CHAPTER - II

RESULTS AND DISCUSSION

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There are two general approaches to obtain polymers with pendant chelating ligands (Section 1.3.1).In the first approach chelating ligands containing vinyl group or acrylic acid derivatives of chelating ligands are polymerized. In the second approach a functionalized polymer is reacted with appropriate reagents to form chelating ligands or reacted with a ligand containing a suitable functional group. The latter approach has been adopted in the present investigation.

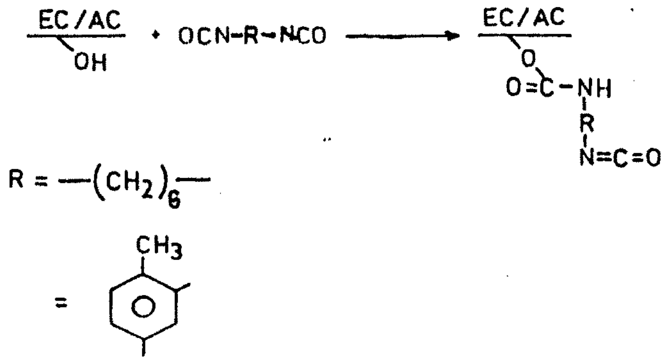
Divinylbenzene crosslinked polystyrene or polyacrylates similarly crosslinked using difunctional monomers (26,33) are among the most commonly used polymer supports. Owing to the low cost and the capacity to be constantly replenished, natural polymers such as waste lignin, chitin, starch and cellulose also are attractive candidates for use as polymer support(34).

In the present work, linear(uncrosslinked) cellulose derivatives such as ethyl cellulose (EC) and cellulose acetate (AC) were used as the starting material. However, crosslinking occured during subsequent modification reaction. Commercially available crosslinked chloromethylated polystyrene was also used for comparison purposes.

2.1 Cellulosic Based Polymer Supports Containing Pendant Amino Groups.

Ethyl cellulose (s.d.Fine Chem.Ltd.), with ethoxy content 48% which corresponds to degree of substitution = 2.48 was used. Commercial cellulose acetate was ~~s~~Soxhlet extracted with ethanol/benzene mixture and its acetyl content was determined by saponification with standard alkali and back titrating the excess of alkali with standard acid using phenolphthalein as an indicator (74). The acetyl content was found to be 40 % which corresponds to the D.S. = 2.5. This means, both ethyl cellulose and acetyl cellulose have one free hydroxyl group for every two anhydroglucopyranose units.

AC and EC were reacted with diisocyanates, hexamethylene diisocyanate (HMDI), or tolylene -2,4-diisocyanate (TDI). Excess of the diisocynate was used to minimise crosslinking and to obtain pendant isocyanate groups onto the cellulosic backbone. The reaction can be shown schematically as

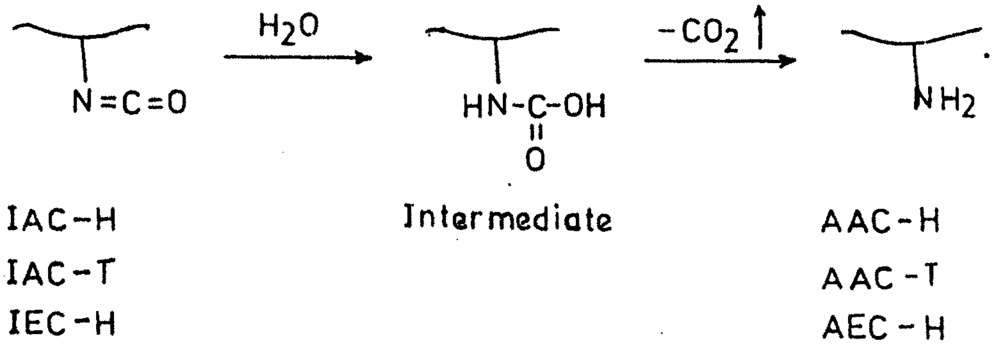


The products, cellulose derivatives with pendant isocynato groups, were referred to as isocyanato acetyl cellulose (IAC-H or IAC-T) or isocyanato ethyl cellulose (IEC-H), where the last letter H or T represent the use of either HMDI or TDI, respectively.

Reaction of AC with HMDI was studied by varying reaction parameters in order to optimize the reaction conditions. Because of the high reactivity (moisture sensitivity) of the diisocyanates, all manipulations were performed under nitrogen atmosphere. As a first attempt, the reaction was carried out in toluene under nitrogen atmosphere using dibutyltindilaurate (DBTDL) as the urethanation catalyst. Reaction time was varied from 1 to 6 h keeping reaction temperature at 40°C in all the cases. AC is insoluble in toluene and therefore the reaction proceeded in heterogeneous medium,which offered the advantage of easy removal of excess of isocynate reagent, after end of the stipulated reaction time. All these reactions were repeated using benzene as the reaction medium.However, the extent of urethanation was found to be low in all these cases as judged by the intensity of absorption due to - N=C=O group at2273 cm^{-1}in the IR spectra of the products. The low extent of urethanation was attributed to the nonpolar nature and the inability of toluene or benzene to swell AC. Therefore, to overcome these problems a polar solvent dichloromethane was used to react AC/EC with HMDI/TDI. The detailed procedure is described in Section 3.2.1

IR spectra of AC, EC, IAC-H, IAC-T, and IEC-H are shown in Fig. 1. The products, IAC-H, IAC-T and IEC-H show a strong and sharp band at 2273 cm $^{-1}$ indicating the presence of free isocyanate group.Dichloromethane is a polar solvent and both AC and EC are soluble in it. Therefore , the reaction proceeds in homogeneous medium which accounts for the greater extent of urethanation. The peak at 2273 cm^{-1} is absent in the IR spectra of AC and EC. Because of the homogeneous nature of the reaction medium, removal of excess of diisocyanate and washing of the product is a bit more difficult compared to the system where benzene or toluene were used. However, the greater extent of urethanation outweighs the disadvantage in workup. The products containing pendant isocyanate groups were washed thoroughly with, dry hexane to remove traces of unreacted diisocyanate, dried at room temperature under vacuum, and stored in an inert atmosphere. IR spectra of IAC-H, IAC-T and IEC-H taken after two weeks of storage in an inert atmosphere did not reveal any significant decrease in the intensity of the $-N=C=O$ peak at 2273 cm^{-1}, indicating that they were reasonably stable. However, they were immidiately used for subsequent reactions in order to avoid any loss in the isocyanate functionality.

Cellulose derivatives with pendant amino groups were obtained by reacting IAC-H, IAC-T, and IEC-H with excess of water. Hydrolysis of isocyanate group produces carbamic acid group as an intermediate, which upon loosing carbon dioxide is converted in to amino groups.



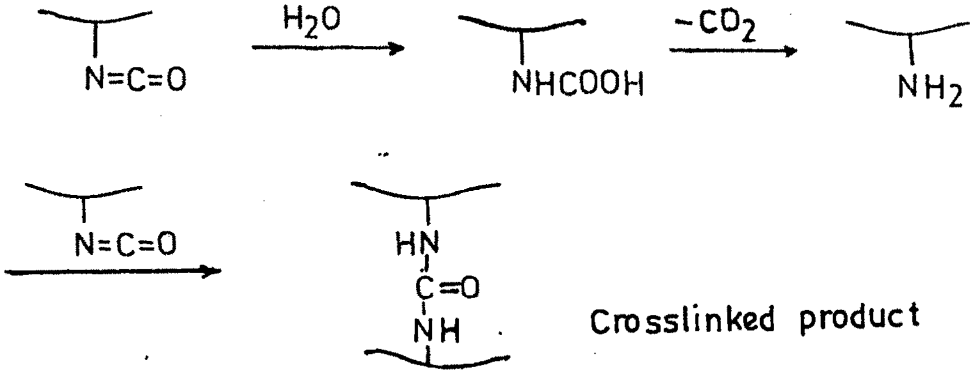
IR spectra of amino acetyl cellulose (AAC-H and AAC-T) and amino-ethyl cellulose (AEC-H) are included into Fig.1, which reveal complete disappearance of isocyanate peak at 2273 cm^{-1}, which was present in their respective precursors, indicating that hydrolysis of isocyanate group was complete. Also, N-H stretching vibrations appear at 3350-3400 cm^{-1}. The presence of primary amino groups was further confirmed in case of AAC-T by its diazotization followed by reaction with β-naphthol to form orange coloured dye. AAC-H and AEC-H could not be tested in the same manner since they contain aliphatic amino groups in contrast to the aromatic amino groups of AAC-T.

Amino group capacity of the above polymers was determined by chemical method, that is by titration and also by nitrogen analysis. The results are given in the Table 2.1.

Table 2.1 : Amino group capacity of polymer supports with pendant amino groups.

Polymer Support	Amino group capacity , meq / g Calculated	by titration	by N analysis
AAC-H	1.47	1.04	2.30
AAC-T	1.46	0.76	1.98
AEC-H	1.65	0.63	2.15
A-PS	1.9 (Ref68)	1.1	-

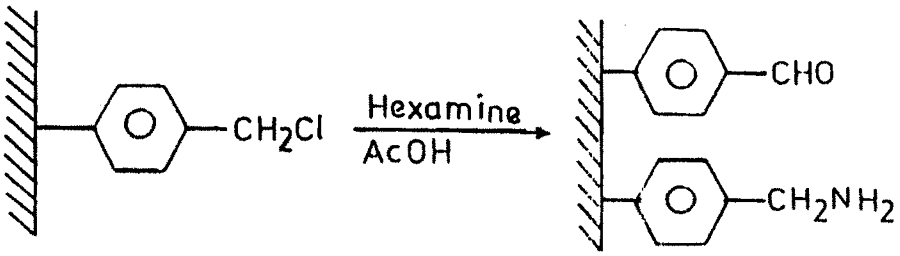
The values of amino group capacity determined by titration are lower than the calculated values in each case. This is probably bacause that all of the amino functions are not accessible to the reagents used in titration. Though the starting polymers AC/EC were linear polymers and soluble in common organic solvent (dichloromethane, for example), the products of urethanation, IAC-H, IAC-T, and IEC-H were insoluble in all solvents indicating that crosslinking occured during urethanation, despite of using the diisocyanates in excess. Additional crosslinking may also occur during the conversion of isocyanate groups to amino groups. Amino group formed may react with isocyanate group till to be hydrolyzed, to form crosslinked structures.



Thus, the low amino group capacity values by titration may be due to :(i) "wastage" of some amino function in crosslinking side reaction, and (ii) decrease in accessibility owing to the crosslinked structure. The values of amino group capacity determined by nitrogen analysis are higher compared to the calculated values,probably because of side reaction of isocyanate groups such as biuret and allophonate formation.

2.2 Polystyrene Support Containing Pendant Amino Groups.

Aminomethylpolystyrene (A-PS) was obtained from DVB crosslinked chloromethylated polystyrene by the Delepine reaction with hexamethylenetetramine (68)

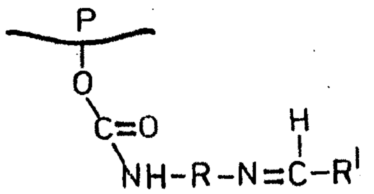


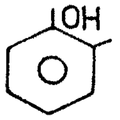
Amino group capacity of A-PS, determined by titration, was found to be 1.1 meq/mol.

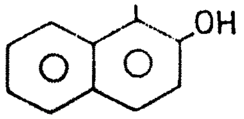
2.3 Polymer Supported Schiff Bases

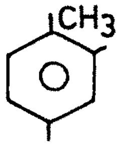
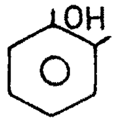
AAC-H, AAC-T and AEC-H, were reacted with aldehyde or ketone to obtain polymer anchored Schiff Bases. Salicylaldehyde, 2-hydroxy-1-naphthaldehyde, and diacetylmonoxime were used as the carbonyl compounds to condense with the pendant amino groups of the polymer supports. The general procedure is given in Section (3.3).

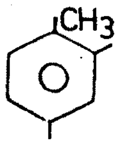
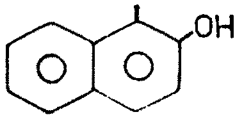
The carbonyl compounds were used in excess, about five times the required stoichiometry. The reaction was carried out in dimethyl acetamide. In some cases yields were lower than expected. This is probably bacause that DMAc is a good solvent for cellulose derivatives and even though the materials were crosslinked and insoluble, it is possible that a part of product remained in solution even after addition of ethanol.The structure of these polymers is shown below.

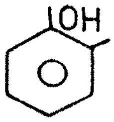


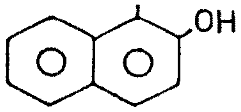
AAC-H-1 P = AC R = $-(CH_2)_6-$ R^1 = 

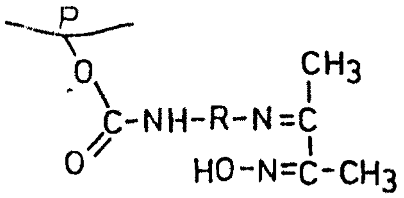
AAC-H-2 P = AC R = $-(CH_2)_6-$ R^1 = 

AAC-T-1 P = AC R =  R^1 = 

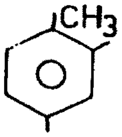
AAC-T-2 P = AC R =  R^1 = 

AEC-H-1 P = EC R = $-(CH_2)_6-$ R^1 = 

AEC-H-2 P = EC R = $-(CH_2)_6-$ R^1 = 



AAC-H-3 P = AC R = $-(CH_2)_6-$

AAC-T-3 P = AC R = 

AEC-H-3 P = EC R = $-(CH_2)_6-$

The polymers syntesized along with the results of nitrogen analyses are given in Table 2.2

Table 2.2 POLYMER SUPPORTED SCHIFF BASES

Sr.No.	Polymer	N% calculated	N% Found
1	AAC-H	4.14	6.69
2	AAC-H-1	3.73	2.95
3	AAC-H-2	3.56	2.97
4	AAC-H-3	5.15	-
5	AAC-T	4.10	5.59
6	AAC-T-1	3.80	2.95
7	AAC-T-2	3.67	5.31
8	AAC-T-3	4.86	5.49
9	AEC-H	4.62	6.08
10	AEC-H-1	4.27	5.59
11	AEC-H-2	4.48	-
12	AEC-H-3	5.50	5.64

Similarly A-PS was also condensed with salicylaldehyde, 2-hydroxy-1-naphthaldehyde and diacetyl monoxime.

2.4 Characterization

Establishing the detailed structure of these polymer is difficult because of their insolubility in all, common solvents and because of the unavoidable complex side reactions that occur during the reactions involving highly reactive diisocyanates.

A difference between the observed and the calculated values of nitrogen analysis is not uncommon in systems involving modifications of crosslinked polymers(68).Except when DAMO is used, the nitrogen content of the polymeric Schiff bases is expected to be lower than that of the polymer support. This is, indeed, found to be the case.

IR spectra of the Schiff bases anchored onto AACH are shown in Fig.2. AACH revealed a high intensity broad band at 3408 cm^{-1} with a large hump at 3500 cm^{-1} characteristic of N-H stretching vibrations. Aliphatic C-H stretch appear at 2942 cm^{-1}. Carbonyl stretching of urethane group is seen at 1744 cm^{-1} with a very small shoulder at about 1625 cm^{-1} which may be due to the aliphatic primary amine groups (73). C-O-C skeletal valence vibrations, characteristics of cellulosics, are seen at 1040-1050 cm^{-1}. A comparison of the IR spectrum of IACH with those of the polymeric Schiff bases, AAC-H-1, AAC-H-2, and AAC-H-3 revealed many common features including urethane carbonyl stretching at 1740 cm^{-1} and C-O-C skeletal valence vibrations of anhydroglucopyranose rings. However, some subtle differences are also observed. The peak due to N-H stretching at 3400 cm^{-1} has 'almost' disappeared indicating that the primary amino groups have reacted. The most significant feature of the IR spectra of polymeric Schiff bases is the appearance of small but sharp peak at 1620 cm^{-1} with a shoulder at 1610 cm^{-1} in contrast to a very small shoulder at 1625 cm^{-1} in case of AAC-H. The peak at 1620 cm^{-1} has been ascribed to >C=N- stretching(71). In addition, AACH-1 and AACH-2 revealed a sharp peak of medium intensity at 1150 cm^{-1} due to 1,2-disubstituted aromatic structure, which was absent in AACH. Thus, the large decrease in the intensity of N-H stretching band at 3400 cm^{-1} and the appearance of sharp peak of low to medium intensity at 1610-1620 cm^{-1} and at 1150 cm^{-1} confirms the formation of Schiff bases. The intensity of >C=N- stretching at 1610-1620 cm^{-1} is much greater in case of AACH-3 compared that for AACH-1 and AACH-2.This is due to presence of >C=N-OH (oxime) group in AACH-3.

IR spectra of AAC-T and the corresponding Schiff bases AAC-T-1, AAC-T-2 and AAC-T-3 are shown in Fig.3. The carbonyl urethane stretch at 1740 cm^{-1} appeared as a much broad peak in the IR spectrum of AACT while it is much sharper for polymeric Schiff bases, especially in the case of AACT-1. The strong N-H stretching absorption band at 3400 cm^{-1} present in IR spectrum of AACT disappeared completely in AACT-1 and decreased in intensity to a great extent in the case of AAC-T-2 and AACT-3.

The >C=N- stretching absorption characteristic of Schiff bases is seen in AACT-1, AACT-2 and AACT-3 and is absent in AACT. In AACT-1 and AACT-2 the peak appears at 1640 cm^{-1} while in case of AACT-3 it appears at 1625 cm^{-1}. Schiff bases anchored onto AACH (Fig.2) show the >C=N- stretching at 1620 cm^{-1}. The shifting of this peak in various Schiff bases can be explained on the basis of substituents on the >C=N- group. AACH was obtained by reacting AC with HMDI and AACT was obtained by reacting AC with TDI. Therefore, the nitrogen of >C=N- group is linked to aliphatic methylene groups in the former and aromatic nucleus in the latter case. Linking of >C=N- to aromatic nucleus increases its double bond character and increase in double bond character shifts the absorption at higher wavenumber. This explain the appearance of >C=N stretching vibrations at 1640 cm^{-1} in AACT-1 and AACT-2 and at 1620 cm^{-1} in AACH-1, AACH-2 and AACH-3. In AACT-3 the band is of considerably high intensity and appears as in

AACH-3, as a doublet, which is probably due to the presence of oxime group.

As in the case of AACH-1 and AACH-2, AACT-1 and AACT-2 revealed a peak at 1150cm^{-1} which has been ascribed to the presence of 1,2 disubstituted aromatic structures. The intensity of peaks at 1640 cm^{-1} (>C=N-) and 1150 cm^{-1} (1,2-disubstituted aromatics) is low in AACT-2 compared to that of AAC-T-1. Similarly, while the intensity of N-H absorption at 3400 cm^{-1} decreased considerably in AAC-T-2 indicating that most of the amino groups have been reacted, it disappeared completely in AACT-1. This leads to the inference that the extent of Schiff base formation is greater in AACT-1 than in AACT-2.

Ethyl cellulose with pendant amino groups was used as another cellulosic support to anchor Schiff bases. IR spectra of AECH,AECH-1,AECH-2 and AECH-3 are shown in Fig.4. Among the common features in these spectra and the other cellulosic polymers used in this study is the presence of C-O-C skeletal valence vibration appearing as a broad peak at around 1050 cm^{-1}. Urethane carbonyl stretching appears in the 1710-1730 cm^{-1} range. In the IR spectra of the polymers based on AACH and AACT the carbonyl peak was seen at the slightly higher wavenumber (1740 cm^{-1}) and was of much higher intensity. This was because of the contribution from the ester groups of acetyl cellulose.

The intensity of the peak due to N-H stretching vibration decreased to some extent in the spectra of AECH-1 and AECH-3 compared to that in AECH, while it disappeared completely in AECH-2 indicating that Schiff base formation occured, to more or less extent, in all these cases.

A peak at around 1620 cm^{-1} is seen in all the four spectra shown in Fig.4. This peak has been attributed to >C=N- group of Schiff bases in case of AECH-1, AECH-2, and AECH-3 and may be attributed to free amino group in case of AECH, though it is not visible in the spectra of AACH (Fig.2) and AACT (Fig.3). The much higher intensity of the peak (at 1620 cm^{-1}) in the spectra of AECH-1, AECH-2, and AECH-3 compared to that in AECH indicates the formation of Schiff bases.

To dispel the doubts about Schiff base formation,"difference" spectra were obtained using the information storage and data analysis facility of the IR spectrophotomer. IR spectra of the samples after scanning were stored in the memory of the instrument and "difference" spectra were obtained by substracting the spectrum of AECH from that of Schiff bases. An example the "difference"spectrum is shown in Fig.5 where a IR spectrum of AECH was substracted from that of AECH-1 (condensation product of salicylaldehyde and AECH). The spectrum confirms the formation of Schiff base. All the peaks common in AECH and AECH-1 such as those arising from cellulosic backbone, urethane linkage, etc, have disappeared and new peaks due to the condensation reaction of salicylaldehyde with AECH are seen in the spectrum. The peak at 1619 cm^{-1} is due to >C=N- stretching vibrations and confirms the formation of Schiff base. The peaks at 1370 and 763 cm^{-1} are the prominent peaks seen in the IR spectrum of salicylaldehyde.

Bacause of availability, renewability and low cost, many natural polymers including cellulose have been modified in many ways to yield chelating resins selective for almost every type of metals (34). However, no work has been reported on the use and modification of cellulose derivatives such as acetyl cellulose, ethyl cellulose in the manner undertaken in the present investigation to yield materials potentially useful as polymer supports in the preparation of chelating resins. Therefore it would be more in order to compare the performance of these materials with that of a more commonly used polymer support anchored with the same type of chelating ligands.DVB crosslinked chloromethylated polystyrene is one of the most commonly used polymer support. In the present investigation, polystyrene supported Schiff bases, A-PS-1, A-PS-2, and A-PS-3 (see Section 3.3) were synthesized following an earlier report(68).Of these polymer supported Schiff bases A-PS-1 has been reported in reference (68).

Figure 6 depicts IR spectra of polystyrene anchored Schiff bases APS-1, APS-2,and APS-3, which show absorptions at 1600 cm^{-1} (>C=N str) indicating the formation of Schiff bases.

2.5 Adsorption of Metal Ions

well-known

Schiff bases are welknown and most widely used ligands for complexation with metal ions. The extent of complexation is a function of temperature and p^H of the solution. When the Schiff bases are anchored onto polymer, the extent of complexation further depends upon the microenvironment of the resin such as hydrophilicity/hydrophobicity balance, polymer backbone/ligand interactions etc. The main objective of the present investigation was to check the feasibility of use of cellulosic backbone in preparation of chelating resins for metal ion separation. Therefore, a detailed study of the effect of various parameters such as p^H, temperature on the metal ion adsorption was beyond the scope of present investigation.

To determine metal ion binding capacity, 20 ml of metal ion solution (400 μg/ml) was added to the polymeric Schiff bases,and stirred for 20 min. The concentration of metal ion in the supernatant clear solution was determined by complexometric titration. The p^H of the solution was 5.3 in all cases. The selection of optimum p^H was based on the earlier work of Sreekumar et al. (68). In some cases the polymer-metal complexes were filtered, washed copiously with deionized water, and metal ions were desorped using 2N HCl, and their concetration was determined by complexometric titration. The values obtained by the two methods were in good agreement.

The results of metal adsorption experiments are given in Table 2.3. It is seen from the Table 2.3. that the amount of metal adsorbed ranges from 0.12 to 0.46 m mol/g depending upon the metal ion in question. For Ni^{++} and Zn^{++} the amount of metal ion complexed was low in the range of 0.12 to 0.20 mmol/g. While for the remaining metal ~~in~~ ions it ranged from 0.3 to 0.46 mmol/g. The results are in good agreement with earlier reported work (68,69).

It also seems that the polymer backbone had negligible role in determining the extent of complexation. This is in contrast to the generally acknowledged role of polymer matrices on the performance of polymer anchored reagents, catalysts and ligands. In the present investigation two different diisocyanates were used in the syntheses of the polymer supported Schiff bases. The polymer backbone and the Schiff base are separated by an urethane linkage and a single aromatic ring when TDI was used (AACT-1, AACT-2, and

AACT-3) while they are separated by an urethane linkage and six methylene units when HMDI was used (AACH-1, AACH-2, AACH-3, AECH-1,AECH-2,AECH-3) as a reagent to introduce pendant amino groups onto AC/EC. It appears from the results shown in Table 2.3 that the "Spacer effect" has been negated by the polar interactions of urethane groups.

Table 2.3 Metal Ion Adsorption by Polymer Anchored Schiff bases

Sr. No.	Polymer	Metal Ions m mol/g				
		Cu^{+2}	Co^{+2}	Ni^{+2}	Zn^{+2}	Mn^{+2}
1	**AAC-H-1**	**0.46**	**0.37**	**0.14**	**0.2**	**0.35**
2	**AAC-H-2**	**0.31**	**0.34**	**0.15**	**0.21**	**0.39**
3	**AAC-H-3**	**0.32**	**0.40**	**0.17**	**0.21**	**0.35**
4	**AAC-T-1**	**0.36**	**0.36**	**0.17**	**0.19**	**0.42**
5	**AAC-T-2**	---	**0.43**	**0.12**	---	**0.41**
6	**AAC-T-3**	**0.36**	**0.3**	**0.13**	**0.21**	**0.38**
7	**AEC-H-1**	**0.34**	**0.45**	**0.14**	**0.13**	**0.39**
8	**AEC-H-2**	**0.36**	**0.35**	**0.17**	**0.14**	**0.37**
9	**AEC-H-3**	**0.35**	**0.35**	**0.14**	**0.16**	**0.35**
10	A-PS-1	0.32 (0.48)[a]	0.39 (0.93)[a]	0.15 (0.03)[a]	0.12 (0.12)[a]	0.38
11	A-PS-2	0.35	0.37	0.15	0.09	0.35
12	APS-3	0.34	0.38	0.18	0.15	0.35

[a] **Values from reference 68.**

Also, it may be noted that the polymer supports used were in dense form and not in a well defined microporous or macroporous bead form where the spacer group has a prominent role to play.

Polymer-metal complex formation was further confirmed by IR spectroscopy. IR spectra of AACH-2, AACH-2/Cu^{2+} complex, AACH-3 and AACH-3/Cu^{++} complex are shown in Fig.7. Coordination reduces the electron density on nitrogen of azomethine linkage and there fore expected to shift the absorption at lower frequency.In the present case, such a shifting of >C=N absortion could not be conclusively detected. However, the intensity of the absorption at about 1620 cm^{-1} (>C=N stretching) is decreased to a great extent in the IR spectrum of AACH-2/Cu^{++} complex while it disappeared almost completely in the IR spectrum of AACH-3/Cu^{++} complex compared to that in the IR spectra of AACH-2 and AACH-3, respectively. This indicates the involvement of >C=N- group in complex formation. Furthermore a weak peak at 550 cm^{-1} is seen in the IR spectrum of AACH-2/Cu^{++} complex indicating Cu-N bond formation (69). Similar inference can be drawn from the IR spectra of AACH-2 and AACH-2/Mn^{++} complex shown in Fig.8.

2.6 Conclusion

AC and EC were modified by reaction with HMDI/TDI to obtain polymers with pendant isocyanato and subsequently, amino groups. The amino group capacity, determined by titration, ranged from 0.63 to 1.04 meq.g^{-1}. They were subsequently condensed with salicylaldehyde, 2-hydroxy -1-naphthaldehyde,and diacetylmonoxime to yield polymer anchored Schiff bases. Schiff base formation was confirmed mainly by appearance of absorption peak at 1620 (or 1640) cm^{-1},(>C=N stretching) in the IR spectra of the Schiff base resins. The polymer Schiff bases were examined for complex formation with transition metals. The metal binding capacity was found to range between 0.12 to 0.2 mMol/g for Ni^{++} and Zn^{++} and between 0.3 to 0.46 for Cu^{++}, Co^{++}, and Mn^{++}. The metal binding capacity was found to be unaffected by the type of polymer backbone. This has been attributed to the presence of polar linkage in the spacer group and to the use of polymer supports in the dense form rather than in bead form. DVB crosslinked Polystyrene was also used as polymer support for comparison purpose.