Reduction of methylene blue (MB) by ammonia in micelles catalyzed by metal nanoparticles†

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The increased encounter probability between ammonia and an immobilized cationic dye in non-ionic micelles demonstrates the reduction capability of ammonia while present even at ppm levels. Catalytic amounts of silver nanoparticles ($\sim$7 nm in size) have been shown to enhance the reaction rate of the reduction reaction, explained by the strong affinity between Ag nanoparticles and the nitrogen atom of the donor ammonia molecule. Furthermore, the preferential participation of the ammonia molecule as reductant has been proven unequivocally by taking micelle-bound dye as the reagent in the presence of phenolphthalein. The proper choice of micelle, influence of different ''salting-in'' and ''salting-out'' agents, catalysis involving nanoparticles and the thermodynamic parameters of the reaction support the possible quantification process of ammonia in solution.

Introduction

Aqueous micellar solutions are a unique media characterized, in contrast to common mixed aqueous organic solvents, by a non-homogeneous distribution of solutes, which gives rise to an alteration of their reactivity, spectroscopic and acid-base properties, extraction and chromatographic behaviour, *etc.* These effects find numerous applications in analytical chemistry.[1–4] Currently much attention is directed towards the use of micellar catalysis for the improvement of kinetic[5–9] and flow injection[10] methods. Micellar effects on reaction equilibria (other than shifts of pK_a values of solubilized molecules), a well-studied topic[11–13] have not yet found application in analysis although they can be utilized in principle.[14]

In general, micellar effects can be used to promote processes strongly reversible in water, such as Schiff base and hydrazone formation condensation reactions, which are widely used for the determination of both carbonyl compounds and amines or hydrazines.[15–17] All these reactions are, however, strongly reversible and sometimes strictly anhydrous conditions are necessary to obtain a close to quantitative yield of the product.[18,19] Another disadvantage is the slow rate of condensation reactions under mild conditions in the absence of specific or general acid catalysts.[20]

Keeping an eye on all these possibilities, suitable micelle solutions have been chosen to immobilize reducible organic compounds. In the next step, ammonia encounters the immobilized molecule and has been observed for the first time to play the role of a reductant. This observation has generated interest in developing a quantification technique for ammonia detection.

In general, colourimetric methods[21,22] are used for the determination of ammonia in aqueous environments. However, colour or turbidity interferes with these methods and therefore, a time-consuming preliminary distillation step[23] is required before analysis. Thus, a fast and highly sensitive method is desired. At present, an ammonia selective electrode method[24,25] has been widely used for determining ammonia in environmental samples. However, this method is susceptible to interferences by amines.[26] A few years ago, a gas phase molecular absorption method[27,28] has been reported but this method is not quite as sensitive.

The ammonia selective electrode method has also been applied in combination with flow-injection systems. Apart from direct sensing of ammonia, the electrodes have also been used as transducers for monitoring enzymatic reactions during which ammonia is released or consumed. The determination of urea, which by catalytic action of urease, is hydrolyzed to give ammonia and carbon dioxide, is a representative example.[29] Ammonia electrodes can also be exploited to monitor the binding of antigens to antibodies.[30] Despite the utility of present day electrochemical ammonia sensors, they have some disadvantages: (1) they do not lend themselves to miniaturization; (2) it is not easy to sterilize them; (3) their performance can be affected by surface potentials, resulting in drifting signal; (4) as in other potentiometric methods, a reference electrode is required, along with its troublesome liquid–liquid junction.

For the determination of the air vapour concentration (AVC) of ammonia several methods are available, but none is rapid, simple and sensitive for practical applications. The Berthelot reaction[31] is time consuming and unsuitable for AVC studies. The AVC of ammonia can be determined by other methods[32,33] but none of them is suitable for use as a personal dosimeter. Other techniques that include molecular absorption, gas chromatography with chemiluminescence detection and fluorimetric methods[34,35] are well-documented but require sophisticated apparatus.

The assay of ammonia has found increasing importance in the diagnosis of several disease states, such as hepatic coma, Eck's fistula and Rey's syndrome.[36] Higher dosages of ammonia may cause iritis, bronchoconstriction and dyspnca.[37] Hence the detection of ammonia is very important not only for air quality studies but also for diagnostic purposes.

Previously, we reported two fluorimetric methods[34,35] for the determination of ammonia concentration in aqueous solution. In this paper, it is reported for the first time a simple demonstration of the unusual reducing capability of ammonia

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that leads to a cost effective and sensitive spectrophotometric method for the determination of ammonia concentration. This method utilizes the quantitative colour bleaching of methylene blue (MB), a well-known non-toxic cationic dye, by ammonia in micellar medium. The decrease in colour intensity of MB is a direct measure of the ammonia concentration and hence is suitable for routine analysis. Ammonia concentration can be detected at the parts-per-million (ppm) level. Possible interferences have been investigated and the standard deviation of the method has been estimated to be ±3%. Furthermore, coinage metal nanoparticles have been found to catalyze the reaction. Thus, the importance of the micelles in dealing with the reducing property of ammonia and acting as an electron relay *via* metal particles, especially silver nanoparticles, for enhancement of the reduction rate have been examined in detail.

Experimental

Reagents and apparatus

All reagents used were of AR grade. All aqueous solutions were prepared in doubly distilled water with the second distillation being carried out from alkaline permanganate in an all-pyrex still. Ammonia solution (6.0 mol l^{-1}) was prepared form a stock ammonia solution (17.0 mol l^{-1}) by proper dilution methods using distilled water and standardized by standard HCl solution. Phenolphthalein (PH) and MB were purchased from Qualigens Fine Chemicals, India and were used after repeated crystallization from alcohol. Stock solutions of PH (3.9×10^{-5} mol l^{-1}) and MB (5.0×10^{-4} mol l^{-1}) were prepared in ethanol water and water, respectively. 1,9-Dimethylmethylene blue (DMMB) was purchased from Sigma and the stock solution (5.0×10^{-4} mol l^{-1}) was prepared in water. Poly(oxyethylene) iso-octyl phenyl ether (Triton X-100 or TX-100), sodium dodecyl sulfate (SDS) and cetyl trimethyl ammonium bromide (CTAB) were purchased from Aldrich. Urea (Loba Chemie) and NaCl (SRL, India) were used as received. Silver and gold solutions were prepared from $AgNO_3$ or $HAuCl_4$ (Johnson and Matthey) by the UV-photoactivation technique and by chemical reduction, which are described below.

All UV-visible absorption spectra were measured in a Shimadzu (Kyoto, Japan) UV-160 digital spectrophotometer equipped with a 1 cm quartz cuvette. The dynamic light scattering (DLS) study was done in a dynamic light scattering (DLS-7000, Otsuka electronics, Osaka, Japan) instrument. A Gilson micropipette with disposable tips was used to add samples.

Preparation of metal nanoparticles

Preparation of gold nanoparticles by the photochemical method. Gold nanoparticles showing a beautiful pink colour and containing 3.3–5.0×10^{-4} mol l^{-1} gold in 10^{-2} mol l^{-1} TX-100 were photochemically prepared from $HAuCl_4$ following a procedure reported earlier.[38a] During the preparation TX-100 acts as both stabilizer and reducing agent. The plasmon absorption for gold nanoparticles is at 523 nm. The average particle size was in the 5–7 nm size regime.

Preparation of silver nanoparticles by the photochemical method. An aliquot of standard $AgNO_3$ solution (final concentration in solution of 7.5×10^{-5} mol l^{-1}) and TX-100 solution (10^{-2} mol l^{-1}) were mixed together and irradiated in the photoreactor with a flux of 850 Lux for 45–60 min. After photo-irradiation the solution turned yellow. The characteristic plasmon absorption band for the silver nanoparticle solutions[38b] appeared at 415 nm. The average size of the particles was 8–10 nm.

Preparation of silver nanoparticles by a chemical method. An aliquot of 10 mL of 10^{-2} mol l^{-1} $AgNO_3$ was taken in 100 mL distilled water in a 250 mL conical flask. The solution was boiled for a few minutes and while boiling 0.5 mL of a 0.2 mol l^{-1} sodium citrate solution was added all at once. Boiling was continued for about 60–90 min and final volume of the solution was maintained at 100 mL. The greenish-yellow coloured silver sol[39a] that was generated had a λ_{max} of 420 nm. The average size of the particle varied in the 30–40 nm range. These are the larger sized particles. Smaller sized particles are prepared as follows: an aliquot of 20 μL of 10^{-2} mol l^{-1} $AgNO_3$ was taken in 2 mL distilled water. The solution was then purged with N_2 and stirred by a magnetic stirrer. Then 5 μL of 0.1 mol l^{-1} $NaBH_4$ was added all at once and stirring was continued for another 30 min. The yellow silver sol that was generated had a λ_{max} at 400 nm. The average size of these particles was ~7 nm.[39b]

Preparation of gold nanoparticles by a chemical method. Similarly, a 1 mL aliquot of 5×10^{-3} mol l^{-1} $HAuCl_4$ was added to 9 mL distilled water. The solution was boiled for a few minutes and then 100 μL of sodium citrate solution (0.2 mol l^{-1}) was added drop by drop while stirring. Boiling and stirring was then continued for another 30 min. The solution turned violet. It was then cooled to room temperature and showed a λ_{max} at 520 nm. The average particle size was ~7 nm.[39c]

Procedure

In a stoppered cuvette 2 mL of TX-100 (0.1 mol l^{-1}) and 50 μL of MB (5×10^{-4} mol l^{-1}) were placed. The solution showed a λ_{max} at 664 nm. Then this solution was mixed with 10–400 μL of an aqueous ammonia solution (0.6 mol l^{-1}). After 2 min (the time required for manipulation) the decrease in the absorbance value of the micelle-stabilized dye (MB) was monitored at 664 nm (Fig. 1). The bleaching of MB colour gives a quantitative measure of the ammonia concentration present in the solution.

Results and discussion

Micellar catalysis leading to quantitative colour bleaching of methylene blue (MB) by NH_3

Methylene blue (MB) is a water-soluble non-toxic cationic dye, which is blue in colour (λ_{max} 662 nm). In TX-100 micelle its λ_{max} shifts to 664 nm. But in the presence of acid or alkali the λ_{max} remains unaffected. This remains true in the micellar environment. Upon reduction, it becomes colourless (Scheme 1). In water, the rate of reduction of MB by NH_3 has been observed to be negligibly small and it takes a long time to

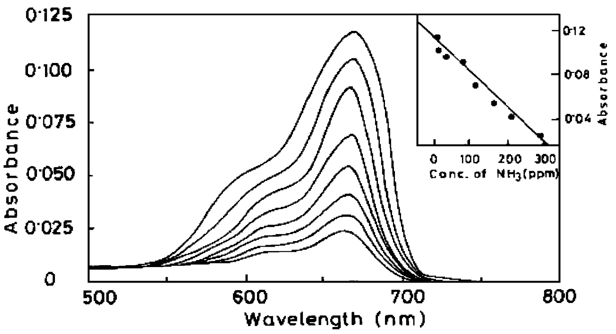
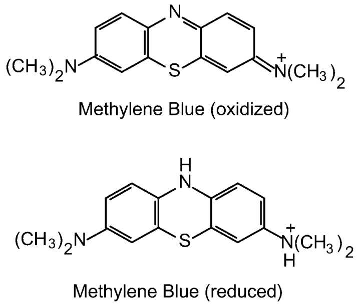


Fig. 1 UV-visible spectra of the reduction of MB by varying amounts of NH_3 in TX-100 micelles. Conditions: final concentration of MB = 1.02–1.21×10^{-5} mol l^{-1}, TX-100 = 8.1–9.7×10^{-2} mol l^{-1}. Inset shows the absorbance *vs.* concentration of ammonia (ppm) plot.



Scheme 1 Oxidized and reduced forms of MB.

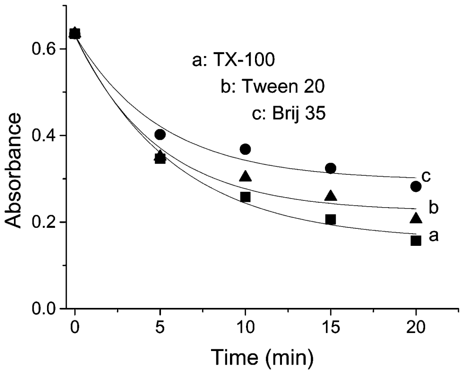


Fig. 3 Absorbance *vs.* time plot for the reduction of MB by ammonia in three different neutral micelles: (a) TX-100, (b) Tween 20 and (c) Brij 35. Conditions: final concentration of TX-100 = Tween 20 = Brij Brij 35 = 8.16×10^{-2} mol l^{-1}; final concentration of MB = 1.02×10^{-5} mol l^{-1}. Absorbance was measured at 664 nm.

observe an appreciable change in colour of the dye. A similar observation was noted in the case of the MB–ascorbic acid reaction in water in the absence of any surfactant.[40] In a likewise fashion, the slow reaction of NH_3 with MB in water is thought to be due to low encounter probability.

From the electrochemical data it was found that the reduction reaction between MB and NH_3 is thermodynamically allowed but does not occur appreciably in water. A "kinetic barrier" arising from a low encounter probability due to the solvated nature of the reactants may explain why the reduction reaction is not observed on the experimental time scale. To remove this barrier and to increase the encounter probability in the MB reduction by NH_3 different micelles were used and the order of reaction was found to be as follows (Fig. 2):

$$\mathrm{Rate}_{\mathrm{TX\text{-}100}} > \mathrm{Rate}_{\mathrm{CTAB}} > \mathrm{Rate}_{\mathrm{SDS}} \sim \mathrm{Rate}_{\mathrm{H2O}}$$

that is, the rate of colour bleaching of MB was found to be fastest in the non-ionic micelle. The site of incorporation of solubilized molecules depends on their relative hydrophobic and hydrophilic tendencies. The molecules may be entrapped in the hydrocarbon core of the micelles,[41] they may be oriented radially in the micelle with the polar group buried (deep penetration as in the CTAB case) or near the surface (short penetration as in TX-100) or they may be adsorbed (as in the SDS case) on the surface of the micelle. Additionally, for non-ionic surfactants, incorporation of the molecule can occur in the polyoxyethylene shell of the surfactant. In order to generalize this statement we studied the reaction in other non-ionic micelles: Brij-35 [polyoxyethylene (20) sorbitan monolaurate] and Tween 20 [polyoxyethylene (35) lauryl ether], both purchased from Aldrich. Here also we found that the rate of reduction in these non-ionic micelles is faster than in the case of charged micelles. However, TX-100 has been found to be the most effective when we compared the effect of TX-100 with other non-ionic micelles with higher hydrophobicity; the order is (Fig. 3):

$$\mathrm{Rate}_{\mathrm{TX\text{-}100}} > \mathrm{Rate}_{\mathrm{Tween\ 20}} > \mathrm{Rate}_{\mathrm{Brij\text{-}35}}$$

and the rate constant values are 6.6×10^{-2}, 5.1×10^{-2} and 3.7×10^{-2} min^{-1}, respectively.

We next tried to see the effect of TX-100 concentration (ranging from 10^{-1} to 10^{-4} mol l^{-1}) on the reduction of MB by NH_3. It was found that the reduction is fastest in 10^{-1} mol l^{-1} TX-100 and slowest in 10^{-4} mol l^{-1}, that is the rate decreases with decreasing TX-100 concentration (Fig. 4) and below 10^{-4} mol l^{-1} the rate of reduction was found to be negligibly small (comparable to the reaction in water), requiring a long time before an appreciable change in colour of the dye was observable, as mentioned earlier.

MB being a cationic dye is bound to TX-100 micelles by hydrophobic forces. As the reaction is favoured in the presence of TX-100 micelle this might be due to enhanced collision probability between NH_3 and MB after MB is micelle-bound. Another important observation was made in TX-100 medium: after complete disappearance of the colour of the dye the back-oxidation of MB never took place, that is the blue colour of MB never reappeared, unlike the back-oxidation of the dye observed in the CTAB–ascorbic acid[40] and SDS–arsine[42] systems.

Insignificant colour bleaching of the dye was observed in cationic or anionic micellar solutions. This might be due to deeper penetration of the dye in the CTAB micelle due to hydrophobic as well as repulsive interactions. Once MB is

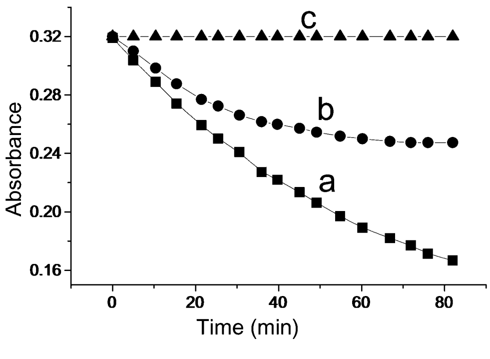


Fig. 2 Absorbance *vs.* time plot for the reduction of MB by ammonia in (a) TX-100, (b) CTAB, and (c) SDS micelles. Conditions: final concentration of TX-100 = CTAB = SDS = 8.1×10^{-2} mol l^{-1}; final concentration of MB = 1.02×10^{-5} mol l^{-1}. Absorbance was measured at 664 nm.

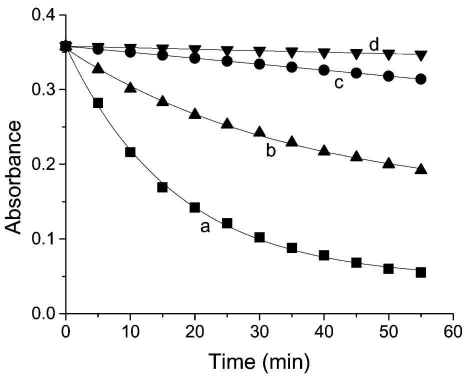
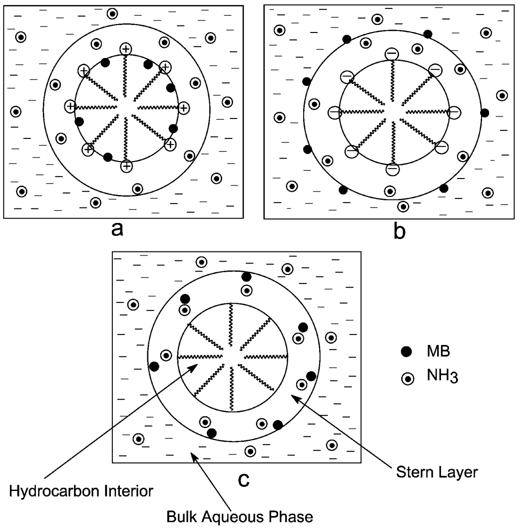


Fig. 4 Absorbance *vs.* time plot for the reduction of MB by ammonia with varying concentrations of TX-100: (a) 10^{-1}, (b) 10^{-2}, (c) 10^{-3} and (d) 10^{-4} mol l^{-1}. Final concentration of MB = 1.02×10^{-5} mol l^{-1}. Absorbance was measured at 664 nm.



Scheme 2 Model of the reaction conditions prevailing in (a) cationic, (b) anionic and (c) neutral micelles.

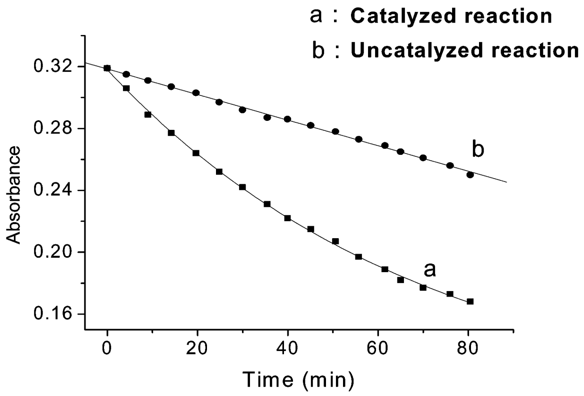


Fig. 5 Absorbance *vs.* time plot for the reduction of MB by ammonia in TX-100 micelles (a) in the presence of metal particles and (b) in the absence of metal particles. Conditions: final concentration of the silver metal particles in solution is 1.6×10^{-5} mol l^{-1}; final concentration of MB = 1.00×10^{-5} mol l^{-1}. Absorbance was measured at 664 nm.

incorporated in a micelle by hydrophobic forces, the dye is pushed further into the core region of the micelle by the repulsive forces. On the other hand, the SDS micelle restricts the penetration of the dye due to the ionic interactions and hence the dye remains bound onto the micelle surface. These might be the reasons for the low collision probability between MB and NH$_3$. The position of the dye and ammonia molecules in the three micelles is shown in Scheme 2.

The sequence of addition of the substrates has been found to be extremely important for some cases of micellar catalysis, as we have already shown.[40,42] But MB reduction by NH$_3$ has been found to be spontaneous, whether NH$_3$ is added prior to MB or the reverse. So here the sequence of addition does not affect the efficiency of the reaction.

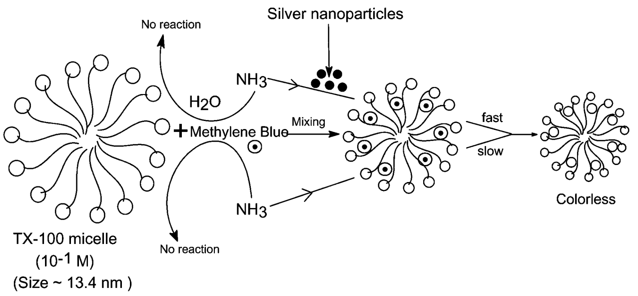
No significant change in the electronic spectrum of MB was observed when micelle-bound MB interacts with NH$_3$. So a proton transfer reaction cannot account for the observations.

Effect of addition of metal particles

The redox reaction between MB and the reductant can be viewed as an electron transfer reaction. The reaction has been observed to be catalyzed by metal nanoparticles in which NH$_3$ (the reductant) readily transfer electrons *via* metal particles to the micelle-bound dye. The rate of the catalyzed reaction was found to be enhanced in comparison to the uncatalyzed reaction (Fig. 5). The reason for the rate enhancement in the presence of metal particles can be simply explained as follows. Metal particles in the nanometer size range can serve as efficient catalysts[43,44] in many redox reactions due to the fact that they possess a large surface area that acts as a substrate on which the electron transfer reaction occurs. Initially, both reactants are adsorbed on the surface of the metal particles. Subsequently, the reductant releases two electrons to the surface of the metal particle from where MB gains two electrons[45] and is thus reduced. In the absence of the particles, the reacting species exhibit a rapid diffusion,[40] thus reducing the chances of fruitful encounters.

The rate of reduction of MB (in the concentration range of $1.0\text{–}1.2 \times 10^{-5}$ mol l^{-1}) by NH$_3$ in TX-100 micellar medium has been found to be accelerated when silver/gold nanoparticles were present in the system (Scheme 3). These metal particles were prepared in different ways, either by photochemical reduction or by wet chemical processes. Nanoparticles, because of their inherent hydrophobic surfaces, are entrapped in the micellar core.[41] Thereby both reactants have an avenue in which to come into contact with the entrapped metal particles and thus an effective electron transfer takes place. This is another plausible way of looking at the nanoparticle catalyzed MB reduction in TX-100 micelles. Repeated kinetic rate measurements (25 °C) revealed that both the nanoparticles catalyzed the redox reaction but the extent of reaction was different: silver nanoparticles served better than gold (in terms of enhancing the rate of reduction). Under the said experimental conditions, gold particles might be capped with the S-containing ligands.[46] Presumably, because of the presence of the sulfur heteroatom in the MB skeleton, gold particle surfaces are reserved for preferential dye adsorption. This might be viewed as poisoning of the gold surface due to a soft-soft interaction. Under these circumstances, dye-covered Au particles did not provide a reasonable avenue for NH$_3$ adsorption onto the Au surfaces. Hence electron transfer was not observed to be as efficient in the case of gold as in the case of silver.

The rate of bleaching of MB by NH$_3$ was found to be best enhanced in the presence of Ag nanoparticles. Ag(0) presumably has a stronger affinity to bind with N-containing ligands[47] in comparison to Au(0). In the presence of MB, presumably Ag surfaces are not as easily poisoned as the gold surfaces. Moreover, the hard-hard interaction and the preference for linear coordination between Ag(0) and NH$_3$ presumably help the electron transfer. So, we studied the catalysis with silver nanoparticles prepared in different ways and observed that chemically prepared silver nanoparticles act as a better catalyst than photochemically produced ones. We also compared the results of the reduction with bulk silver (shots) metal and silver nanoparticles of different size regimes. The catalytic efficiency of the different silver particles is as follows: Ag^0 (prepared by wet chemical method[39a,b]) > Ag^0 (photochemically prepared[38b]s) > Ag^0 (bulk metal used as shot) and Ag^0 (wet



Scheme 3 Schematic representation of the reduction of MB by ammonia in TX-100 micelles catalyzed by metal nanoparticles.

chemical method $_{\text{small-sized particle}}$[39b]) > Ag^0 (wet chemical method $_{\text{large-sized particle}}$[39a]). It was found that the smaller silver nanoparticles (average diameter 7–10 nm) act more efficiently than the larger silver particles (average diameter 30–40 nm). This is due to the fact that the smaller particles have a more negative potential[48] and larger surface area that provides the sufficient and necessary condition for electron relay for the dye reduction.

Calibration graph and other statistical parameters

The analytical utility of this study was investigated using the calibration curve for variable amounts of ammonia addition. The ammonia dependent decrease in absorbance of the dye (due to the reduction of MB by NH_3) gives a quantitative measure of ammonia concentration in solution. The plot is linear in the range of $1.63–4.7 \times 10^{-4}$ mol l^{-1} (final concentration) of ammonia (due to the addition of 10–400 μL of 10^{-1} mol l^{-1} ammonia to 2 mL of reagent). The MB concentration in the solution was 1.1×10^{-5} mol l^{-1}. The absorbance values, A, are related to the concentration ammonia, C_{NH3} (mg mL^{-1}) by the equation:

$$A = -3.408 \times 10^{-4}\ C_{NH3} + 0.1148$$

with a correlation coefficient equal to 0.9913. The estimate for the standard deviation from 8 blank measurements is 19.6×10^{-4} absorbance units. The limit of detection (LOD) is 0.8427 ppm and calculated as LOD $= 3S_B/m$ where S_B is the standard deviation of the blank and m is the slope of the calibration graph.

Interference by other species

Interferences due to various cations and anions were studied in detail. Large excesses of urea, boric acid, Na_2-EDTA, EDTA, nitrate, sulfate, chloride, carbonate, iodide ion, sodium ion, potassium ion and pyridine do not interfere at all in the determination. Even a thousand times excess of NH_4Cl, NH_4NO_3, NH_4Br, NH_4OOCH_3 did not react with the micelle-bound MB while their final concentrations in solution become 9.8×10^{-1} mol l^{-1}. However, a mixture of ammonium salts along with NaOH at room temperature reduced the blue colour of the micelle-bound MB quantitatively as in the case of NH_3. This speaks for the reduction of MB by ammonia. Hydrazine, 1,1-dimethyl hydrazine, aniline, *N*,*N*-dimethyl aniline, dimethyl amine, triethyl amine and triethanol amine interfere strongly.

Effect of temperature

The decrease of spectrophotometric intensity increased with increase in temperature (15–60 °C). This is due to the fact that the rate of reaction of the micelle-bound dye (MB) with ammonia increases with increasing temperature. Therefore, it is necessary for the temperature of the solutions to be held constant. All experiments were carried out at room temperature (25 °C).

Plausible mechanism of the reaction

Effect of "salting-in" and "salting-out" agents. Water-hydrocarbon interactions are modified in the presence of additives.[49] It is widely known that large ions such as guanidinium (used as $GdmClO_4$) and molecules like urea disrupt the water structure. These compounds lead to increased solubility of organic molecules in aqueous medium; they are called "salting-in agents".[49b] Small ions (Li^+, Na^+, Cl^-, *etc.*) reduce the solubility of organic compounds in water and hence are called "salting-out agents".[49] The latter facilitate hydrophobic binding.

To further strengthen the contention that the hydrophobic effect is an important factor affecting the rate of reduction of MB by NH_3 in aqueous TX-100, the effect of "salting-in"[49b] and "salting-out"[49] agents on MB reduction by NH_3 were studied. Experimentally, it was found that, at a dye concentration of 1.1×10^{-5} mol l^{-1}, the extent of bleaching by 9.6×10^{-1} mol l^{-1} ammonia was diminished when 1.0 mol l^{-1} urea was added to an aqueous solution of TX-100. The surfactant concentration was maintained at 8.6×10^{-2} mol l^{-1}, which is above the CMC of TX-100 (2×10^{-4} mol l^{-1}). In the presence of 1.0 mol l^{-1} NaCl, however, the extent of reduction was increased. One explanation may be the "salting- out" behaviour exhibited by NaCl, so that the reactants MB and NH_3 are squeezed out of the bulk aqueous medium into the micellar pseudo phase. To check this phenomenon, a much higher concentration of MB (1.3×10^{-4} mol l^{-1}) was used, so that there is no discharge of the blue colour by 9.6×10^{-1} mol l^{-1} ammonia in a TX-100 medium. Under the same experimental conditions, on introduction of 1.0 mol l^{-1} NaCl, the blue colour of MB is seen to be discharged. This proves the importance of the "salting-out" action of NaCl in this reaction. Similar salt-induced rate enhancements of micelle-catalyzed reactions have been observed earlier.[50] However, NaCl, in the absence of a surfactant, does not show any rate acceleration, thus proving that the action of NaCl is not a mere electrolytic effect. Another important fact is that, for urea, the question of competitive binding does not arise, nevertheless a retardation in the rate of reduction is obtained. One reason may be that urea directly enters the micellar pseudo phase, thus squeezing out MB from the micellar phase to the bulk aqueous phase and consequently decreasing the interaction of the dye with ammonia (no micellar catalysis). As a result there is a decrease in the rate of reduction. This phenomenon indirectly proves that the incorporation of ammonia in the micelle is a prime condition for dye reduction. A similar observation was noted when DMMB was used as a cationic dye in the place of MB.

Evidence for the participation of ammonia and other amines in the reduction of micelle-bound MB. An acid-base indicator, phenolphthalein (PH) was introduced judiciously in the reaction medium to conclusively prove the involvement of ammonia in the reduction reaction of micelle-bound MB. Absorbance measurements on the reaction mixture TX-100 + MB + NH_3 along with PH initially showed the two usual and desired peaks, one at 555 nm (basic pink form of PH) and the other at 664 nm (oxidized form of MB). Thus the pink colour of phenolphthalein did not interfere with the blue colour of MB while bound in the micelles. On standing the reaction mixture with PH showed a simultaneous decrease in MB colour (monitored spectrophotometrically with the stepwise reduction of the peak at 664 nm) and also the consequent decrease in the peak height at 555 nm due to the PH-ammonia entity. This observation suggests the involvement of ammonia (the same ammonia that is responsible for the basic form of PH) in the MB reduction.

This phenomenon was monitored while keeping the final concentrations of the reagents fixed as follows: NH_3 (9.5×10^{-2} mol l^{-1}), MB (7.9×10^{-6} mol l^{-1}), PH (6.2×10^{-7} mol l^{-1}). At first, added ammonia (lower than the stoichiometric concentration of PH) readily converts the acidic form of PH instantaneously into its basic form (responsible for the 555 nm peak). As time passes, PH reverts to its acidic form slowly releasing NH_3. Hence a steady decrease in the 555 nm peak was observed and ultimately it vanished completely. Consequently the released ammonia plays its role in the redox reaction to bleach the micelle-bound MB. The MB peak successively decreases to a constant absorbance value when MB was kept in small excess in comparison to NH_3. Due to the presence of excess MB (with reference to ammonia concentration) the peak due to the PH-ammonia entity dies down

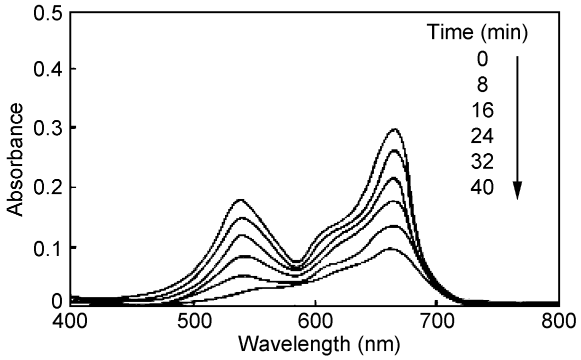


Fig. 6 Kinetics of reduction of micelle-bound MB through the stepwise release of ammonia from ammoniacal phenolphthalein (PH) solution. Conditions: final concentration of MB = 7.9×10^{-6} mol l^{-1}, PH = 6.2×10^{-7} mol l^{-1}, $NH_3 = 9.5 \times 10^{-2}$ mol l^{-1} and TX-100 = 9.5×10^{-2} mol l^{-1}.

completely and a constant absorbance value (no further decrease) at 664 nm was noticed for the remaining amount of MB (Fig. 6). At this stage introduction of a fresh batch of ammonia into the reaction mixture (containing a small excess of unreacted MB) again regenerates the basic form of PH. This interesting observation unequivocally proves the presence of the acidic form of PH, which remained intact even after releasing ammonia for the reduction of MB.

As has been mentioned above, possible and potential interferences arise from different amines. Their action as reductants has been compared with the behaviour of ammonia in micelles and follows the sequence: $Et_3N > NH_3 > (CH_2CH_2OH)_3N > Me_2NH$. Thus the p$K_b$ values of these amines explains their action as expected. The only exception arises in the case of Me_2NH, which might be due to the alteration of solvation process in micelles.

DLS study and thermodynamic parameters

The incorporation of NH_3 in the micelle can be well-understood from the dynamic light scattering (DLS) studies, which show that the micelle size increases gradually with the addition of ammonia. The size of the micelle TX-100 (10^{-1} mol l^{-1}) was 13.7 nm at 25 °C and after incorporation of 3 ml of 0.01 mol l^{-1} ammonia the size was found to be 14.4 nm; the size of the micelles then increases step-by-step with the addition of more ammonia (50 ml of 0.01 mol l^{-1}). From the above measurements it is clear that ammonia is definitely incorporated in the micelles. Thus there exists no restriction for the movement of NH_3 into the micelle and hence it can easily reduce micelle-bound MB. The reaction was found to be first-order with respect to ammonia and the activation energy was calculated to be 29.87 kJ mol^{-1} [from the reaction carried out at four different (15, 30, 45, 60 °C) temperatures].

Comparison of colour bleaching of MB with 1,9-dimethylmethylene blue (DMMB)

The importance of the immobilization of dye molecules in TX-100 micelles and then the dye reduction were tested using the bulkier dye DMMB. This dye has similar skeletal features as that of MB but two additional methyl groups make the molecule bulkier, which restricts its incorporation/immobilization into an already crowded environment as in higher TX-100 concentrations. The final concentration of both the dyes was kept very low (8.0×10^{-6} mol l^{-1}). Under these conditions the dye molecules do not perturb the micellar shape, however, their colour bleaching could be monitored easily, even at this low dye concentration. This is possible due to the high molar extinction coefficient ($\sim 1 \times 10^5$ l mol^{-1} cm^{-1}) of the dyes. The colour bleaching, that is the rate of reduction of the blue colour of MB (λ_{max} 664 nm) and DMMB (λ_{max} 658 nm) in TX-100 micelle by NH_3, was compared. As mentioned earlier, MB reduction has been observed to be fastest in 10^{-1} mol l^{-1} TX-100 surfactant. But in DMMB (final concentration 1.0×10^{-5} mol l^{-1}), the fastest reduction has been noted with 10^{-2} mol l^{-1} surfactant concentration. With the increase in surfactant concentration, the number of micelles increases and the possibility of a change in micellar shape also exists. Presumably this helps the immobilization of MB *via* increased hydrophobic interactions, whereas with DMMB, because of its bulkier structure, immobilization (penetration) becomes more difficult at higher surfactant concentrations.[41] Thus, reduction is faster with comparatively lower concentrations of surfactant in the case of DMMB than in the case of MB.

Conclusion

This paper not only describes a method for ammonia determination *via* the colour bleaching of the cationic dye MB housed in a non-ionic micellar medium but also explains the "micelle-catalyzed redox reaction". The organized assemblies, though dynamic, provide geometric control of the reaction and solubilization sites for the reactant. However, they are not only passive hosts. This study reports the catalytic effect offered by the restricted geometric and atypical environment of various organized assemblies on the well-known redox reaction of methylene blue. The importance of encounter probability has been focused on, explaining its dominating influence in the case of catalysis by micelles. Thus, micelles provide a method of organizing the reactant on a molecular scale and enhancing the rate of reaction. A delicate balance of the interacting forces (electrostatic and hydrophobic) gives rise to the optimum conditions for catalysis. In addition, nanoparticle induced catalysis has been successfully exploited in which electron relay between the reactants is exposed. The difference in the rate of reaction exhibited by silver and gold nanoparticles may provide a clue to the possible interaction in light of "Hard-Soft Acid Base" theory. Thus, this study may provide insights into many aspects of catalysis.

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References

1 W. L. Hinze, in *Solution Chemistry of Surfactants*, ed. K. L. Mittal, Plenum Press, New York, 1979, vol. 1, pp. 79–127.
2 *Ordered Media in Chemical Separations*, eds. W. L. Hinze and D. W. Armstrong, ACS Symposium Series, American Chemical Society, Washington, DC, 1987, vol. 342.
3 J. G. Dorsey, *Adv. Chromatogr.*, 1987, **27**, 167.
4 G. L. McIntire, *Crit. Rev. Anal. Chem.*, 1990, **21**, 257.
5 H. A. Mottola and D. Perez-Bendito, *Anal. Chem.*, 1992, **64**, 407.
6 D. Perez-Bendito and S. Rubio, *Trends Anal. Chem.*, 1993, **12**, 9.
7 E. Iglesias, J. R. Leis and M. E. Pena, *Langmuir*, 1994, **10**, 662.
8 E. Iglesias, *New J. Chem.*, 2002, **26**, 1352.
9 S. Kopp-Marsaudon, Ph. Leclere, F. Dubourg, R. Lazzaroni and J.-P. Aime, *Langmuir*, 2000, **16**, 8432.
10 B. F. Johnson, R. E. Malick, B. Ghearing and J. G. Dorsey, *Analyst*, 1992, **117**, 1833.
11 L. S. Romsted and D. Zanette, *J. Phys. Chem.*, 1988, **92**, 4690.
12 C. A. Bunton, L. S. Romsted and L. Sepulveda, *J. Phys. Chem.*, 1980, **84**, 2611.
13 L. S. Romsted, *J. Phys. Chem.*, 1985, **89**, 5107.

14 I. V. Berezin, K. Martinek and A. K. Yatsimirsky, *Russ. Chem. Rev. (Engl. Transl.)*, 1973, **42**, 787.

15 S. Siggia and J. G. Hanna, *Quantitative Organic Analysis via Functional Groups*, Wiley-Interscience, New York, 4th edn., 1979.

16 E. Sawicki and C. R. Sawicki, *Aldehydes Photometric Analysis*, Academic Press, London, 1975–1978, vols. 1–5.

17 L. Mazor, in *Wilson and Wilson's Comprehensive Analytical Chemistry*, ed. G. Svehla, Elsevier, Budapest, 1983, vol. 15, pp. 1–529.

18 M. Lopez-Nieves, P. D. Wentzell and S. R. Crouch, *Anal. Chem.*, 1990, **62**, 304.

19 M. Lopez-Nieves, P. D. Wentzell and S. R. Crouch, *Anal. Chim. Acta.*, 1992, **258**, 253.

20 W. P. Jencks, *Catalysis in Chemistry and Enzymology*, Dover Publications, New York, 1987.

21 C. J. Patton and S. R. Crouch, *Anal. Chem.*, 1977, **49**, 464.

22 T. T. Ngo, P. H. A. Phan and F. C. Yam, *Anal. Chem.*, 1982, **54**, 49.

23 *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC, 15th edn., 1980, pp. 351–366.

24 D. Mldgley and K. Torrance, *Analyst (London)*, 1972, **57**, 626.

25 M. J. Beckett and A. C. Wilson, *Water Res.*, 1974, **8**, 333.

26 M. E. Lopez and G. A. Rechnitz, *Anal. Chem.*, 1982, **54**, 2085.

27 P. N. Vijan and R. G. Wood, *Anal. Chem.*, 1981, **53**, 1447.

28 P. N. Vijan and R. G. Wood, *Anal. Lett.*, 1982, **15**, 699.

29 J. D. Joseph, *Anal. Chim. Acta.*, 1985, **169**, 249.

30 S. B. Brontam and M. E. Meyerhoff, *Anal. Chim. Acta.*, 1984, **162**, 363.

31 M. Berthelot, *Rep. Chim. Appl.*, 1859, **1**, 85.

32 O. S. Wolfbeis and H. Eposch, *Anal. Chim. Acta.*, 1986, **185**, 321.

33 P. Cagler and R. Narayanaswamy, *Analyst*, 1987, **112**, 1285.

34 A. Pal, T. K. Sau and T. Pal, *Indian J. Chem., Sect. A: Inorg., Bioinorg., Phys., Theor. Anal. Chem.*, 1998, **37**, 753.

35 T. Pal, A. Pal, G. H. Miller and T. Vo-Dinh, *Anal. Chim. Acta.*, 1992, **263**, 175.

36 M. Weigele, S. L. DeBernardo, J. P. Tengi and W. Leimgruber, *J. Am. Chem. Soc.*, 1972, **94**, 5927.

37 J. I. Routh, in *Fundamentals of Clinical Chemistry*, ed. N. W. Tietz, Saunders, Philadelphia, 1976, ch. 16.

38 (*a*) A. Pal, *Talanta*, 1998, **46**, 583; (*b*) S. K. Ghosh, S. Kundu and T. Pal, *Bull. Mater. Sci.*, 2002, **25**, 581.

39 (*a*) P. C. Lel and D. Meisel, *J. Phys. Chem.*, 1982, **86**, 3391; (*b*) N. Pradhan, N. R. Jana, K. Mallick and T. Pal, *J. Surf. Sci. Technol.*, 2000, **16**, 188; (*c*) G. Frens, *Nature (London)*, 1973, **241**, 20.

40 T. Pal, S. De, N. R. Jana, N. Pradhan, R. Mandal, A. Pal, A. E. Beezer and J. C. Mitchell, *Langmuir*, 1998, **14**, 4724.

41 J. H. Fendler and E. J. Fendler, *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York-San Francisco-London, 1975, pp. 43–45.

42 S. Kundu, S. K. Ghosh, M. Mandal and T. Pal, *New J. Chem.*, 2002, **26**, 1081.

43 N. Pradhan, A. Pal and T. Pal, *Langmuir*, 2001, **17**, 1800.

44 T. K. Sau, A. Pal and T. Pal, *J. Phys. Chem. B.*, 2001, **105**, 9266.

45 *CRC Handbook of Organic Analytical Reagents*, 1982, CRC Press, Inc., Boca Raton, Florida, 195.

46 N. R. Jana and T. Pal, *Langmuir*, 1999, **15**, 3458.

47 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 5th edn., 1988, p. 939.

48 P. Mulvaney, L. M. Liz-Marzan, M. Giersig and T. Ung, *J. Mater. Chem.*, 2000, **10**, 1259.

49 (*a*) A. Loupy, B. Tchouber and A. Astruc, *Chem. Rev.*, 1992, **92**, 1141; (*b*) P. A. Greico, P. Garner and Z. M. He, *Tetrahedron Lett.*, 1983, **24**, 1897.

50 C. A. Bunton, M. J. Minch, J. Hidalgo and L. Sepulveda, *J. Am. Chem. Soc.*, 1973, **95**, 3262.