, irrespective of the size of the pool. However, the location of the dye molecules is nearer to the inner periphery of the reverse micelles (adjacent to the water pool) rather than the outer periphery which is directly exposed to the completely non-polar bulk *n*-heptane phase. The situation is similar to normal micelles where it was inferred that MB resides in the palisade layer. The difference in reaction rate with differing w_0 arises due to the location of SC ion, which is more likely to be present in the aqueous phase. For small water pools, the probability of SC ion being exposed to MB increases as the water-containing reductant is in close proximity to the surfactant chains¹⁹. The motion of the reductant is restricted in the small water pools and this leads to an increased number of encounters. For the larger water pool (i.e. $w_0 = 16$), a fraction of the added water which is in excess of the bound and interfacial water is not exposed directly to the surfactant¹⁹. Hence the MB molecules are less vulnerable to attack by these more mobile complex SC ions contained in the water comprising the central water pool. Thus the probability of reduction decreases and hence a slower reaction rate compared to $w_0 = 8$ is observed.

However, in both cases (i.e. $w_0 = 8$ and $w_0 = 16$) it is found that the reduction rate of MB by the reductant is slower than that in normal micelles of CTAB. The reaction rate in reverse micelle is, however, faster than that in plain water. For alcohol too, the reduction rate is between that in plain water and CTAB micelles. The effective dielectric constant (D) of the water pool has been determined earlier employing fluorescence techniques. From the reported data, the value of D is found to be in the range 30–40, which is close to that in methanol^{20,21}. This result also shows that there may be a similarity between the effective D of the water pool of reverse micelles and that of methanol.

This article discusses how a conventional chemical reaction, often studied in homogeneous solution, has been studied to be advantageous in organized systems. The present study reports the catalytic effect offered by the restricted geometry and atypical environments of various organized assemblies on the well-known redox reaction of

MB. Of the two factors affecting the rate of reactions, i.e. free energy of activation and encounter probability, the latter has been found to exert a dominating influence in the case of catalysis by micelles and reverse micelles. Thus, micelles provide a method of organizing the reactants on a molecular scale and enhancing the reaction rate. Electrostatic and hydrophobic forces exert a profound influence on the encounter probability. A delicate balance of both gives rise to an optimum condition for catalysis. However, it was found that the hydrophobic effect is a very important factor determining the rate of the micellar catalysis. In conclusion, this report demonstrates the significance of hydrophobic interaction of dye in micelle that supplements the enhancement of reduction rate by removing the kinetic barrier, to lead to a thermodynamically favourable reaction in micelles.

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