

# Redox Catalytic Properties of Palladium Nanoparticles: Surfactant and Electron Donor–Acceptor Effects

Nikhil R. Jana,<sup>†</sup> Z. L. Wang,<sup>‡</sup> and Tarasankar Pal<sup>\*,§</sup>

Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India,  
Department of Chemistry, R. R. R. Mahavidyalaya, Radhanagar, Hooghly, W. B., India, and  
Georgia Institute of Technology, Materials Engineering, Atlanta, Georgia 30332-0245

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Dye reduction catalyzed by palladium nanoparticles has been investigated in water and surfactant media. The initial rate of dye reduction strongly depends on the nature of the reducing agent and dye. In most cases the rate becomes surface controlled and depends on the  $E_{1/2}$  values of the dye and the reducing agent. However, stronger reducing agents make the reduction process a diffusion controlled one. A detailed study has been carried out to understand the effect of surfactant on the reaction rate. A variation of the reaction rates has been observed in surfactants above and below the critical micelle concentration (cmc). Below the cmc, surfactants are adsorbed onto the Pd surface and act as a binding site for both the dye and the reducing agent. Above the cmc, surfactants form micelles which provide additional binding sites. Catalytic selectivity was also achieved by proper selection of reducing agent and surfactant.

## 1. Introduction

The electron-transfer step is important in many homogeneous and heterogeneous reactions.<sup>1,2</sup> In the electron-transfer step there may be a large redox potential difference between the donor and the acceptor, which may restrict the passage of an electron. An effective catalyst with an intermediate redox potential value of the donor–acceptor partner helps electron transfer and acts as an electron relay system. Metal ions or metal particles are well-known examples of this type of redox catalyst. Recent experiments suggest that when metal particles become small in size their redox properties differ from the bulk metal and their redox potential changes in the presence of adsorbed foreign ions.<sup>3,4</sup> Thus the electronic interaction between a metal particle and the substrate as well as the role of the metal particle as an electron-transfer catalyst is expected to vary with particle size; and the nature of adsorbed foreign ions is also expected to vary with particle size.

Metal particles are frequently used as a heterogeneous catalyst for hydrogenation, hydroformylation, carbonylation, etc.<sup>5–16</sup> where the importance of the electronic

contribution of the metal particles has been the subject of long-term debate. Often, the catalyst particles are stabilized in a suitable solid matrix<sup>5–9</sup> or by surface modification using polymers<sup>10,12</sup> or ligands.<sup>13,14</sup> This type of stabilization leads to the loss of catalytic activity to a great extent, but in some cases the selectivity of the catalyst increases. Solid matrixes or ligands interact strongly; the surface atoms occupy a good number of catalyst active sites with a change in the electronic properties of the catalyst. However, polymers and surfactants interact weakly with the catalyst surface although steric effects of the polymer come into play in the vicinity of the catalyst surface. In this regard, surfactants are recommended as a viable alternative for particle stabilization.<sup>11,15,16</sup> Their loosely packed but dynamic structure around the catalyst surface stabilizes the particle but hardly affects the accessibility of particles to reacting molecules.

Colloidal metal particles of platinum and gold have been used previously as model catalyst in electron-transfer reactions due to their better stability and well understood physicochemical properties.<sup>2,17–20</sup> They are very important for the mechanistic study of heterogeneous catalysis. We have studied the role of metal nanoparticles as electron-transfer catalysts,<sup>21–24</sup> and shown that the redox catalytic property of still growing and fully grown palladium particles differs. This difference is attributed to the size dependent redox properties of the metal particles and their different interactions with substrates and reagents. In this work we present the influence of electron donors and acceptors on the redox catalytic properties of palladium

\* To whom correspondence should be addressed. Email: tpal@hijli.iitkgp.ernet.in.

<sup>†</sup> Radhanagar.

<sup>‡</sup> Georgia Institute of Technology.

<sup>§</sup> Indian Institute of Technology.

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particles. In addition, the effect of surfactants is also studied in detail. Surfactants are generally used as particle stabilizers, which may sometimes play a key role in catalysis by altering the mechanism of reactions.<sup>15,21–23</sup>

Palladium particles were produced in aqueous surfactant media and their catalytic properties toward the reduction of a number of dyes in the presence of different reducing agents, viz. NaBH<sub>4</sub>, N<sub>2</sub>H<sub>4</sub>, and ascorbic acid, were studied. The dyes used were methylene blue (MB), phenosafranin (PS), fluorescein (F), 2,7-dichlorofluorescein (DCF), eosin (E), and rose bengal (RB). The selection of these dyes is based on the following three factors. First, the reductions of all the dyes are thermodynamically favorable but not kinetically. Second, these dyes have different colors in their oxidized and reduced forms. Finally, the  $E_{1/2}$  value of the dyes varies over a wide range of potentials that facilitates the study of the catalytic activity of palladium nanoparticles for a wide range of  $E_{1/2}$  values of the electron acceptor dyes.

## 2. Experimental Section

**2.1. Reagents and Apparatus.** Palladium nanoparticles were produced by the solution reduction of PdCl<sub>2</sub> (BDH) by NaBH<sub>4</sub>/ascorbic acid. Surfactants used for particle stabilization were cetyltrimethylammonium bromide (CTAB), polyoxyethylene isooctyl phenyl ether (TX-100), and sodium dodecyl sulfate (SDS), purchased from Aldrich, USA. Dyes used were from Fluka, S.D. Fine, or Sigma. Dye solutions ( $\sim 10^{-2}$  mol dm<sup>-3</sup>) were prepared in distilled water. The NaBH<sub>4</sub> ( $10^{-2}$  mol dm<sup>-3</sup>) solution was prepared in ice-cold distilled water. A buffer solution of pH 9.5 was prepared by mixing 0.02 mol dm<sup>-3</sup> NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> solutions. Hydrazine acts as self-buffering agent at pH 6.2. The pH of the solution was measured using a pH meter. All other reagents used were of AR/GR grade and distilled water was used for all purposes.

UV-visible spectra were measured in Shimadzu UV-160 digital spectrophotometer (Kyoto, Japan) with 1 cm quartz cuvettes. Transmission electron microscopic (TEM) study of the particles were carried out at 200 kV using a Hitachi HF-2000 TEM equipped with a field emission source. An energy-dispersive X-ray spectrometer (EDS) attached to the Hitachi HF-2000 TEM was used to determine the chemical composition of the sample. TEM specimens were prepared by placing microdrops of colloid solutions on a carbon film supported by a copper grid.

**2.2. Procedure.** Small metallic particles of palladium were prepared by earlier methods<sup>24</sup> from different aliquots of PdCl<sub>2</sub> solution in buffer solution with reducing agents such as NaBH<sub>4</sub>, ascorbic acid, or N<sub>2</sub>H<sub>4</sub> at room temperature. The generation of Pd metal particles was monitored following the increase and decrease in absorbance values at  $\sim 400$  and 250 nm respectively. PdCl<sub>2</sub> in water has a  $\lambda_{\max}$  at  $\sim 250$  nm which vanished completely after the reduction; and Pd particles showed an absorption profile in the 300–500 nm range. Details are given elsewhere.<sup>24</sup> These solutions were used for TEM study. For catalytic studies, surfactant solutions were mixed with the already produced Pd particle dispersions. The presence of surfactant during the formation of metal nanoparticle influence the particle size and shape.<sup>10,15,16</sup> Hence surfactants were added after the formation of Pd particles.

In a typical experiment 0.03 mL ( $2 \times 10^{-3}$  mol dm<sup>-3</sup>) PdCl<sub>2</sub> solution was mixed with 2.8 mL buffer solution and purged with N<sub>2</sub> gas for 5–6 min, to remove all dissolved oxygen. Then 0.15 mL (0.1 mol dm<sup>-3</sup>) freshly prepared reducing agent solution was added to it. Pd particles appeared in the solution in about 1–5 min depending on the reducing agent. To the Pd containing solution 0.05 mL (0.1 mol dm<sup>-3</sup>) surfactant solution and 0.015 mL ( $10^{-2}$  mol dm<sup>-3</sup>) dye were successively added to the aqueous Pd nanoparticle reducing agent solution. Both the surfactant and dye solutions were purged using nitrogen to remove all dissolved oxygen. The progress of the reaction was followed using a spectrophotometer.

**Table 1. Initial Rates (mol dm<sup>-3</sup> sec<sup>-1</sup>)  $\times 10^{-7}$  of Catalytic Reduction of Dyes in the Presence of Different Reducing Agents at 25 °C<sup>a</sup>**

dye	reducing agents		
	NaBH <sub>4</sub> (-1.33V)	N <sub>2</sub> H <sub>4</sub> (-0.23 V in acid & -1.16 V in alkali)	Ascorbate ion (+0.13 V at pH 9)
MB (662 nm, -0.21V)	3750 <sup>b</sup>	3.1 and 9.6 (at pH 6.2)	0.08 <sup>d</sup>
PS (525 nm, -0.22V)	2140 <sup>b</sup>	0.8 and 0.2 (at pH 6.2)	—
F (490 nm, -0.28V <sup>c</sup> )	3	—	—
DCF (500 nm, -0.10V <sup>c</sup> )	10	—	—
E (515 nm, -0.53V)	196 <sup>b</sup>	—	—
RB (549 nm, -0.48V)	180 <sup>b</sup>	—	—

<sup>a</sup> Conditions: [PdCl<sub>2</sub>] =  $0.86 \times 10^{-5}$  mol dm<sup>-3</sup>, [NaBH<sub>4</sub>] = [N<sub>2</sub>H<sub>4</sub>] = [Ascorbate] =  $5 \times 10^{-3}$  mol dm<sup>-3</sup>, [Dye] =  $5 \times 10^{-5}$  mol dm<sup>-3</sup> and pH 9.5 wherever not mentioned. Values in parentheses are  $\lambda_{\max}$  in water and  $E_{1/2}$  (versus NHE) values in acetonitrile of the dyes, respectively. <sup>b</sup> These reactions are very fast under the above conditions and so the rates were measured at the lower concentration range of the reducing agents and PdCl<sub>2</sub>. The rates were calculated under the above mentioned conditions by considering the first order dependence on borohydride and PdCl<sub>2</sub> concentrations. <sup>c</sup> Irreversible reduction. <sup>d</sup> Catalytic rate was obtained by subtracting the noncatalytic rate.

## 3. Results

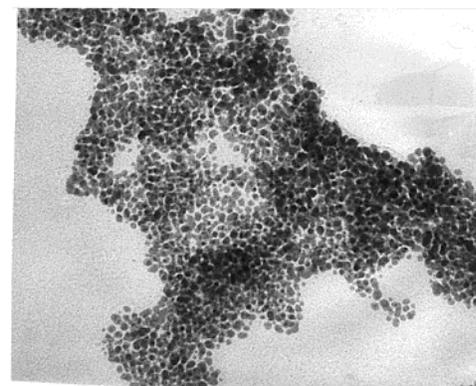
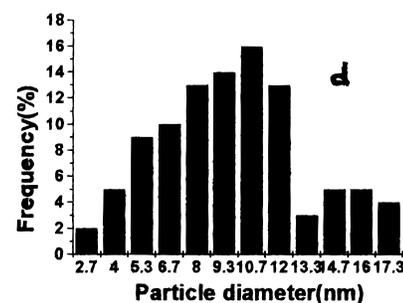
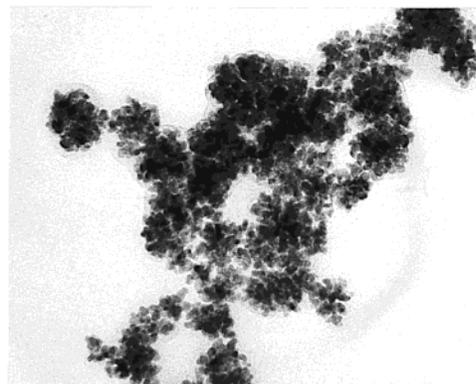
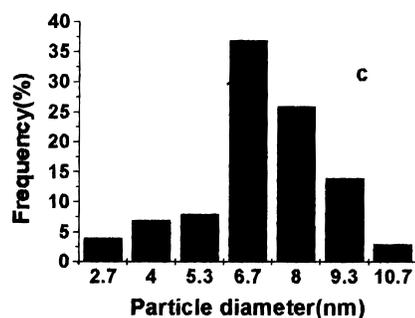
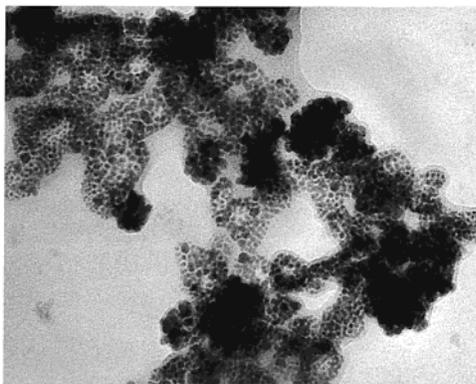
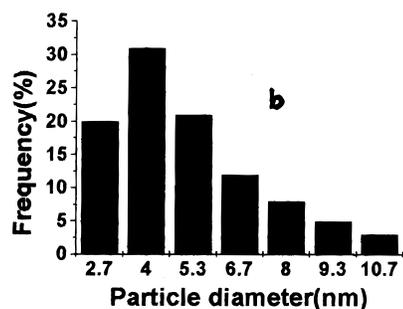
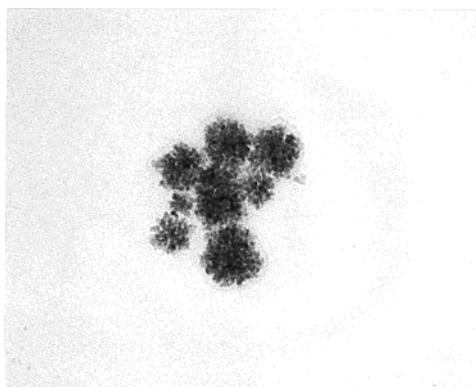
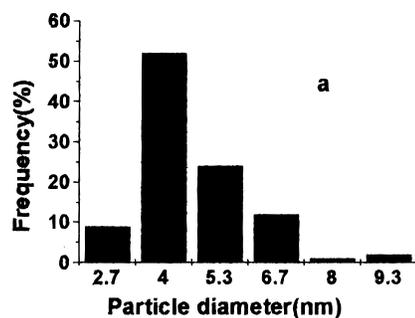
**3.1. Size Distribution of Palladium Particles.** It is well-known that the particle size distribution strongly depends on the nature of the reducing agent used.<sup>25</sup> Figure 1 shows the TEM and the size distribution histograms of Pd nanoparticles prepared by different reducing agents. The particles formed were in the range of 3–20 nm. The average sizes were 5 nm for (NaBH<sub>4</sub>) 5 and 7 nm (for N<sub>2</sub>H<sub>4</sub> at pH 9.5 and 6.2) and 10 nm (for ascorbate ion), respectively. The size distribution is broad for ascorbate but very sharp for NaBH<sub>4</sub>. With increasing reduction potential of the reducing agent, the average size of the particle increases and the size distribution becomes broad. The average size increases with decreasing pH for hydrazine. This is due to the lower reducing power of hydrazine at low pH.

**3.2. Properties of the Dyes.** Spectroscopic and redox properties of the dyes were reported earlier.<sup>21,23</sup> The  $\lambda_{\max}$  and  $E_{1/2}$  values of the dyes are given in Table 1. The reduced forms of all the dyes are colorless. Depending on the charges of the dyes, in the working condition MB and PS become cationic whereas F, DCF, E, and RB are anionic.

**3.3. Pd Nanoparticle as Redox Catalyst.** MB undergoes slow reduction in the presence of NaBH<sub>4</sub>/ascorbic acid; and micellar catalysis was also observed.<sup>22,26</sup> The reduction of other dyes becomes redundant in the absence of catalyst. Dye reduction occurs very fast in the presence of Pd metal particles and for MB the reduction rate is enhanced with PD, indicating a catalytic effect of the particles. Catalytic reduction of all the dyes occurs when NaBH<sub>4</sub> is used as the reducing agent. However, in some cases dye reduction become thermodynamically unfavorable with N<sub>2</sub>H<sub>4</sub> or ascorbic acid due to their weaker reducing power compared to NaBH<sub>4</sub>. Hydrazine being a stronger reducing agent than ascorbic acid could reduce MB and PS but ascorbic acid reduces only MB.

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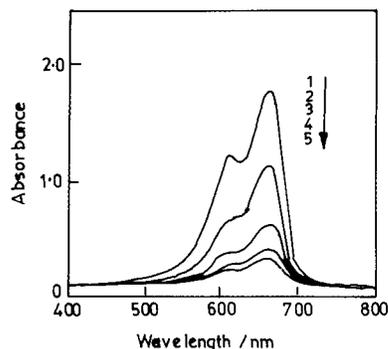


**Figure 1.** TEM image and size distribution histogram of Pd nanoparticles prepared by different reducing agents. (a)  $\text{NaBH}_4$ , (b)  $\text{N}_2\text{H}_4$  at pH 9.5, (c)  $\text{N}_2\text{H}_4$  at pH 6.2, and (d) Ascorbate. Conditions:  $[\text{PdCl}_2] = 0.86 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{NaBH}_4] = [\text{N}_2\text{H}_4] = [\text{Ascorbate}] = 5 \times 10^{-3} \text{ mol dm}^{-3}$  and pH = 9.5 where not otherwise indicated.

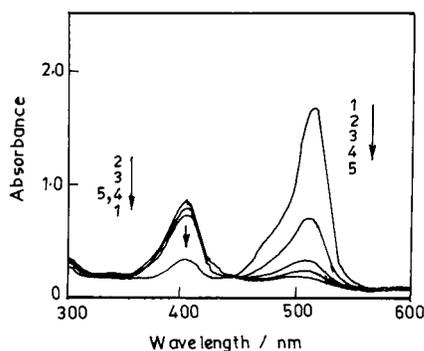
Successive UV-visible spectra of the dye reduction in the presence of Pd nanoparticles are shown in Figures 1 and 2. Pd particles have no intense plasmon band in the visible region<sup>27</sup> and do not interfere with the spectra of the dyes. The absorption bands for all the dyes vanish

gradually without showing any change in shape or position. For F, DCF, E, and RB a distinct absorption

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**Figure 2.** Successive UV-visible spectra of methylene blue (MB) in course of its Pd nanoparticle catalyzed reduction by  $\text{N}_2\text{H}_4$  in water. Successive spectra were taken after 60 s intervals. Conditions:  $[\text{PdCl}_2] = 0.86 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{N}_2\text{H}_4] = 5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{MB}] = 5 \times 10^{-5} \text{ mol dm}^{-3}$  and  $\text{pH} = 9.5$ .



**Figure 3.** Successive UV-visible spectra of eosin (E) during its Pd nanoparticle catalyzed reduction by  $\text{NaBH}_4$  in water. Successive spectra were taken after 30 s intervals. Conditions:  $[\text{PdCl}_2] = 0.43 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{NaBH}_4] = 5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{E}] = 2 \times 10^{-5} \text{ mol dm}^{-3}$  and  $\text{pH} = 9.5$ .

band for the intermediate semiquinone product<sup>28</sup> having  $\lambda_{\text{max}} \approx 400 \text{ nm}$ , was observed during the course of reduction (Figure 3). The progress of the catalytic dye reduction was followed from the time dependent decrease in absorbance value at the dye  $\lambda_{\text{max}}$ . Initial rates of reduction were obtained from the slopes of the absorbance-time plots at  $t = 0$ . As the rate of the uncatalyzed reduction is practically insignificant under the chosen conditions (except for the MB-ascorbate system), the initial rates measured in this way are due to catalysis. The initial rates of catalyzed dye reduction by different reducing agents are given in Table 1.

**3.4. Influence of Reducing Agents and Dye.** When all other conditions remain unchanged, the rate of dye reduction depends on the nature of the reducing agent. The catalytic reduction rate of MB/PS in the presence of  $\text{NaBH}_4$  is  $10^3$  times faster compared to  $\text{N}_2\text{H}_4$ /ascorbate system. Since the rate depends on the solution pH, we have studied the reduction in buffer solutions having a pH of 9.5. In this pH condition  $\text{BH}_4^-$ ,  $\text{N}_2\text{H}_4$ , and ascorbate anion will be the active reductants. We have also measured the rate of dye- $\text{N}_2\text{H}_4$  system at pH 6.2 where  $\text{N}_2\text{H}_5^+$  is the active reductant.<sup>29</sup> The reduction rate for MB and PS with borohydride increases with stirring, indicating a mass-transport controlled rate.<sup>2</sup>

**3.5. Influence of Surfactant on Catalysis.** The initial rates of catalyzed reduction of dyes were measured in the presence of a cationic surfactant, CTAB, an anionic

surfactant, SDS, and a nonionic surfactant, TX-100. The surfactant concentration was maintained below and above the cmc. The rate of Pd catalyzed reduction strongly depends on the nature and concentration of the surfactant stabilizer.

Detailed kinetic study of the influence of surfactant was done for a cationic dye (MB) and an anionic dye (F) (Figure 4). In TX-100 or SDS, media reduction rates were comparable for the F- $\text{NaBH}_4$  system but increases sharply with [CTAB] below cmc. Above the cmc the reduction rate gradually decreases. In the case of the MB- $\text{NaBH}_4$  system, the rate decreases sharply when the surfactant concentration increases well below the cmc of the surfactant. This is true for all the three surfactants. As the [CTAB]/[TX-100] ratio increases, the rate decreases to a minimum and then increases sharply near and above the cmc. However, for SDS there is a further decrease before its cmc without showing a minimum rate.

In the case of the MB- $\text{N}_2\text{H}_4$  system, the rate increases sharply with increasing [TX-100] far below its cmc and then remains almost unaltered. In the presence of CTAB, the rate decreases first and it does not increase further in the case of pH 6.2 but for pH 9.5 the rate increases again only above the rate value typical of the cmc. In SDS, the rate has two maxima and one minimum at pH 6.2 and one maximum at pH 9.5 and all these occur below the cmc. For the MB-ascorbate system, the rate decreases with increasing [TX-100]/[SDS]. But it increases for [CTAB].

**3.6. Catalyst Selectivity.** Borohydride reduction of the cationic dyes MB and PS in the presence of Pd nanoparticles is faster than for other dyes (Table 1). This fact has been used in determining the kinetic selectivity. Catalytic reduction of a dye mixture having one cationic dye and one anionic dye was carried out using  $\text{NaBH}_4$ . The cationic dye was reduced first followed by reduction of the anionic dye (Figure 5). Mixtures of cationic or anionic dyes do not indicate such selectivity. However, the use of surfactant may improve reduction selectivity. The catalytic reduction of a mixture of RB and DCF overlaps with each other (Figure 6a). The overlap becomes more prominent in  $5 \times 10^{-4} \text{ mol dm}^{-3}$  CTAB (Figure 6b) but RB is reduced almost selectively in  $5 \times 10^{-4} \text{ mol dm}^{-3}$  (Figure 6c).

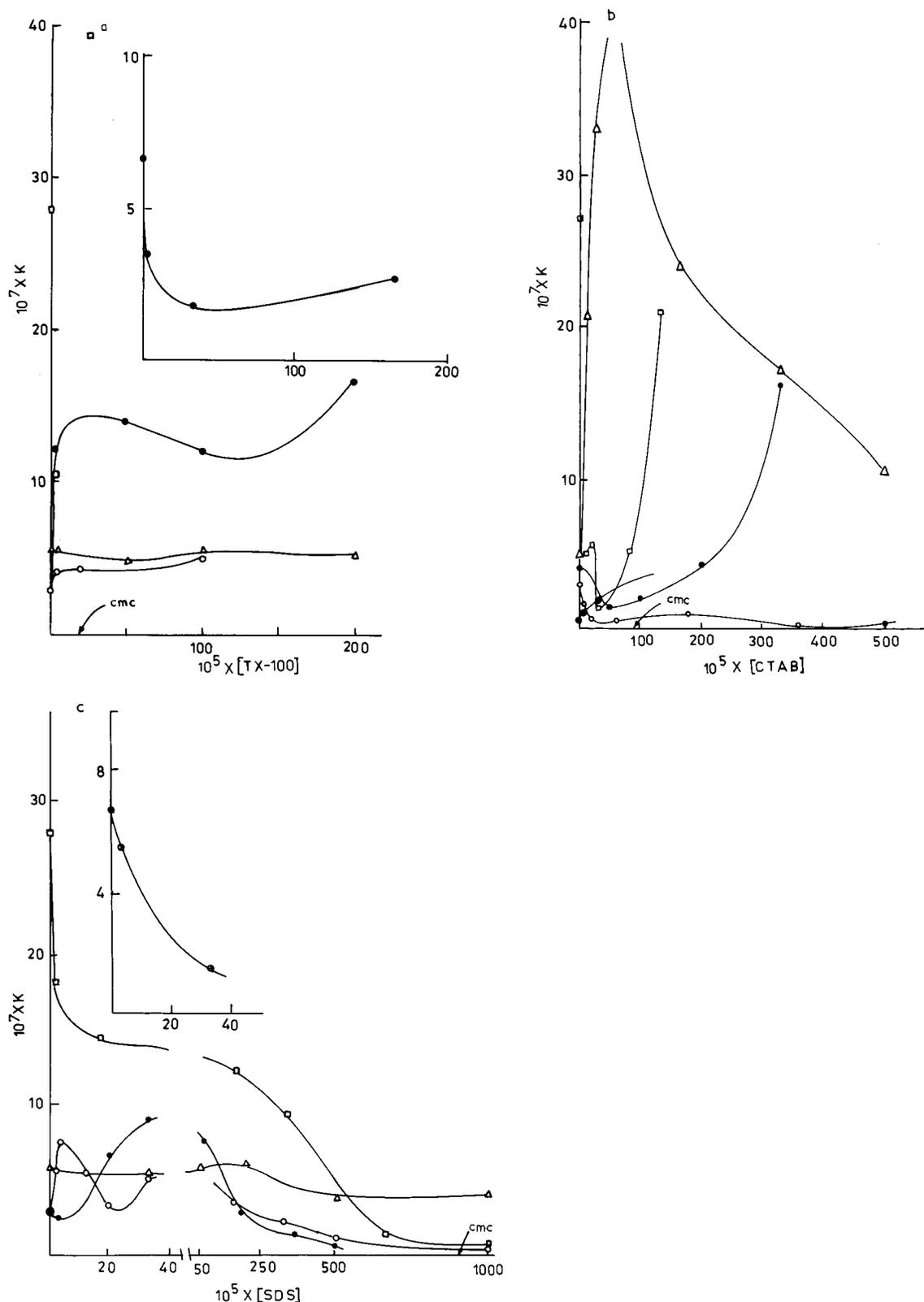
## 4. Discussion

**4.1. Mechanism of Catalysis and Role of Electron Donor-Acceptor.** The catalyzed redox reaction of small metal particles proceeds through an electrochemical mechanism where electron transfer occurs via the metal particles.<sup>2,17-20</sup> The electrochemical potential of the particles should be intermediate between the electron donor and acceptor. The reduction potential of the  $\text{Pd}^{\text{II}}/\text{Pd}_{\text{metal}}$  (aqueous) system is +0.987 V (Vs NHE) which becomes lower for  $\text{Pd}^{\text{II}}/\text{Pd}_{\text{nanoparticle}}$  system and depends on particle size and the nature of the adsorbed ions at the particle surface.<sup>30</sup> The average particle sizes (5–10 nm) do not change appreciably among the different preparations so this would not influence the particle potential to a significant extent. However, the small palladium particles have a large surface-to-volume ratio compared to bulk metal. As a result, adsorption of large number of foreign ions onto the nanoparticles surface is possible.<sup>2-4,13-24</sup> In the reaction mixture both dye and reducing agent are adsorbed at the particle surface and a resultant potential is adopted by the particle. The adsorption equilibrium of reducing agent and dye depends on their concentration, hydrophobic character, chemical interaction, etc.

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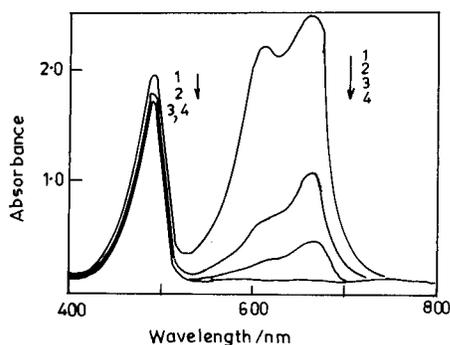
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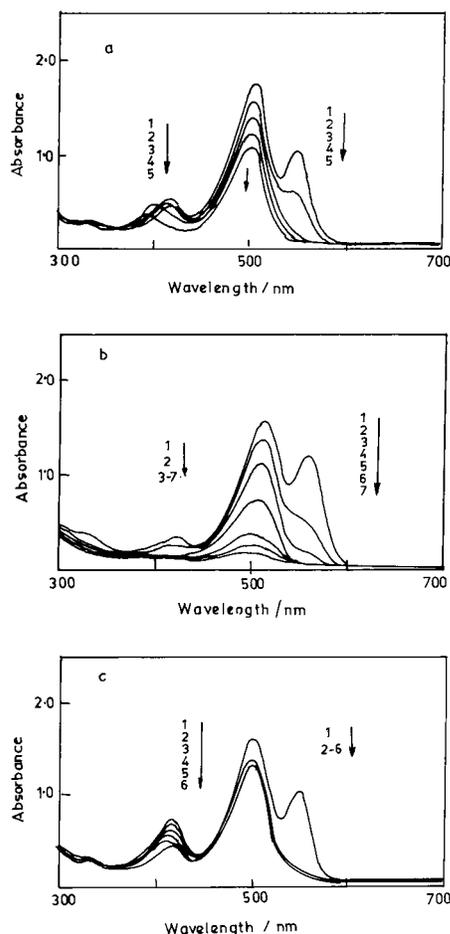
**Figure 4.** Plot of initial rates ( $\text{mol dm}^{-3} \text{sec}^{-1}$ ) against surfactant concentration. (a) in TX-100, (b) in CTAB, and (c) in SDS.  $\otimes$  for the MB-ascorbate system having  $[\text{PdCl}_2] = 1.43 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{ascorbate}] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{MB}] = 3.3 \times 10^{-5} \text{ mol dm}^{-3}$ , and  $\text{pH} = 9.5$ .  $\circ$  for the MB- $\text{N}_2\text{H}_4$  system having  $[\text{PdCl}_2] = 0.86 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{N}_2\text{H}_4] = 5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{MB}] = 5 \times 10^{-5} \text{ mol dm}^{-3}$ , and  $\text{pH} = 6.2$ .  $\bullet$  for the MB- $\text{N}_2\text{H}_4$  system having  $[\text{PdCl}_2] = 0.86 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{N}_2\text{H}_4] = 1.67 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{MB}] = 5 \times 10^{-5} \text{ mol dm}^{-3}$ , and  $\text{pH} = 9.5$ .  $\square$  for the MB- $\text{NaBH}_4$  system having  $[\text{PdCl}_2] = 2.85 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{NaBH}_4] = 5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{F}] = 3.3 \times 10^{-5} \text{ mol dm}^{-3}$ , and  $\text{pH} = 9.5$ .  $\triangle$  for the F- $\text{NaBH}_4$  system having  $[\text{PdCl}_2] = 1.71 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{NaBH}_4] = 5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{F}] = 5 \times 10^{-5} \text{ mol dm}^{-3}$ , and  $\text{pH} = 9.5$ .

The catalytic reduction rate should be surface and/or diffusion controlled. Most reaction rates are independent of stirring, indicating that they are surface controlled.<sup>2</sup>

Borohydride reduction of MB and PS are partly diffusion controlled at least as their rate increases on stirring. The rate of surface controlled reactions are determined by the



**Figure 5.** Successive UV-visible spectra of a mixture of methylene blue (MB) and fluorescein (F) during their Pd nanoparticle catalyzed reduction in water. Successive spectra were taken after 30 s intervals. Conditions:  $[\text{PdCl}_2] = 2.85 \times 10^{-6} \text{ mol dm}^{-3}$ ,  $[\text{NaBH}_4] = 1.67 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{MB}] = 1.43 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{F}] = 2.4 \times 10^{-5} \text{ mol dm}^{-3}$ , and  $\text{pH} = 9.5$ .



**Figure 6.** Successive UV-visible spectra of mixture of rose bengal (RB) and 2,7-dichlorofluorescein (DCF) during their Pd nanoparticle catalyzed reduction in water (a) in  $5 \times 10^{-4} \text{ mol dm}^{-3}$  CTAB (b), and in  $5 \times 10^{-4} \text{ mol dm}^{-3}$  SDS (c). Successive spectra were taken after 60 s intervals. Conditions:  $[\text{PdCl}_2] = 2.85 \times 10^{-6} \text{ mol dm}^{-3}$ ,  $[\text{NaBH}_4] = 1.67 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{DCF}] = 3.6 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{RB}] = 2.1 \times 10^{-5} \text{ mol dm}^{-3}$ , and  $\text{pH} = 9.5$ .

difference in resultant potential of the Pd nanoparticles and the potential of the dye.<sup>2</sup> The higher the differences, the higher would be the rate. Rates of MB and PS reduction decreased by  $10^3$  fold when  $\text{BH}_4^-$  is replaced by  $\text{N}_2\text{H}_4/\text{ascorbate}$  ions. Their borohydride reductions are strongly catalyzed compared to the other dyes, leading to diffusion controlled rates. This can be explained by considering the adsorption of more diffusing  $\text{BH}_4^-$  ions (compared to  $\text{N}_2\text{H}_4/\text{ascorbate}$

ions) onto the surface of the Pd nanoparticles resulting in a more negative reduction potential value making it a stronger reductant. The resultant particle potential can be correlated from the comparative electron injection capabilities of these reducing agents, which can be assessed from their standard reduction potential values (Table 1).

At this stage any correlation between the reduction potential of the dye and the rate is difficult to predict. Although the reduction potentials of MB, PS, F, and DCF are almost comparable, borohydride reduction rates become faster for MB and PS. Probably, the nature of the dyes (i.e., charge, hydrophobicity, presence of S/N donor atom, etc.) is also an important feature.<sup>24</sup> The nature of the dye determines its adsorption equilibrium with the catalyst surface and thus controls the effective concentration of the dye at the catalyst surface. Of the four anionic dyes, F and DCF have a higher reduction potential than E and RB. Still, borohydride reduction rates are higher for E and RB. Here, increased hydrophobicity of E and RB, due to the presence of Br and I in their skeleton, may be a plausible reason.

**4.2. Role of Surfactant.** In many cases the catalyzed dye reduction stops after some time in the absence of surfactant. This is due to the deactivation or poisoning of the catalyst surface through adsorption of the dye. In the presence of surfactant, the static adsorption of dye onto the catalyst surface is inhibited due to the predominant and dynamic adsorption of surfactant. This type of adsorption of surfactants on the surface of bulk metal and nanoparticle is well documented in the literature.<sup>15,16,21,31</sup> Above the cmc surfactants form micelles which can interact with dye molecules preventing static adsorption of the dye on the catalyst surface. Thus deactivation of catalyst becomes inhibited in the presence of a surfactant.

Below the cmc, surfactants form a monolayer, bilayer, etc. on the surface of the Pd particles depending upon the concentration of surfactant.<sup>31</sup> Organized assemblies of surfactants act as a catalyst in a way that is distinctly different from micellar catalysis.<sup>32</sup> In this case the surfactant layer acts as a binding site for the dye/reducing agent. As a result, reactants are concentrated onto the catalyst surface, leading to rate enhancement. The extent of binding depends on the hydrophobic character and charge of the reactants and surfactant, which has recently been explained by Pal et al.<sup>22</sup> When a nonionic surfactant is used, only hydrophobic effects are important; while for charged surfactant both the hydrophobic and electrostatic factors play equally important roles.

Nonionic surfactants sometimes decrease the rate only below the cmc. The reasons for the decrease are competitive adsorption of surfactant and substrates, and hindered electron transfer due to the presence of surfactant layers.

When both dye and reducing agent are of similar charges, the reduction rates increase sharply upon the addition of a small amount of oppositely charged surfactant. The monolayer of the surfactant formed on the particle surface attracts dyes and reducing agent from the bulk by both hydrophobic and electrostatic interactions. The observed oscillation of rates with increased surfactant concentration is probably due to the formation of surfactant multilayers. When the surfactants have a similar charge to that of the dye and the reducing agent, the electrostatic repulsion may predominate over the hydrophobic interaction and this causes a decrease in rate.

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When the dye and the reducing agent are oppositely charged, the charged surfactant layer can attract one of them but repel the other, and the rate will be the resultant of the two effects.

The decrease in rate above the cmc is due to the competitive binding of dye and reducing agent between the micellar surface<sup>33,34</sup> and the catalyst surface. Sometimes the rate increases as in the case of MB–NaBH<sub>4</sub> and MB–N<sub>2</sub>H<sub>4</sub> (pH 9.5) systems in CTAB, where a rate decrease is observed below the cmc. In this case a reverse mechanism probably operates between the surfactant and substrates in the presence of micelle.

**4.3. Origin of Catalytic Selectivity.** The present investigation shows that the nature of the electron donor and acceptor influences the rate through electrochemical properties and the preferential adsorption property at the catalyst surface. With this information it is possible to obtain a kinetic selectivity. The borohydride reduction of MB occurs almost selectively in the presence of F, because of the faster rate of reduction of MB than that of F (Figure 5). The choice of a proper surfactant further enhances the catalytic selectivity of borohydride reduction (Figure 6). RB is reduced almost selectively in the presence of DCF in aqueous SDS medium (below the cmc) although both

reductions occur simultaneously in water/CTAB. This is due to the different interaction of the two dyes (due to the presence of different halogen atoms in their structure) with the SDS layer at the Pd surface.

## 5. Conclusion

Small palladium particles act as electron transfer catalysts. Catalytic rates depend on the  $E_{1/2}$  of both the dye and the reducing agent. The presence of surfactant can alter the rate. However, the charge of the surfactant headgroup and the substrates also influences the catalytic property of Pd nanoparticles. The judicious selection of a surfactant may result in an enhanced or suppressed catalytic efficiency/selectivity for a given reaction. This report also indicates that the choice of a proper nucleophilic reducing agent for a particular metal could give a unique catalytic selectivity. It should be mentioned that the redox potential difference between the oxidant and reductant might not be the only factor, which contributes to the observed reaction rate. The chemical interaction, proximity, favorable orientation of the reactants relative to the catalytic surface, microscopic environment surrounding the reacting molecules, etc. might have a bearing on the chemical reactivity.

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