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Metal tetrasulfophthalocyanines catalysed co-oxidation of phenol with 4-aminoantipyrine using hydrogen peroxide as oxidant in aqueous microheterogeneous system

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Abstract

Co-oxidation reaction of hydrogen peroxide with phenol, 4-aminoantipyrine catalysed by metal tetrasulfophthalocyanines (MPcTs) has been studied by UV–vis spectroscopy in the presence and absence of microheterogeneous media. The rate of antipyrilquinoneimine dye formation depends on the nature of metal ion, pH, and microheterogeneous medium. Hence, the activation of hydrogen peroxide is in the following order: MnPcTs > FePcTs > ZnPcTs > CuPcTs > NiPcTs. In basic pH, the rate of dye formation is greater than the acidic pH and maximum rate is observed at pH 9.0. The role of microheterogeneous medium on the activation of MPcTs complexes towards higher rate value is found to be increasing the stability of metaloxo cationic radical and free radical species of 4-aminoantipyrine and phenol in the following order: SDS > TX-100 > CTAB. The enzyme mimic models also quantitatively sense the H_2O_2 compositional variations.

Keywords: Phthalocyanine complex; Phenol; Microheterogeneous medium; Co-oxidation; Antipyrilquinoneimine

1. Introduction

Applications of transition metal ion as a catalyst for oxidation of organic substrates in basic aqueous medium face major limitations like precipitation of catalytically active metals and competitive substrate coordination to active metal center, etc. [1,2]. Regarding the nature of oxidants from the environmental concern, the replacement of toxic oxidants with hydrogen peroxide in aqueous medium forms the primary goal due to the low cost and water being the by product [3–5]. Co-oxidation reactions of hydrogen peroxide with chromogenic hydrogen donor in the presence of peroxidases are widely used in the analysis of biological samples [6,7]. However, the instability and high cost of the peroxidase enzyme has stimulated people to search for suitable alternatives [8]. In peroxidase enzyme the prosthetic centre is constituted by metalloporphyrin [9,10], and synthetic metallo derivatives of porphyrins, have been demonstrated to be catalysts for oxidation reactions using hydrogen peroxide [11–14]. Incidentally such reactions act as models of enzymatic oxidation by peroxidases [10]. In many instances metalloporphyrin catalysed hydrogen peroxide decompositions have been coupled with organic substrates that require one pot oxidation producing single product [15,16].

For this purpose, oxidative coupling reactions of phenolic compounds in the presence of hydrogen peroxide have been widely used with 4-aminoantipyrine ($AmNH_2$) [15,17]. In the same oxidation states, the central metal phthalocyanines are expected to be efficient oxidants than their porphyrin counterparts. Hence, phthalocyanine ligands tend to stabilize lower oxidation states of the metal ions compared to porphyrins [18]. This property has been utilised in reactions involving hypervalent central metal ion of metal tetrasulfophthalocyanine (MPcTs) for oxidation catalysts enabling easier conversion to lower oxidation states.

The present investigation has been under-taken to develop a precise quantitative detection of lower amounts of H_2O_2 in basic aqueous medium, which mimics enzyme like reactions and find utility in the oxidative removal of phenol (PhOH) containing pollutants in wastewaters of cellulose, oil-processing and dye-fine chemical manufacturing industries. The

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co-oxidation reactions of PhOH and $AmNH_2$ with H_2O_2 produce a antipyrilquinoneimine dye with the characteristic absorption at $\lambda_{max} = 505$ nm which is catalysed by metalloporphyrin [18]. Thus, in par with metalloporphyrins, which are treated as enzyme mimics, metallophthalocyanines could serve as enzyme mimic models possessing enhanced water solubility and catalytic activity. UV–vis spectrophotometry is a popular and easy tool for the kinetic study of the evaluation of rate and rate constants of such reactions in aqueous medium. Inspired by these, effects of oxidant, pH, metal ion substitutions in catalyst, various microheterogeneous medium are under taken in this work. To assess the performance of the catalyst, various MPcTs containing Mn(III), Fe(III), Ni(II), Cu(II) and Zn(II) as central metal ions are examined. The dye was characterised using FT-IR spectra.

2. Experimental

2.1. Materials

H_2O_2 (30% wt./vol.) was used after iodometric titration to verify its concentration [19]. Phenol (Merck) was used after distillation in an inert atmosphere. 4-Aminoantipyrine was used as received from Aldrich. KNO_3 for supporting electrolyte in cyclic voltammetry, acetic acid–sodium acetate, disodium hydrogen phosphate–monosodium hydrogen phosphate and sodium carbonate–sodium bicarbonate as pH buffers were of analytical grade and purchased from Fluka. Sodiumdodecyl sulfate (SDS), Triton X100 (TX-100) and cetyltrimethylammoniumbromide (CTAB) were purchased from Sigma. Triply distilled water was used for solution preparations. Metal tetrasulfophthalocyanines as dihydrates were synthesized from sodium salt of 4-sulfophthalic acid, ammonium chloride, urea, ammonium molybdate and metal (II) sulfate according to the procedure described by Weber and Busch [20]. MPcTs containing Mn(II), Fe(III), Co(II) and Ni(II) metal ions are also prepared according to this procedure and the yields were found to be slightly lower. The starting chemicals were the sulfate salts of metals [21,22]. The initial product was treated successively with NaCl, 0.1N NaOH, and 80% aqueous ethanol in the prescribed manner. Pure catalyst was obtained by extracting the solid with absolute ethanol for 4 h in a Soxhlet apparatus. The blue crystalline complex was then dried in vacuo over P_2O_5 prior to analysis. The structure of the complexes were characterised by UV–vis and FT-IR spectra. The MnPcTs and FePcTs system exists in +3 oxidation state, which is confirmed from UV–vis, and FT-IR techniques with published data [23,24].

2.2. Cyclic voltammetry

Cyclic voltammogramms were obtained from a CHI model 600 voltammetric analyser using a disk type glassy carbon working electrode (2 mm diameter) and platinum wire as the counter electrode. The supporting electrolyte is KNO_3 in aqueous medium. The reference electrode was Ag/AgCl wire dipped in 0.01 M $AgNO_3$ in aqueous solvent. GCE was polished with alumina, soaking in dilute nitric acid and rinsed repeatedly in triple distilled water.

2.3. Kinetic measurements

UV–vis spectra were recorded on Shimadzu UV-1601 spectrometer containing double beam in identical compartments each for reference and test solution fitted with 1 cm path length quartz cuvettes. pH measurements were done with an Elico-India digital pH meter. Preparation of H_2O_2 (0.2 M) stock solutions were made by adding 10 ml of 30% H_2O_2 to 490 ml of purified water. Subsequent dilutions were made from this stock solution. All kinetic data were obtained with fresh solutions only. The initiation of the reaction was considered as the time of addition of H_2O_2 into the reaction mixture containing PhOH, $AmNH_2$ and catalyst. In the absence of the MPcTs catalyst, when the reaction was studied only with PhOH, $AmNH_2$ and H_2O_2 reactants under all compositions, there was no dye formation, which will be indicated by the appearance of pink color, even after the reaction 24 h of reaction time. However, when the MPcTs was included light pink coloration was developed immediately. Increasing absorbance values at 505 nm indicates the dye formation and the difference in the absorbance of spectrum recorded at various time intervals indicate the progress of the reaction. The kinetic parameters log S where $S = (OD_\infty/OD_\infty - OD_t)$ are calculated from absorbance values versus time measurements.

In order to optimise the reaction conditions the maximum rate for different stoichiometric mole ratio of H_2O_2 and the MPcTs catalysts were also investigated. Here 1:1 mole ratio of H_2O_2 and MPcTs produced the maximum rate. Thus, effects of PhOH, $AmNH_2$, pH and microheterogeneous media are carried out at constant composition of H_2O_2 and catalyst.

3. Results and discussion

3.1. Activation of hydrogen peroxide by metal tetrasulfophthalocyanines

The inception of the dye formation only in the presence of MPcTs shows that catalyst activity of MPcTs is necessary for the activation of H_2O_2. The UV–vis spectrum of MnPcTs (1×10^{-5} M) in aqueous solution exhibits monomer/dimer equilibrium. The dimer peak corresponds to 630 nm and the monomeric peak being observed near 716 nm is shown in Fig. 1(a). On addition of H_2O_2 the blue color solution of MnPcTs complex turns to green color indicating the formation of the MnPcTs–H_2O_2 adduct. The dimeric peak of the MnPcTs system is suppressed completely while the intensity of monomeric peak increases along with longer wavelength shift as shown in Fig. 1(b). The splitting of the S band in the UV region and shifting of monomer peak at 720 nm confirms the axial coordination of hydroperoxide anion (MnPcTs-OOH). Also, a new peak appears at 620 nm, which is attributed to the formation of MnPcTs = O adduct [25]. Fig. 1(c) shows the dye formation reaction of solution containing phenol, $AmNH_2$ and MnPcTs in the presence of H_2O_2. The presence of new peak at 505 nm confirms the antipyriloquinoneiminium dye formation.

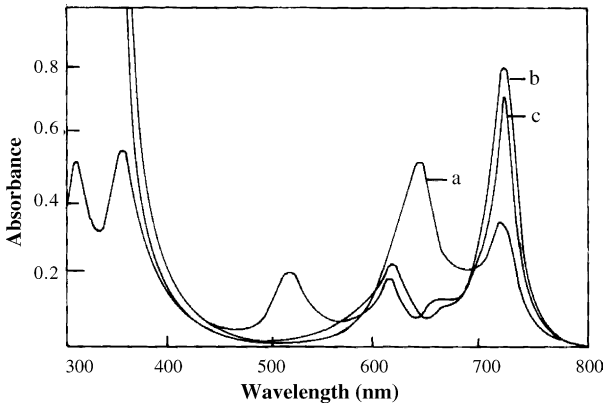


Fig. 1. Electronic absorption spectra in aqueous solution, at pH 7.0 and 25 °C, containing MnPcTs with (a) no additive (b) H_2O_2 (c) PhOH + $AmNH_2$ + H_2O_2. [MnPcTs] = 1×10^{-5} M; [H_2O_2] = 1×10^{-3} M; [PhOH] = [AmNH] = 2×10^{-3} M.

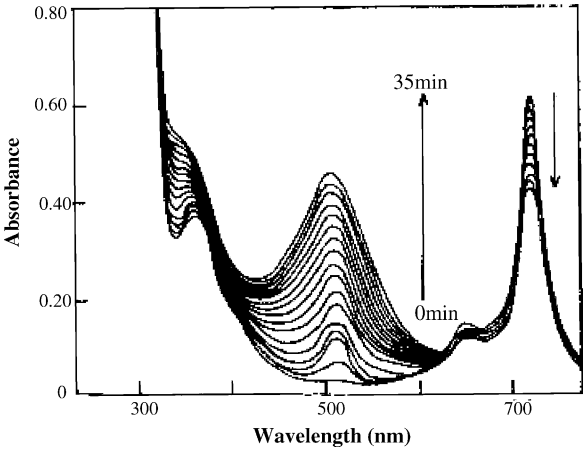


Fig. 2. Stacked UV–vis spectra of dye formation at 2 min time intervals in the aqueous solution at pH 7.0 containing [MnPcTs] = 1×10^{-5} M; [PhOH] = [$AmNH_2$] = 2×10^{-3} M and [H_2O_2] = 0.1 M at 25 °C.

The stacked UV–vis spectra of dye formation in PhOH, $AmNH_2$ and H_2O_2 solutions catalysed by MnPcTs at two minutes time intervals are shown in Fig. 2. The dye formation is inferred from the green color change to pink color which is responsible for the peak appearance at λ_{max} = 505 nm [18]. At the same time the intensity of the peak at λ_{max} = 720 nm decreases due to consumptions of the MnPcTs–H_2O_2 adduct as reaction proceeds. The kinetic plots for different MPcTs systems at constant compositions of $AmNH_2$, PhOH and H_2O_2

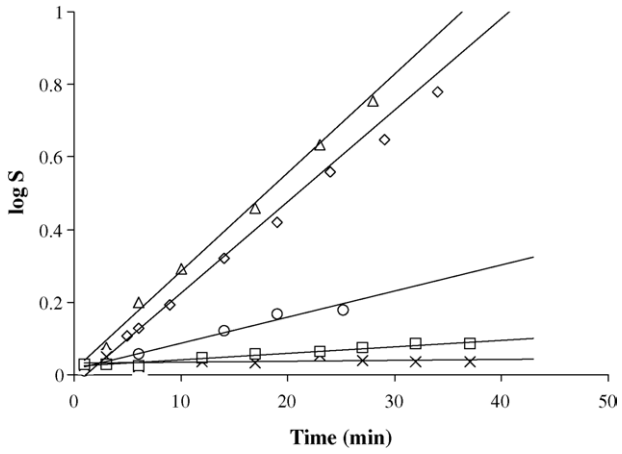


Fig. 3. Kinetic plots of dye fomation from PhOH and $AmNH_2$ in presence of different [MPcTs] = 1×10^{-5} M and [H_2O_2] = 0.1 M in neutral pH. (Δ) MnPcTs; (◊) FePcTs; (◯) ZnPcTs (□) NiPcTs; (×) CuPcTs.

in pH 7.0 are shown in Fig. 3. The overall rate constant is obtained from the plot being equal to slope/2.303. By doing so for different MPcTs systems, the results are given in Table 1. The catalytic activity of MPcTs follows the trend MnPcTs > FePcTs > ZnPcTs > CuPcTs > NiPcTs. The observed trend indicates the possibility of difference in H_2O_2 activation by various MPcTs and the stability of the resulting oxo radical formation.

3.2. Effect of hydrogen peroxide concentration

The spectra of dye formation from PhOH, $AmNH_2$ and 0.1 M H_2O_2 catalysed by MnPcTs at regular time intervals in neutral pH are shown in Fig. 4. The OD versus time plots of MnPcTs catalysed reaction at different hydrogen peroxide concentrations are presented in Fig. 5. The log *S* versus time plots derived from the OD–time dependences are shown in Fig. 6. The linear plots passing through the origin confirms that the overall reaction is first order. From the effect of H_2O_2 concentration studies, the sensitivity of the reaction for the H_2O_2 detection falls within the range (0.1–1.0 mM) when M(II)PcTs (1×10^{-5} M) is utilized as the catalyst. Scheme 1 represents the overall peroxidase mimic model reaction of $AmNH_2$ and PhOH with H_2O_2 in the presence of MPcTs yielding the antipyrilquinoneimine dye. In this reaction the μ-oxo radical species formed initially triggers the radical generation in successive steps, which may be assumed to be cascadic [26,27].

Table 1
Rate constant values of dye formation from PhOH and $AmNH_2$ catalysed by different tetrasulfometalphthalocyanine in presence of various reaction mediums at 25 °C

MPcTs	pH 9.0 $k \times 10^{+3}$ (s^{-1})	SDS $k \times 10^{+3}$ (s^{-1})	TX-100 $k \times 10^{+3}$ (s^{-1})	pH 11 $k \times 10^{+3}$ (s^{-1})	CTAB $k \times 10^{+3}$ (s^{-1})	pH 7.0 $k \times 10^{+3}$ (s^{-1})	pH 6.0 $k \times 10^{+4}$ (s^{-1})	pH 4.0 $k \times 10^{+4}$ (s^{-1})
MnPcTs	3.87	3.69	1.76	1.87	1.52	1.03	6.14	4.22
FePcTs	3.27	2.51	1.58	1.36	1.26	0.98	5.72	4.12
ZnPcTs	2.15	1.12	0.92	0.52	0.72	0.28	0.20	0.09
CuPcTs	0.91	0.50	0.40	0.34	0.05	0.03	0.02	0.01
NiPcTs	0.32	0.23	0.21	0.12	0.04	0.01	0.005	0.001

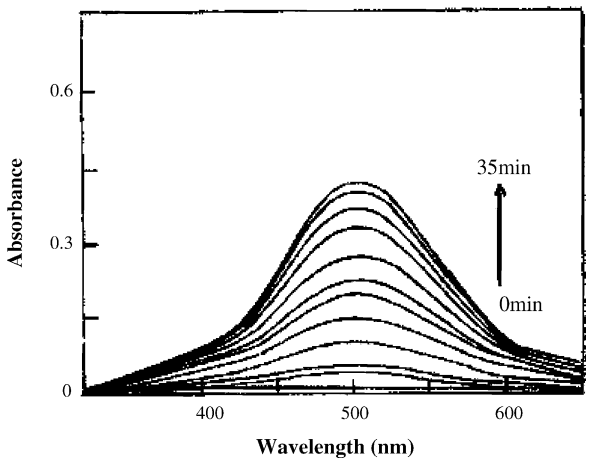


Fig. 4. Stacked visible spectra of dye formation in aqueous medium, pH 7.0 at 2 min time intervals containing [MPcTs] = 1×10^{-5} M with [PhOH] = [$AmNH_2$] = 2×10^{-3} M and [H_2O_2] = 0.1 M at 25 °C.

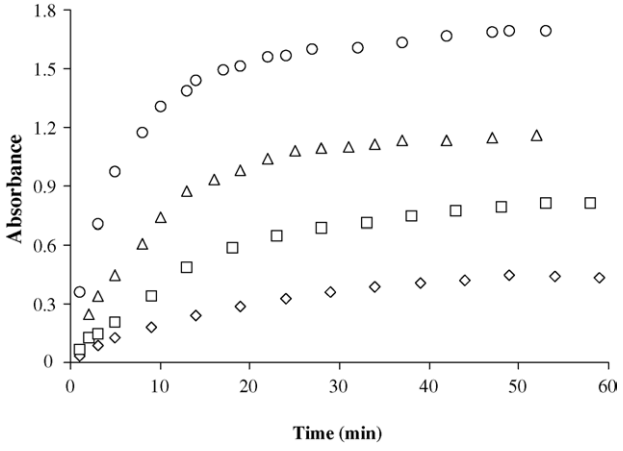


Fig. 5. Optical density–time dependence plots of dye formation in presence of MnPcTs = 1×10^{-5} M at various hydrogen peroxide concentrations, containing [PhOH] = [$AmNH_2$] = 2×10^{-3} M at pH = 7.0. [H_2O_2]M = (◯) 0.2; (Δ) 0.18; (□) 0.15; (◊) 0.1.

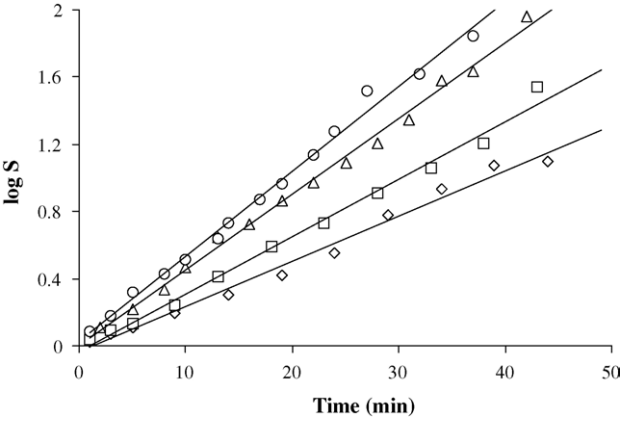
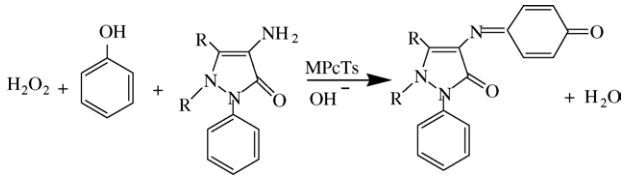


Fig. 6. Kinetic plot of dye formation from [PhOH] = [$AmNH_2$] = 0.002 M, in presence of MnPcTs = 1×10^{-5} M catalyst for various hydrogen peroxide concentration, at neutral pH. λ_{max} = 405 nm. [H_2O_2] M = (◯) 0.2; (Δ) 0.18; (□) 0.15; (◊) 0.1.



Scheme 1.

3.3. Effect of pH

In aqueous solution the dissociation constant of H_2O_2 is sensitive to pH variations. However, dependence of the rate of dye formation on the pH of the medium is studied for different MPcTs systems. The rate constant-pH profiles for corresponding reactions are shown in Fig. 7. An enzyme like catalytic behaviour of MPcTs is also detected with pH variation. In acidic pH, the observed rate constant values are low due to existence of low proportion of hydroperoxide anion. It increases significantly when pH is raised and the maximum rate constant is attained at pH 9.0 (listed in Table 1). This may be due to the pK_a value of PhOH, which falls at 9.8. In a more alkaline region, (pH > 11) the rate constant decreases remarkably due to the possibility of dimerisation of MPcTs through μ-oxo bridge. The MPcTs dimeric species are catalytically inactive because of its inability to activate H_2O_2.

3.4. Effect of microheterogeneous medium

The dimeric and other aggregated forms of MPcTs are transferred to larger proportions of monomeric forms in the presence of surfactant micelles [28]. This effect is attributed to the possibility of hydrophobic and hydrophilic interactions of MPcTs with SDS (anionic), CTAB (cationic) and TX-100 (nonionic) micelles. In the CTAB micelle system, the negatively charged sulfonated group of the phthalocyanine part of MPcTs interacts strongly with the positively charged micelles [29]. In the SDS micelles system, the central metal part of MPcTs interacts strongly via columbic forces most probably in the axial direction, which results in the monomerisation of aggregated MPcTs

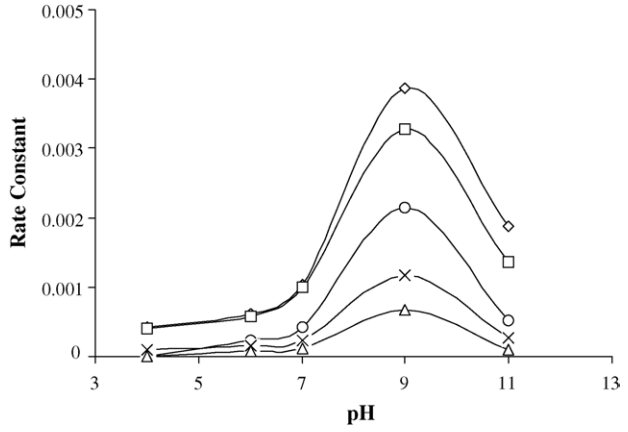


Fig. 7. Overall rate constant—pH profile of dye formation from PhOH and $AmNH_2$ in presence of different MPcTs = 1×10^{-5} M at neutral pH. (◊) MnPcTs; (□) FePcTs; (◯) ZnPcTs; (×) NiPcTs; (Δ) CuPcTs.

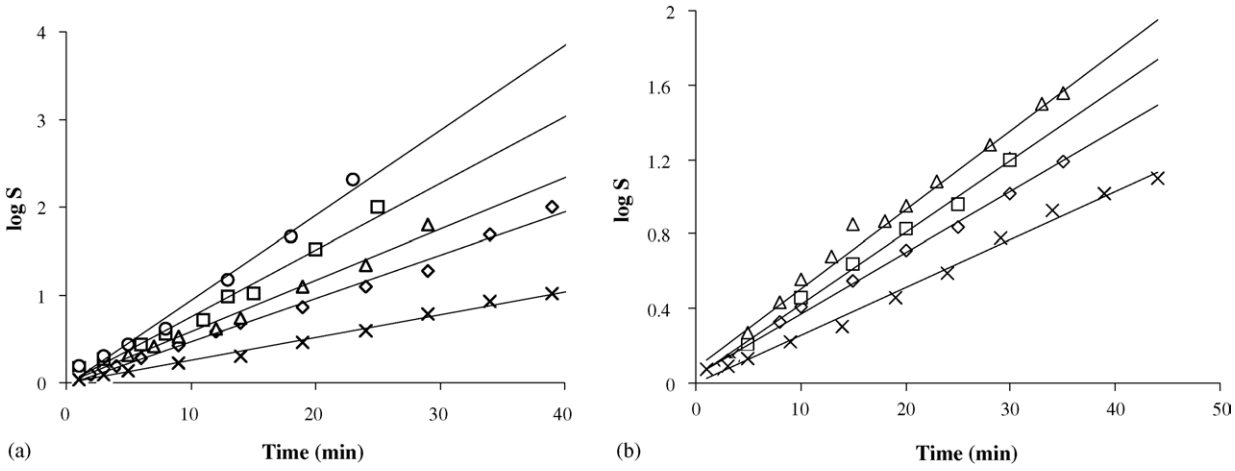


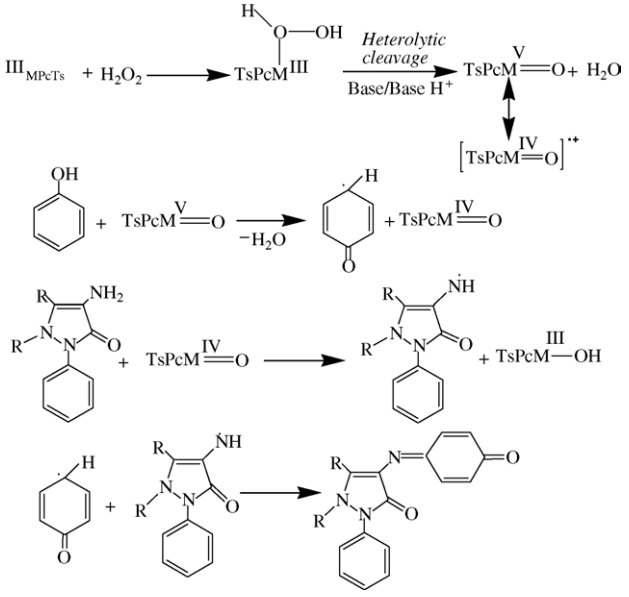
Fig. 8. (a) Effect of SDS concentration on the kinetic plots of dye formation from PhOH, $AmNH_2$ and [MnPcTs] = 1×10^{-5} M in presence of [H_2O_2] = 0.1 M and at neutral pH. [SDS]: (×) 0 M; (◊) 0.003 M; (Δ) 0.005 M; (□) 0.008 M; (○) 0.01 M. (b) Effect of CTAB concentration on the kinetic plots of the dye formation from PhOH and $AmNH_2$ and [MnPcTs] = 1×10^{-5} M in presence of [H_2O_2] 0.1 M at neutral pH. [CTAB]: (×) 0.001 M; (◊) 0.003 M; (□) 0.005 M; (Δ) 0.008 M.

molecules [30]. Additionally, the phthalocyanine part of MPcTs interacts with the micelle cores via the hydrophobic force, which also enhances the monomerisation effect on the aggregated form of MPcTs. In TX-100 micelles, the interaction forces of MPcTs aggregates with the micelles lies in between the extent of effects of SDS and CTAB micelles and in this system also monomerisation of MPcTs occurs.

The process of enhanced monomerisation of MPcTs is evident from the significant increase in the intensity of the characteristic monomeric peaks in the UV–vis spectrum for each of the MPcTs. That is, in the MnPcTs system the intensity of λ_{max} = 720 nm peak and in the of CoPcTs, the intensity of λ_{max} = 670 nm significantly increases. This effect is reflected in the increased rate of dye formation in the presence of micelle medium and more dominant with increase in the compositions of micelles. That is, the peroxidase like activity of MPcTs still prevails in the presence of micelles and due to the increase in the proportion of the monomeric forms, the catalytic activity seems enhanced in the microheterogeneous medium. Also, the microheterogeneous medium increases the stability of metal oxo cationic radical. The kinetic plots of dye formation at various concentration of SDS and CTAB micelles (TX-100 not shown) catalysed by the MnPcTs systems are shown in Fig. 8(a) and (b). The effect of microheterogeneous media on the rate of formation of the dye is observed to be SDS > TX-100 > CTAB micellar system (shown in Table 1).

3.5. Proposed reaction mechanism

The peroxidase mimic catalytic activities of MnPcTs and FePcTs have been revealed in the presence PhOH and $AmNH_2$ using H_2O_2 as oxidant. Recently, Sorokin and co-workers reported that the high valent metal oxo (^{V}MPcTs = O) complex is formed by heterolytic cleavage of MPcTs-OOH [31,32]. Similar observations were also reported by Meunier for water soluble monomeric porphyrin with H_2O_2 [33]. The hyper valent state of metallophthalocyanine is less accessible than porphyrin. Hence, phthalocyanine ligands tend to stabilize lower oxidation states. The electrophilic ^{V}MPcTs = O complex was proposed to be the active species which involved in homogeneous oxidation of electron donor compounds. The possible mechanism of peroxidase like reaction is exemplified in Scheme 2, for the MnPcTs and FePcTs system in the presence of an electron donor species such as PhOH and $AmNH_2$. As proposed earlier by Metelitza et al., in the first step a two electron oxidation of ^{V}MPcTs = O complex proceeds by the reaction of H_2O_2 with MnPcTs or FePcTs which is in equilibrium with ^{IV}MPcTs = O cationic radical species. In the second step the electrophilic character of ^{V}MPcTs = O or ^{IV}MPcTs = O cationic radical complex react with PhOH, resulting in the formation of phenoxy radial (PhO•) and ^{IV}MPcTs = O species. In the following step aminyl radical ($AmNH^{\bullet}$) is formed by the reaction of $AmNH_2$ with ^{IV}MPcTs = O and consequently



Scheme 2.

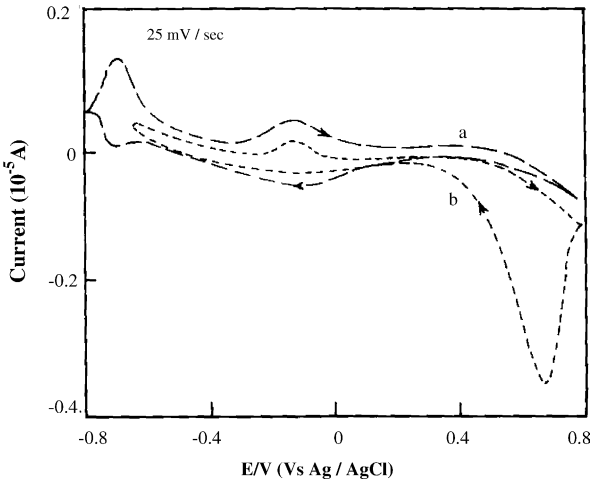


Fig. 9. Cyclic voltammogram of dye formation from PhOH and $AmNH_2$ catalyzed by [MnPcTs] = 1×10^{-5} M. (a) MnPcTs + H_2O_2; (b) CoPcTs + H_2O_2 + PhOH + $AmNH_2$; supporting electrolyte is 0.1 M KNO_3 and scan rate 25 mV s^{-1}.

the MPcTs returns to its native state. Finally, the recombination of these two radical species produces co-oxidised product of red colored antipyrilquinoneimine dye. The redox voltammogram of MnPcTs in the presence of H_2O_2 is shown in Fig. 9(a). The peak at −0.15 V represents the reduction potential of Mn(III)/Mn(II) and the potential −0.72 V corresponds to Mn(II)/Mn(I) species [34]. Fig. 9(b) shows the redox voltammogram of the MnPcTs catalysed reaction mixture containing PhOH and $AmNH_2$ in the presence of H_2O_2. The new peak, which was observed at +0.69 V, corresponds to the oxidized product of dye. The metal based redox process of MnPcTs and FePcTs shows greater catalytic activity than the ring based redox processes of NiPcTs, CuPcTs and ZnPcTs. After the completion of the reaction, the dye was separated out from the solution and characterised by FT-IR spectrum, which is shown in Fig. 10. The spectrum agrees with the literature since the dye formation reaction of PhOH and $AmNH_2$ is well known.

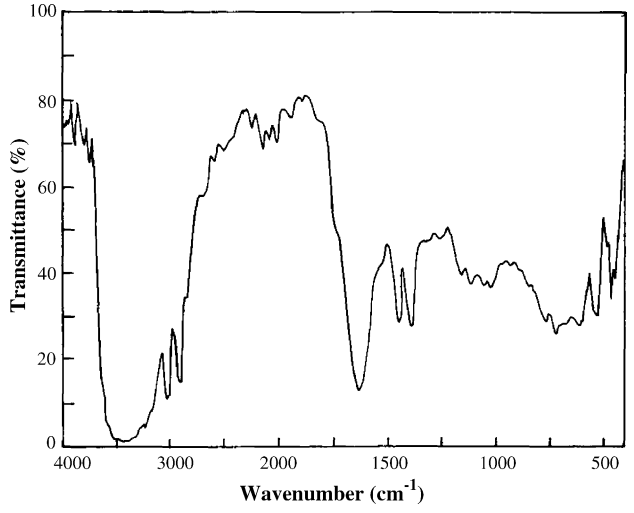


Fig. 10. FT-IR spectrum of the antipyrilquinoneimine dye formation from PhOH and $AmNH_2$, in KBr pellet at 25 °C.

4. Conclusion

The peroxidase mimic activity of water soluble anionic MPcTs has been found to be a promising alternative to the HRP for co-oxidation reaction of PhOH and $AmNH_2$ in the presence of H_2O_2. The difference in catalytic activity of MPcTs depends on the activation of H_2O_2 and stability of metal oxo adduct formed in the axial positions. The trend in the metal ion activity of different MPcTs is as follows: MnPcTs > FePcTs > ZnPcTs > CuPcTs > NiPcTs. In acidic pH, the lower rate constant values are observed than at pH 9.0 for all the MPcTs systems. In the presence of microheterogeneous media the overall rate constant values increase. The catalytic effects are found to be more in SDS micelles, when compared to the TX-100 and CTAB micelles. The effect of microheterogeneous media is SDS > TX-100 > CTAB. The change in the oxidation potential of MnPcTs and oxidized product of dye is confirmed by cyclic voltammetry. Hence, the rate constant values of dye formation showing peroxidase like activity gives the overall trend pH 9.0 > SDS > TX-100 > pH 11.0 > CTAB > pH 7.0 > pH 6.0 > pH 4.0.

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