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CATALASE-LIKE ACTIVITY OF DIVINYLBENZENE (DVB)-CROSSLINKED POLYACRYLAMIDE SUPPORTED AMINO METAL COMPLEXES

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Abstract—The catalytic properties of the complexes resulting from the interaction between a DVB-crosslinked polyacrylamide supported amine and Cu(II), Cr(III), Fe(III), Mn(II) and Pb(II) ions have been investigated. The study of hydrogen peroxide decomposition was employed as a model reaction for this purpose. The phenomenological aspects of this process such as time-course, dependence of H_2O_2 concentration, complex concentration, temperature and pH were evaluated. The activation energy of decomposition was calculated to be 16.35 kJ/mol. The results indicate a catalase-like activity for these metal complexes. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Polymer–metal complexes are useful as immobilized catalysts for practical application and sometimes they are much more reactive than the corresponding monomeric analogues due to the specificities arising from the large ligand molecule [1–6]. The isolation of products from the support catalyst is facilitated and the catalyst can be used repeatedly by a simple procedure. The advantages, apart from recovery and reuse, are isolation of catalytic sites and prevention of agglomeration leading to inactivation and coordinate unsaturation introduced by the polymeric matrix resulting in enhanced specificity. The decomposition of hydrogen peroxide has been used as a model reaction for the investigation of the catalytic activity of various metal complexes [7, 8]. Although the catalytic mechanism has not been thoroughly elucidated, this decomposition of H_2O_2 is often employed as a standard reaction to determine the catalytic activity of a polymer metal complex [9]. This paper describes the preparation of DVB-crosslinked polyacrylamides with 2–20 mol% DVB, their functionalisation with ethylenediamine to afford the amino resin, complexation of the polymeric amino ligands with Cu(II), Cr(III), Fe(III), Mn(II) and Pb(II) ions and the catalytic activity of these supported metal complexes in the decomposition of H_2O_2. The decomposition of H_2O_2 has been studied as a catalase model [10].

EXPERIMENTAL

General

Commercially available samples of acrylamide, DVB, potassium persulphate and ethylenediamine were used. All the reagents and metal salts were of certified ACS grade.

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Preparation of DVB-crosslinked polyacrylamide

DVB-crosslinked polyacrylamides were prepared by solution polymerization of the monomers in ethanol at 70°C using benzoyl peroxide as the initiator [11]. For the preparation of 2 mol% DVB-crosslinked polymer, acrylamide (20.87 g) and DVB (0.78 g) were dissolved in ethanol (100 mL). Benzoyl peroxide (300 mg) dissolved in ethanol was mixed with it. The reaction mixture was heated in a water bath with stirring until the polymer was precipitated. The precipitated polymer was separated from the feed by filtration, washed several times with water and methanol and dried in a vacuum. DVB-crosslinked polyacrylamides with 2, 4, 8, 12 and 20 mol% crosslinking were prepared by varying the amount of monomers in the feed (Table 1). The polymers precipitated as amorphous mass and on drying they appeared as bulk masses.

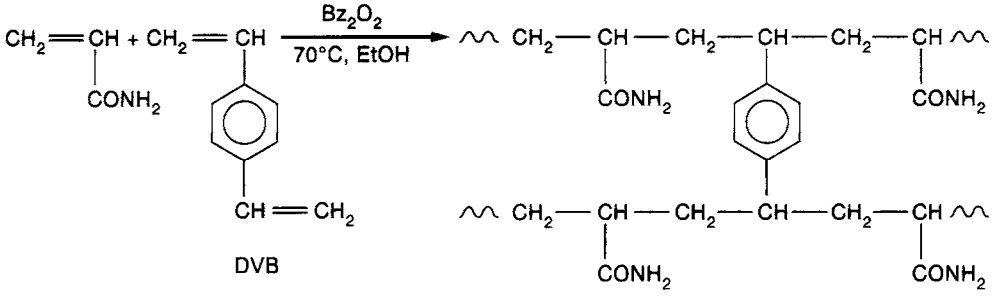
A commercial sample of DVB, which is 55% pure, was used. The mol% was calculated on the basis of the actual DVB isomer present.

Table 1. Preparation of DVB-crosslinked polyacrylamides

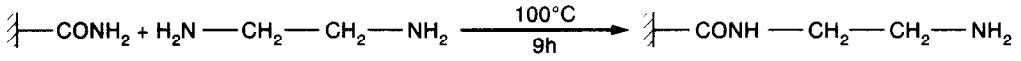
DVB (mol%)	Wt. of acrylamide (g)	Wt. of DVB (g)	Yield (g)
2	20.87	0.78	21.50
4	20.43	1.56	21.88
8	19.59	3.12	22.68
12	18.74	4.68	23.40
20	17.04	7.80	24.80

Table 2. Preparation of DVB-crosslinked poly(*N*-2 aminoethyl acrylamide)s

Crosslinking	Weight of polymer (g)	Yield (g)	Animo capacity (meq/g)
DVB			
2	5	6.50	3.04
4	5	6.15	2.29
8	5	5.95	1.92
12	5	5.25	1.22
20	5	6.00	0.51



Scheme 1. Preparation of TEGDMA-crosslinked polyacrylamides.



Scheme 2. Functionalisation of crosslinked polyacrylamide with ethylenediamine.

Functionalisation of the crosslinked polyacrylamide

The DVB-crosslinked polyacrylamides were functionalised by transamidation with excess ethylenediamine [11]. The polymer was mixed with a five fold excess of ethylenediamine and was refluxed at 100°C for 9 hr with stirring (Table 2). When the reaction was completed, the mixture was poured into crushed ice. The resin was collected by filtration and washed with NaCl (1 M) solution to free from ethylenediamine as indicated by the ninhydrin test, washed several times with distilled water to free from chloride ions and finally with methanol and dried in a vacuum.

Estimation of the amino capacity of the polymer

The DVB-crosslinked poly(*N*-2-aminoethylacrylamide) (100 mg) was neutralised by equilibration with excess HCl (0.2 N, 10 mL) with stirring for 9 hr. The excess unreacted acid was estimated by titration with NaOH to a phenolphthalein end point.

Complexation of the amino resin with metal ions

Complexation studies of Cr(III), Mn(II), Fe(III), Cu(II) and Pb(II) ions were followed using the DVB-crosslinked amino resin with different crosslink densities by batch equilibration technique. The polymer (100 mg) was stirred with excess metal salt solution (0.05 M, 40 mL) for 9 hr. The difference in concentration of metal ion solution before and after complexation was estimated: Pb(II) was estimated by complexometry using xylenol orange as indicator [12], Cu(II), Cr(III), Mn(II) and Fe(III) by spectrophotometry at 814.6, 575, 544 and 299 nm, respectively [13].

Catalytic activity of the metal complexes

The metal complex (50 mg) was stirred with hydrogen peroxide solution (0.01–0.1 N, 20 mL) for 2 hr. The polymer metal complex catalysed the decomposition of H_2O_2 and O_2 was evolved. Since concentration of H_2O_2 was very low the reaction was not at all hazardous in this case. After 2 hr the reaction was arrested by cooling in ice and the supernatant liquid was pipetted and titrated with 0.02 N $KMnO_4$ solution. The difference in titre values of $KMnO_4$ solution before and after the catalysed decomposition was followed. The experiment was similarly conducted with the various metal complexes. The catalytic decomposition of H_2O_2 was studied at various pH values, temperatures, H_2O_2 concentrations and complex concentrations. A blank experiment was also simultaneously conducted with uncomplexed resin (50 mg) under the same conditions.

The time course and kinetics of catalytic decomposition of H_2O_2 were followed at equal intervals of time and titrating with standard $KMnO_4$. 20 mL reactions were performed for the various kinetic measurements.

RESULTS AND DISCUSSION

DVB-crosslinked polyacrylamides were prepared by solution polymerisation of the monomers, acrylamide and DVB, in ethanol at 70°C using benzoylperoxide initiator (Scheme 1).

Polymers with 2, 4, 8, 12 and 20 mol% DVB-crosslinking were prepared by changing the amount of monomers for polymerization (Table 1).

The crosslinked polymers were functionalised by transamidation with a five fold excess of ethylenediamine at 100°C for 9 hr (Scheme 2, Table 2). The presence of excess ethylenediamine prevented the pendant amino group reacting to generate crosslinks.

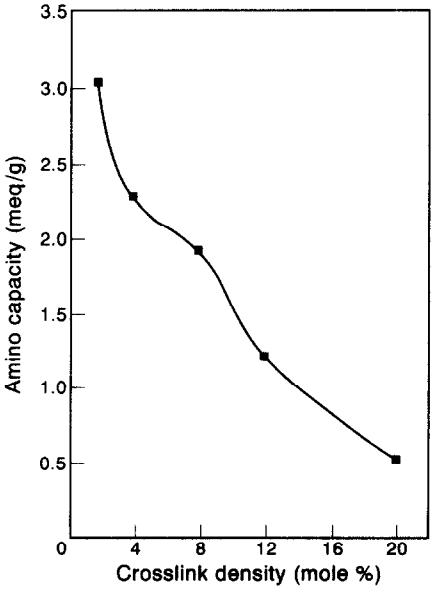


Fig. 1. Amino capacity vs extent of TEGDMA crosslinking.

Table 3. Metal ion intake of DVB-crosslinked resin

DVB (mol%)	Animo capacity (meq/g)	Cr(III) meq/g	Cr(III) M/L[a]	Mn(II) meq/g	Mn(II) M/L	Fe(III) meq/g	Fe(III) M/L	Cu(II) meq/g	Cu(II) M/L	Pb(II) meq/g	Pb(II) M/L
2	3.04	0.63	0.2072	0.72	0.2368	0.39	0.1282	1.13	0.2727	0.55	0.1809
4	2.29	0.31	0.1353	0.50	0.2183	0.26	0.1135	1.02	0.4454	0.48	0.2096
8	1.92	0.24	0.1250	0.38	0.1979	0.23	0.1197	0.83	0.4322	0.36	0.1875
12	1.22	0.05	0.0409	0.19	0.1557	0.14	0.1147	0.65	0.5327	0.26	0.2131
20	0.51	0.04	0.0784	0.08	0.1568	0.00	0.0000	0.50	0.9803	0.10	0.1960

M/L = Metal/ligand ratio.

The aminofunctions were detected from the blue colouration with ninhydrin reagent [14]. The amino capacity was estimated by equilibrating with excess acid and estimating the unreacted acid by titration with standard NaOH. The amino capacity decreases with increase of crosslink density (Fig. 1). This is due to the reduced availability of the amide groups buried within the rigid and hydrophobic crosslink network for transamidation with ethylenediamine [15, 16]. The diffusion of the low molecular weight reagents into the interior of the networks is limited by the increased rigidity of the support.

Complexation of DVB-crosslinked poly(N-2-aminoethylacrylamide

Complexation of Cr(III), Mn(II), Fe(III), Cu(II) and Pb(II) was followed using DVB-crosslinked amino resin. The metal intake was estimated by batch equilibration technique. The values of the metal in intake for the various resins are given in Table 3.

The trend in metal ion intake is Cu(II) > Mn(II) > Cr(III) > Pb(II) > Fe(III). The amount of metal ion complexed decreases as the crosslink density increases. Complexation is maximum for the 2% crosslinked system and is minimum for the 20%. This is in the same order as the amino capacity. The variation of metal intake with increase in crosslinking is shown in Fig. 2.

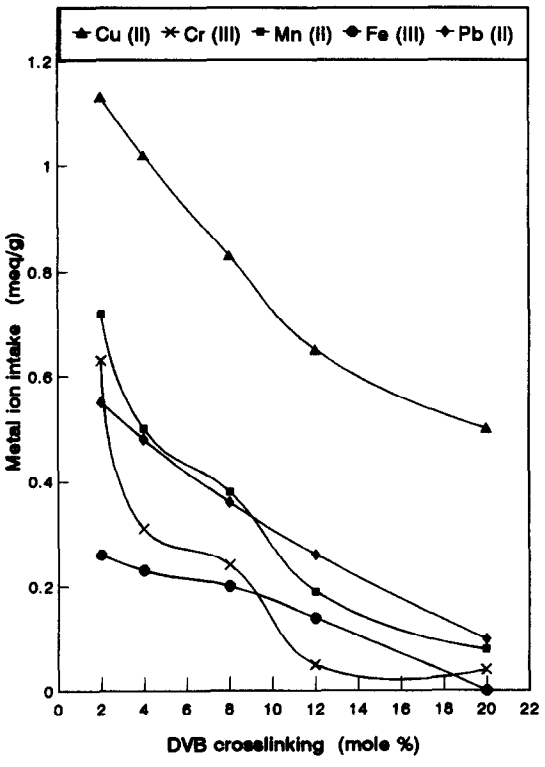


Fig. 2. Metal ion intake vs extent of TEGDMA crosslinking.

Catalysed decomposition of H_2O_2

1. Effect of various metal complexes. The decomposition of H_2O_2 was followed in the presence of Cu(II), Cr(III), Fe(III), Mn(II) and Pb(II) complexes of DVB-crosslinked polyacrylamide amines (Table 4).

The catalytic efficiency is found to be in the order Mn(II) > Cu(II) > Fe(III) > Cr(III) > Pb(II) complexes.

Decomposition of H_2O_2 using crosslinked polyacrylamide amine–Cu(II) complexes of 2–20 mol% DVB-crosslinks was studied. The catalytic efficiency decreases as the crosslinking increases (Table 5). This is in line with the varying hydrophilic/hydrophobic nature of the polymer supports with changing extents of crosslinking.

2. Phenomenological aspects. The catalytic properties of 8% DVB-crosslinked polyacrylamide amine–Cu(II) complexes were studied at various hydrogen peroxide concentrations (Table 6) and complex concentrations (Table 7). Increase in H_2O_2 concentration, and also the increase in complex concentration, increase the extent of the decomposition of hydrogen peroxide.

The dependence of catalytic activity of the 8% crosslinked polymer Cu(II) complex on pH was studied using two buffers: borax (pH 9.2) and ammonium sulphate (pH 5.5). The hydrogen peroxide decomposition was higher at the pH of borax buffer; 78% conversion occurred at pH 9.2 and 60% conversion at pH 5.5.

The catalytic efficiency was found to be enhanced with increasing temperature. The decomposition of H_2O_2 was followed at 301 K and 313 K using the 8 mol% DVB-crosslinked polymer Cu(II) complex. The decomposition was 58% at 301 K and 75% at 313 K.

Table 4. Catalytic decomposition of H_2O_2 using various metal complexes

Crosslinking	Metals	Metal content (meq/g)	$[H_2O_2]$ decomposed (moles decomposed per mole of metal)
8% DVB	Cu(II)	0.83	20.8795
	Cr(III)	0.24	26.2917
	Fe(III)	0.20	47.3000
	Mn(II)	0.38	58.0526
	Pb(II)	0.36	4.3888

$[H_2O_2]$: 0.1 M; Complex: 50 mg; Time: 2 hr; Temperature: 28°C.

Table 5. Catalytic decomposition of H_2O_2 using 2–20 mol% DVB-crosslinked polyacrylamide–Cu(II) complexes

Crosslinking	Metal content (meq/g)	$[H_2O_2]$ decomposed (moles decomposed per mole of metal)
2% DVB	1.13	23.3451
4% DVB	1.02	22.1568
8% DVB	0.83	20.8795
12% DVB	0.65	19.2307
20% DVB	0.50	16.8400

$[H_2O_2]$: 0.1 M; Complex: 50 mg; Time: 2 hr; Temperature: 28°C.

Table 6. Catalytic decomposition of H_2O_2 at various hydrogen peroxide concentrations using 8% DVB-crosslinked polyacrylamide amine–Cu(II) complex

Concentration of H_2O_2 (mol)	$[H_2O_2]$ decomposed (mol/g)
0.1576	22.65
0.0780	20.30
0.0157	10.50
0.0078	5.35
0.0038	2.50

Complex: 50 mg; Time: 2 hr; Temperature: 28°C.

Table 7. Catalytic decomposition of H_2O_2 at various complex concentrations

Complex concentrations (mg)	$[H_2O_2]$ decomposed (mol)
50	17.33
100	20.55
150	25.32
200	28.75

$[H_2O_2]$: 1 M; Time: 2 hr; Temperature: 28°C.
Complex: 8% DVB-crosslinked polyacrylamide amine–Cu(II) complex.

Table 8. Reuse of DVB-crosslinked polyacrylamide amine–Cu(II) complex in catalytic decomposition of H_2O_2

No. of cycles	$[H_2O_2]$ decomposed (mol/g)
1	17.33
2	17.30
3	17.30
4	17.28

The reuse of 8 mol% DVB-crosslinked polyacrylamide amine Cu(II) complex was investigated for four cycles (Table 8). The supported catalyst was found to retain its activity for repeated use.

3. Kinetics of decomposition. The time course of catalytic property of DVB-crosslinked polyacrylamide amino Cu(II) complexes was followed (Fig. 3). The decomposition of H_2O_2 was also followed at two different temperatures 301 and 313 K. The linear plot of $-\log(a-x)$ vs time (Fig. 4) indicates that the reaction follows first order kinetics with respect to H_2O_2 [17]. The rate constants k_1 and k_2 were calculated from the slope of the curve. The activation energy E was calculated using the equation.

$$\ln \frac{k_2}{k_1} = \frac{E}{8.314}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

The activation energy value of DVB-crosslinked polyacrylamide amine Cu(II) complex was found to be 16.35 kJ/mol. The catalytic activities of inorganic oxide supported metal ions and chelated metal complexes are also reported [17]. The catalytic decomposition of H_2O_2 using DVB-crosslinked polystyrene supported ethylene diamine and glycine cobalt complexes follows first order kinetics with respect to $[H_2O_2]$ [18]. The kinetics and mechanism of catalytic decomposition of H_2O_2 in homogeneous systems have been investigated [19–25]. From the literature data of catalase-induced reactions

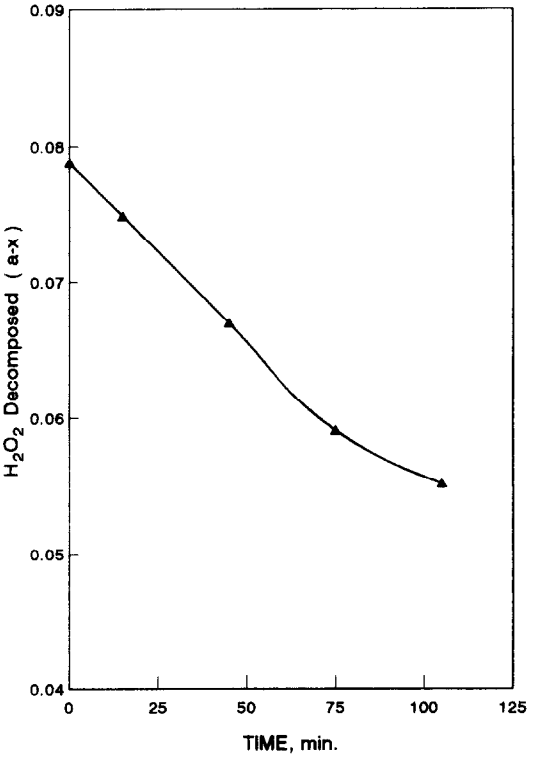


Fig. 3. Catalysis decomposition of H_2O_2 vs time.

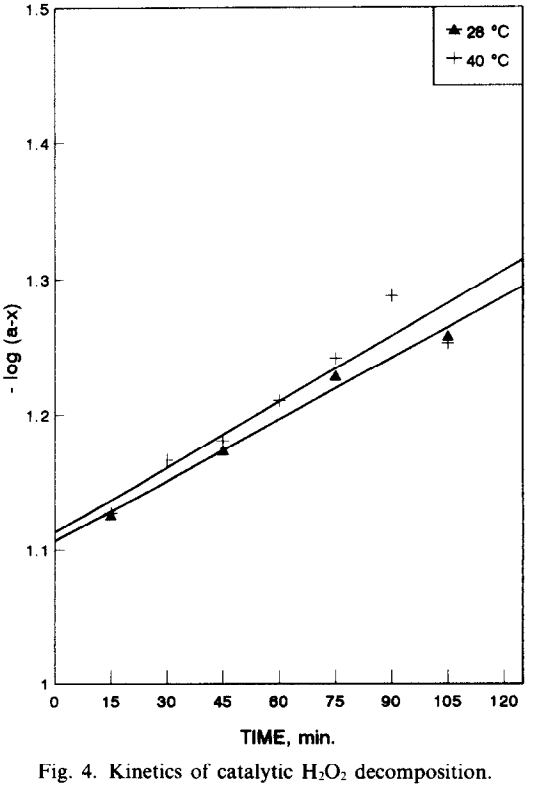


Fig. 4. Kinetics of catalytic H_2O_2 decomposition.

activation energy is only 8.4 kJ/mol [22], whereas the thermal decomposition of H_2O_2 requires 201 kJ/mol [23]. When using a copper complex of a copolymer 2-methyl-5-vinyl-pyridine and acrylic acid this value is 73.5 kJ/mol [24]. The activation energy of the copper complex of polymethacrylate aspartic acid is reported to be 33.6 kJ/mol and of glutamic acid is 23.1 kJ/mol [25]. The decomposition of H_2O_2 in the presence of copper complexes of certain polyelectrolytes has been reported to be proportional to $[H^+]$, $[H_2O_2]$ and $[CuL_2]$ [23].

CONCLUSION

The catalytic activity of the metal complexes of a DVB-crosslinked polyacrylamide amine was investigated for the catalase-model decomposition of H_2O_2. The trend in catalytic efficiency is in the order Mn(II) > Cu(II) > Fe(III) > Cr(III) > Pb(II) complexes. The extent of catalytic activity decreases as the crosslink density increases. The catalytic decomposition depends on the concentration of H_2O_2, the amount of the catalyst, temperature and pH. The rate of the reaction is first order. The activation energy of a 8% DVB-crosslinked polyacrylamide amine–Cu(II) complex was found to be 16.35 kJ/mol.

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