Catalytic Activity of Acrylic Acid Based Polymer-Metal Complexes in the Hydrolysis of p-Nitrophenyl Acetate
Catalysis by transition metal complexes has gained prominence in recent years. A transition metal complex can function as a homogeneous catalyst if it has an open coordination site to bind the reactants. The catalytic activity of such a catalyst arises from the binding of the reactants to the metal complex and their subsequent transfer to the substrate, thereby regenerating the free catalyst. A loss in activity in a homogeneous catalyst takes place when the complex dimerizes during the opening of the active sites.

It was therefore argued that if the transition metal complexes can be bound to a polymer and if the polymer is rigid enough to separate the binding sites, their active catalysts, similar to the homogeneous ones, should be obtained. In addition, these polymer bound catalysts could be easily recovered and reused. For these reasons, a large number of research groups are currently engaged in research on the preparation and application of such catalyst to industrial processes. The advantages apart from recovery and reuse are: (a) isolation of catalytic sites and prevention of agglomeration leading to inactivation, and (b) coordinate unsaturation introduced by the polymeric matrix resulting in enhanced specificity.

The catalytic cycle of a polymer-metal complex catalysed reaction can be schematically represented as

\[ ML_n + S \rightarrow L_{n-1}MS \]

where \( M \) is the metal ion, \( L \) the ligand, and \( S \) the substrate.
In the first step, substrate coordinates to a metal catalyst forming an intermediate mixed complex (LMS). It is then activated by metal ions and dissociates from the catalyst. The complex catalyst, having accomplished its purpose, is regenerated to the original complex. The catalytic action of metal ion depends substantially on the nature of the ligands in the intermediate mixed complex.24

In the present study the catalytic activity of the various metal complexes of 4-20 mol% NN MBA-crosslinked polyacrylic acids and 4 mol% linear and TTEG DMA-, BDDMA-, and NN MBA-crosslinked acrylic acid-(N-vinyl-2-pyrrolidone) copolymers were investigated towards the hydrolysis of \( p \)-nitrophenyl acetate. The dependence of the catalytic activity on the various parameters of the hydrolytic reaction were followed. The extent of hydrolysis was correlated with the nature and degree of the crosslinking, and nature and composition of the polymer support.

5.1 Catalytic Activity of 4-20 mol% NN MBA-crosslinked Polyacrylic Acid-Metal Complexes

Metal complexes of 4-20 mol% NN MBA-crosslinked polyacrylic acids showed variation in reactivity with crosslink density. The reactivity of a ligand function on a crosslinked polymer support is highly dependent on the variables of the polymeric network structure. The catalytic activity of Cr(III), Mn(II), Fe (III), Co(II), Ni(II), Cu(II) and Zn(II) complexes of NN MBA-crosslinked polyacrylic acid of different crosslink densities were investigated in the hydrolysis of \( p \)-nitrophenyl acetate and is depicted in Figure 5.1. The catalytic activity decreased in the order: Co(II) > Ni(II) > Cu (II) \( \approx \) Zn(II) > Cr(III) > Mn(II) > Fe(III).
Catalytic activity of acrylic acid based polymer-metal complexes in the hydrolysis of p-nitrophenyl acetate

Transition metals with their variable valency and unpaired electrons in the d-orbital may form unstable intermediate compounds and hence enhance the reaction. Co(II) complexes of 4-20 mol% polyacrylic acids exhibit maximum catalytic activity. This can be explained by its tetrahedral/octahedral geometry where coordination sites are vacant, thereby form the intermediate compound. Mn(II) and Fe(III) showed less activity compared to Co(II) due to the presence of half filled d-orbital. Complexes where the metal is in the (III) oxidation state are
generally more stable than those where metal is in the (II) state. Hence Fe(III) and Cr(III) have less tendency to form intermediate complex compared to Ni(II) and Co(II) and therefore less catalytic activity.

Catalytic activity was followed by comparing the absorbance at 400 nm for definite time interval of two samples of p-nitrophenyl acetate of known concentration (1) with catalyst, and (2) without catalyst for about 3 hrs. Absorbance at 400 nm is directly proportioned to the amount of p-nitrophenol produced as a result of hydrolysis (Scheme 5.1).

\[
\begin{align*}
\text{O}_2\text{N} & \text{-} \text{OOCCH}_3 \xrightarrow{\text{H}_2\text{O}} \text{O}_2\text{N} & \text{-} \text{OH} + \text{CH}_3\text{COOH}
\end{align*}
\]

**Scheme 5.1** Hydrolysis of p-nitrophenyl acetate

Amount of p-nitrophenol was calculated from the working curve of p-nitrophenol at pH 7.8 prepared by plotting concentration against absorbance at 400 nm of known concentrations of p-nitrophenol.

**5.1.1 Effect of degree of NNMBA-crosslinking on the catalytic activity of metal complexes 4-20 mol% polyacrylic acids**

In order to investigate the effect of degree of NNMBA crosslinking on the catalytic activity, the hydrolysis of p-nitrophenyl acetate was followed using Co(II) complexes of 4-20 mol% NNMBA-crosslinked polyacrylic acids. The variation in reactivity with different crosslink density is given in Figure 5.2. The reactivity of 4 mol% is higher than all other systems. As the crosslink density of the resin increases the accessibility of the reactive site to the reaction medium decreases. In low crosslinked systems, the catalytic site is randomly arranged and it is more easily accessible to the reaction medium. As the crosslink density increases, steric effect by the crosslinks of the entire system increases and the
mobility of active centre becomes difficult. Hence 8 mol% and 20 mol% NNMBBA-crosslinked polyacrylic acid-metal complexes showed less catalytic activity than metal complexes of 4 mol% NNMBBA-crosslinked polyacrylic acid. Due to the unequal distribution of NNMBBA crosslinks, Co(II) complex of 12 mol% polyacrylic acid exhibited more catalytic activity than Co(II) complex of 8 mol% polyacrylic acid.

![Figure 5.2](image)

**Figure 5.2** Variation of catalytic activity with NNMBBA crosslinking

### 5.1.2 Kinetics of hydrolysis of p-nitrophenyl acetate catalysed by Co(II) complex of 4 mol% NNMBBA-crosslinked polyacrylic acid

In the present study, kinetic studies of hydrolysis of p-nitrophenyl acetate was followed by Co(II) complex of 4 mol% NNMBBA-crosslinked polyacrylic acid at three different temperatures (20, 29 & 38°C). The hydrolysis was found to be first order. The variation of rate constants with temperature is given in **Figure 5.3**. Compared to other metal complexes Co(II) complex is very active since it requires less activation energy. The kinetic parameters for the Co(II) complex catalysed hydrolysis were calculated using the Arrhenius equation

\[ k = Ae^{-E/RT} \]

The kinetic parameters are

- \( E = 29.7 \text{ kJ} \)
- \( A = 1.08 \times 10^5 \text{ s}^{-1} \)
- \( \Delta S = -148.69 \text{ J} \)
The less activation energy of Co(II) complex is due to the unsaturation in the coordination sphere making the easy accessibility of \( p \)-nitrophenyl acetate molecule to get involved in the catalytic hydrolysis.

![Graph showing variation of rate constant with temperature in the hydrolysis of NPA catalysed by Co(II) complex of 4 mo\% NN MBA-crosslinked polyacrylic acid.](image)

**Figure 5.3** Variation of rate constant with temperature in the hydrolysis of NPA catalysed by Co(II) complex of 4 mo\% NN MBA-crosslinked polyacrylic acid

### 5.2 Acrylic Acid-N-Vinyl-2-Pyrrolidone Copolymer Systems

The performance of a polymeric catalyst is influenced by the physical and chemical properties of the polymeric support. The distribution and accessibility of the active sites controls the activity of the catalyst. Kinetics of metal ion complexation and its catalytic activity are influenced by the rigidity of the crosslinking agents. Considering all these factors, we investigated the catalytic activity of metal complexes of linear and crosslinked acrylic acid-N-vinyl-2-pyrrolidone copolymers. The reactivities of the metal complexes attached to linear and crosslinked AA-NVP copolymers were investigated with respect to the nature of the crosslinking agent, composition of the polymer support and pH of the reaction medium. The high swelling characteristics and metal uptake
capacities are responsible for the high catalytic activity of metal complexes of NN MBA-crosslinked polyacrylic acid when compared to that of AA-NVP copolymers system. The catalytic activities of metal complexes of linear and crosslinked AA-NVP copolymers are summarised as follows.

5.2.1 Catalytic activity of linear AA-NVP copolymer-metal complexes

The trend of the catalytic activity is same as that of polyacrylic acid and is depicted in Figure 5.4. The linear AA-NVP system is found to be more catalytically active, but it cannot be recycled because of the irrecoverability of the polymer system. The chemical reactivity of attached functional groups is governed by the distribution and accessibility on the polymer backbone. Linear polymers which can attain homogeneous macromolecular solutions can provide their functional groups free in the solution.

![Figure 5.4](image)

**Figure 5.4** Catalytic activity of various metal complexes of linear AA-NVP copolymer
5.2.2 Catalytic activity of 4 mol% TTEGDMA-crosslinked AA-NVP copolymer-metal complexes (1:1 system)

The esterolytic activity of 4 mol% TTEGDMA-crosslinked AA-NVP metal complexes (AA:NVP=1:1) was investigated and is shown in Figure 5.5. The catalytic activity of these complexes was the highest compared to BDDMA- and NNMBKA-crosslinked systems and decreased in the order: Co(II) > Ni(II) > Cu(II) > Zn(II) > Cr (III) > Mn(II) > Fe(III). In the case of TTEGDMA-crosslinked system, the carboxyl capacity, metal ion uptake and catalytic activity were found to be higher than that of BDDMA- and NNMBKA-crosslinked systems. This is due to the greater accessibility of the reactive sites originating from the flexible nature of TTEGDMA crosslinking.

![Figure 5.5](image_url)  
*Figure 5.5 Catalytic activity of various metal complexes of TTEGDMA-crosslinked AA-NVP (1:1) copolymer system*
5.2.3 Catalytic activity of 4 mol% BDDMA-crosslinked AA-NVP copolymer-metal complexes (1:1 system)

Catalytic activity of various metal complexes of BDDMA-crosslinked system was less compared to TTEGDMA-crosslinked system and is shown in Figure 5.6. Here also the catalytic activity decreased in the order: Co(II) > Ni(II) > Cu(II) > Zn(II) > Cr(III) > Mn(II) > Fe(III).

![Figure 5.6. Catalytic activity of various metal complexes of BDDMA-crosslinked AA-NVP (1:1) copolymer system](image)

5.2.4 Catalytic activity of NNMBA-crosslinked AA-NVP copolymer metal complexes (1 : 1 system)

Of the three crosslinked copolymer systems, NNMBA-crosslinked system exhibited least catalytic activity. This is due to the low metal uptake capacity and semi rigid nature of the NNMBA crosslinking agent. The variation in catalytic activity of the various metal complexes of NNMBA-crosslinked AA-NVP copolymer system is summarised in Figure 5.7.
The trend in catalytic activity is similar to that of TTEGDMA- and BDDMA-crosslinked copolymer metal complexes.

5.2.5 Kinetics of hydrolysis of p-nitrophenyl acetate catalysed by Co(II) complex of 4 mol% TTEGDMA-crosslinked AA-NVP copolymer system (1:1)

Co(II) complex of 4 mol% TTEGDMA-crosslinked AA-NVP copolymer was used for the investigation at three different temperatures (20, 29 & 38°C). It was found to be first order. The variation of rate in temperature is given in Figure 5.8. The kinetic parameters calculated are

\[ E = 41.54 \text{ kJ}; \ A = 9.7 \times 10^6 \text{s}^{-1}; \ \Delta S = -64.316 \text{J} \]
5.2.6 Effect of the nature of crosslinking agent on the catalytic activity of copolymer metal-complexes in the hydrolysis of p-nitrophenyl acetate

In order to investigate the effect of the nature of crosslinking agent on the catalytic activity, Co(II) complexes of linear and 4 mol% TTEGDMA-, BDDMA-, and NNMBA-crosslinked AA-NVP (1:1) copolymers were followed. The variation in reactivity with crosslinking agents is given in Figure 5.9. The reactivity varied in the order: linear > TTEGDMA- > BDDMA- > NNMBA-crosslinked AA-NVP (1:1) copolymers.

In the case of flexible crosslinking agents the catalytic site is randomly arranged and therefore is more easily accessible to the reaction medium i.e. as flexibility increases, catalytic activity also increases. Thus TTEGDMA-crosslinked system exhibit maximum catalytic activity among the three crosslinked copolymer systems.
5.3 Effect of Various Parameters on the Catalytic Activity of Acrylic Acid Based Polymer-metal Complexes in the Hydrolysis of \( p \)-Nitrophenyl Acetate

The effect of various parameters like time, temperature, amount of catalyst, pH and concentration of buffer were found to have vital role in the hydrolysis of \( p \)-nitrophenyl acetate. Co(II) complex of 4 mol\% NN MBA-crosslinked polyacrylic acid was used for these investigations and the results are depicted in Figure 5.10. Heterogeneous catalysis normally depends on at least one reactant being adsorbed (usually chemisorbed) and modified to a form in which it readily undergoes reaction. Often this modification takes the form of a fragmentation of the reactant molecules. The activity of a catalyst depends on the strength of chemisorption. To be active, the catalyst should be extensively covered by adsorbate, which is the case if chemisorption is strong. If the strength of the substrate-adsorbate bond...
becomes too great, the activity declines either because the other reactant molecules cannot react with the adsorbate or because the adsorbate molecules are immobilised on the surface. This pattern of behaviour suggests that the reactivity of a catalyst should initially increase and then decrease. This is the reason why the rate of catalysis is not uniform with time. This suggests an acetylation-deacetylation mechanism for the catalytic activity of the polymer-metal complexes in ester hydrolysis. The catalysis starts with the adsorption of the acetyl group which takes place at a higher rate initially. As adsorption increased, rate of catalysis also increases to some extent and then decreases.

The influence of pH was studied using phosphate buffer with pH values 6.8, 7.6, 7.8 and 8.4 and was in the order $6.8 < 7.6 < 7.8 < 8.4$. The absorbance at 400 nm was observed only after 45 minutes at pH 6.8, since the rate of hydrolysis of p-nitrophenyl acetate at pH 6.8 is very low. Though the rate of hydrolysis increased with increase in pH, maximum catalytic activity was observed at pH 7.8 and then decreased. From this it is concluded that acid hydrolysis of p-nitrophenyl acetate is not catalysed by Co(II) complex of polyacrylic acid and the optimum pH is 7.8. Buffer of different concentrations were used and maximum catalytic activity was noticed for 0.05 M buffer. Catalytic activities of Co(II) complex of 4 mol% NNMBA-crosslinked polyacrylic acid at room temperature and 38°C were compared and found that as temperature increased, catalytic activity also increased. This complex could be used several times without loss of efficiency.
Figure 5.10. Effect of various parameters on the hydrolysis of p-nitrophenyl acetate catalysed by Co(II) complex of 4 mol% NNMBA crosslinked polyacrylic acid (a) pH, (b) temperature, (c) amount of the catalyst, and (d) time.
5.4 Comparison Between Crosslinked Polyacrylic Acid System and Crosslinked AA-NVP Copolymer System

Co(II) complex of 4 mol% NN MBA-crosslinked polyacrylic acid system and 4 mol% NN MBA-crosslinked AA-NVP copolymer system (1:1) were used for this investigation. Since the carboxyl capacity of polyacrylic acid system is higher than that of AA-NVP copolymer system, the metal uptake and hence the catalytic activity of polyacrylic acid system was higher than that of copolymer system. The coordinate bond through >C=O of NVP is less stable and hence metal complexation at NVP ring is not stable i.e., in copolymer system, the metal coordination is effected only through carboxylate group of acrylic acid. Hence metal uptake of copolymer system was less than that of polyacrylic acid system i.e. NVP has no vital role on metal complexation and catalytic activity. This was proved by TG analysis where the amount of CuO left is only 10% in the case of Cu(II) complex of 4 mol% NN MBA-crosslinked AA-NVP copolymer whereas it is 26.5% in the case of Cu(II) complex of 4 mol% NN MBA-crosslinked polyacrylic acid. But derivatisation and other reactions are more handy for AA-NVP copolymer system.

5.5. Comparison Between Linear and Crosslinked AA-NVP Copolymer Systems

Co(II) complexes of linear and 4 mol% NN MBA-crosslinked AA/NVP (1:1) copolymer were used for this investigation. Metal uptake and catalytic activity of linear system is higher than that of copolymer system, but it cannot be recycled. The high reactivity of the metal complexes of the linear system is due to the increased availability of metal centres of the polymer chain.