Deanship of Graduate Studies

Al-Quds University

Analysis and Characterization of Polyacrylamide Metal Complexes

Sami Atallah Mahmoud Makharza

M.Sc. Thesis

Jerusalem-Palestine

2005

Analysis and Characterization of Polyacrylamide Metal Complexes

By

Sami Atallah Mahmoud Makharza

B.Sc. Chemistry and Chemical
Technology (2001)

Al-Quds University
Palestine

Supervisor: Dr. Wadie Sultan

Co supervisor: Dr. Hasan Dweik

A THESIS

Submitted in partial fulfillment of requirements for the degree of
Master of Applied and Industrial Technology
Department of Chemistry & Chemical Technology
Deanship of Graduate Studies
Al-Quds University

September, 2005

Program for Postgraduate Studies in Applied and Industrial Technology
Faculty of Science and Technology
Department of Chemistry & Chemical Technology
Deanship of Graduate Studies

Analysis and Characterization of Polyacrylamide Metal Complexes

Student Name: Sami Atallah Mahmoud Makharza
Registration No: 20111567
Supervisor: Dr. Wadie Sultan
Co-supervisor: Dr. Hasan Dweik

Master thesis submitted and accepted, Date 7/9/2005

The names and signatures of the examining committee members are as follows:

1- Head of committee Signature

2- Internal Examiner Signature

3- External Examiner Signature

Al-Quds University

2005

TO MY MOTHER

&

MY BROTHERS

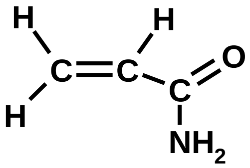
CHAPTER ONE

INTRODUCTION

I. Introduction

I.1 Acrylamide

Acrylamide is a white crystalline solid with a melting point of 84.5 °C[1]. It is soluble in many polar solvents, including acetone, ethanol and water, where 215.5 g can be dissolved in 100 mL of water at 30 °C. Acrylamide contains two principle functional groups, the vinylic carbon-carbon double bond and an amide group (scheme 1.1).

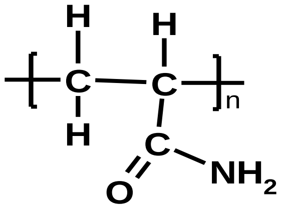


Scheme 1.1: Structure of Acrylamide

Acrylamide is monomer formed from the hydration of acrylonitrile with sulfuric acid at tempreatures between 90 and 100 °C. More recently by catalytic hydration using copper catalyst [2]. The electron deficient double bond of acrylamide is susceptible to a wide range of chemical reactions including nucleophilic additions, and radical reactions [3]. Acrylamide has been classified by the Environmental Protection Agency (EPA) as a Group B2 probable carcinogen [4].

I.2 Polyacrylamide

Polyacrylamide (PAam) is a water-soluble polymer. PAam is the first polymer for which the volume phase transition in the polymer gel was observed [5]. PAam is known within the research community for its use as a cross-linked hydrogel for size-based electrophoresis separation of proteins and nucleic acids, these methods are known as polyacrylamide gel electrophoresis (PAGE). PAam has a hydrophobic main chain and a hydrophilic side group. As can be seen in scheme 1.2, one may consider PAam to be a polyethylene main chain with $-CONH_2$ side groups [6].



Scheme 1.2: Structure of Polyacrylamide

I.2.1 Physical and Chemical Properties of Polyacrylamide

The physical properties of polyacrylamide are influenced by copolymerizing with different vinylic monomers. One of the most useful examples is produced by copolymerizing acrylamide with sodium acrylate to form an ionic polymer at normal pHs [7]. The process of polymerizing acrylamide affords polyacrylamide that has completely different chemical and biological characteristics to the monomer.

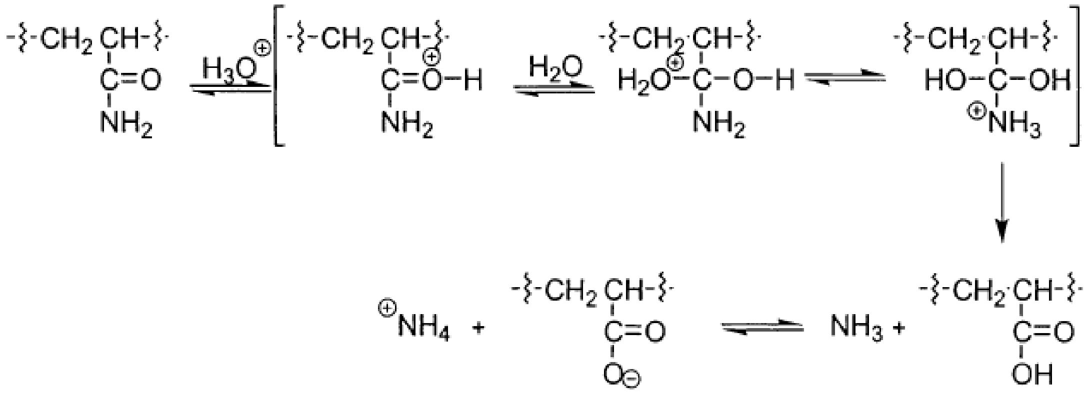
Chemically the reactivity of acrylamide is due to the electron deficient double bond, but the polymerization process to form polyacrylamide removes the double bond and as such, polyacrylamides are relatively chemically inert under normal conditions. Unlike acrylamide, polyacrylamide do not undergo nucleophilic addition across the backbone since they possess only a C-C single bond. The amide group of polyacrylamide and carbonyl group can undergo reactions such as hydrolysis, and dehydration [3].

I.2.2 Stability of polyacrylamide via different temperatures

Below the temperatures of about 200 °C, polyacrylamides are thermally stable and undergo very little physical change apart from a slight mass loss. This slight weight loss is probably due to absorbed water from the environment and other volatile impurities [8, 9]. At temperatures above 200 °C, polyacrylamide begins to undergo irreversible chemical changes resulting from thermal degradation [10]. Above 300 °C polyacrylamide is initially characterized by the decomposition of imides to form nitriles and the release of volatiles such as CO_2 and H_2O [11, 12]. At higher temperatures, the predominant reactions are random bond scission of the polymeric backbone forming long chain hydrocarbons [10, 13].

I.2.3 Hydrolysis of Polyacrylamides under acidic and basic conditions

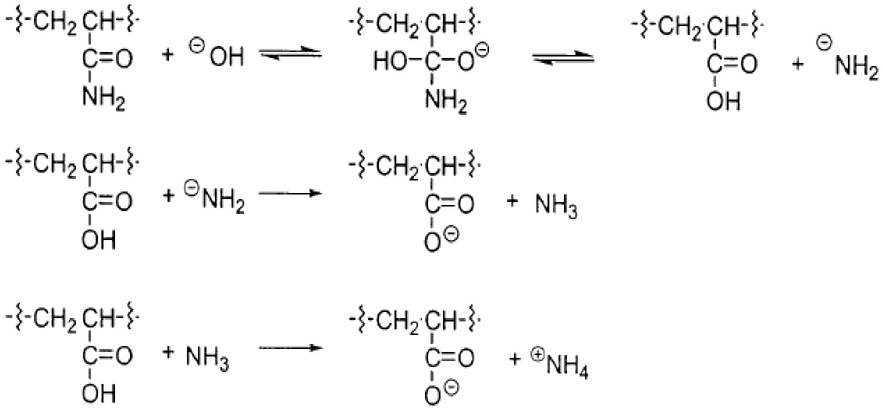
Polyacrylamides undergo hydrolysis under acidic conditions to produce poly (acrylamide-coacrylic acid). Forcing conditions of low pH and long reaction times can provide complete hydrolysis of all the amide groups. The reaction involves the nucleophilic addition of water to the protonated amide, followed by the elimination of NH_3 [14]. The proposed reaction hydrolysis of polyacrylamide is presented in scheme 1.3.



Scheme 1.3: Hydrolysis of PAam under acidic condition.

Also under alkali conditions polyacrylamides are undergoing hydrolysis at moderately low temperatures (60-100 °C). The reaction involves the nucleophilic addition of hydroxide to the amide carbonyl, followed by loss of the amide ion ($-NH_2$) to afford an acrylic acid residue [15, 16].

The amide ion then removes a proton from the acrylic acid to form more stable carboxylate anion and ammonia [14].The proposed reaction hydrolysis of polyacrylamide is presented in scheme 1.4.



Scheme 1.4: Hydrolysis of PAam under basic condition.

The hydrolysis reaction is mainly irreversible as the amide anion readily removes a proton from the acrylic acid residue rather than attack a carbonyl carbon atom, and the carboxylate anion will be unsusceptible to nucleophilic attack from both NH_3 and NH_2 [17,18].

I.2.4 Applications of polyacrylamide

Polyacrylamides (PAam) are among the most widely used synthetic polymers. They are often used in different fields such as:

1. Water treatment
2. Papermaking
3. Petroleum recovery
4. Mineral processing
5. Soil conditioning, etc.

Determining PAam concentration is an important factor for its successful application, since properties of PAam solution, such as rheology, adsorptions, and flocculating ability, are highly concentration dependent [19]. Many techniques have been developed to quantify PAam in aqueous solution [20, 21].

These methods involved of analytical approaches, such as viscosity measurement, flocculation, total organic carbon, N-bromination of amide groups followed by starch triiodide complex measurement, conversion of amide groups to amines which are then determined by fluorescence spectrometry and amide hydrolysis with ammonia detection [22].

I.2.5 Electrical conductivity of polymers

Plastic is used as insulation around the copper wires in ordinary electrical cables. Yet, the Prize Winners of the 2000 Nobel Prize in Chemistry: Alan Heeger, Alan G. MacDiarmid and Hideki Shirakawa, were rewarded for their revolutionary discovery that plastic can be made electrical conductivity after certain modifications.[23]

For a polymer to be electrically conductive it must "imitate" a metal, the electrons in the bonds must be freely mobile and not bound fast to the atoms.

The exciting idea of combining the mould ability and low weight of plastics with the conductivity of metals has prompted intensive development. Since the conductivity can be varied over a very broad area, from poor semi-conductors to metallic-level conductivity, many commercial uses present such as batteries, condensers, anti-static materials and anti-corrosion substances. Now the most intensive development is aimed at conjugated polymers in their un-doped, semiconductive state. This is because it was discovered ten years ago that some conjugated polymers exhibit electro-luminescence, they glow when a voltages passes through them.

Many applications are predicted for luminescent plastic. We shall soon be seeing the first practical use in light displays in mobile telephones and on information boards. In a few years flat TV screens in luminescent plastic may have become a reality.[24, 25]

According to Ohm‘s Law, the current (I) flowing in substrate is proportional to the potential drop along the substrate: $V = IR$, where R, the resistance of the substance, depends on its dimensions. The resistivity (ρ) is defined to be the proportionality constant between the electric field (E) at a point in the substance and the current density (j) that it induces.

$$E = \rho j \qquad (1)$$

The current density j is a vector, parallel to the flow of charge, whose magnitude is the amount of charge per unit time crossing a unit area perpendicular to the flow.

Thus if a uniform current (I) flows through a substance of thickness (L) and cross sectional area (A), the current density will be $j = I/A$, Since the potential drop across the substance will be

$V = EL$

Eq. (1) gives $V = I \rho L/A$ and hence

$R = \rho L / A$ ……….. (2) [26].

Different voltages (*V*) are applied to the outer two probes and the resulting current (*I*) is measured by connecting a Keithley electrometer amplifier in series with inner two probes.

Surface Conductivity (σ) was evaluated using the equation

$\sigma = I/2\pi sV$ mhos cm^{-1}……….. (3)

Where s is the spacing between two probes [27].

The conduction in polymeric systems is to classify materials according to the carriers responsible for conduction.

1. The first species are ionic carriers; these are distinct ionically charged chemical entities: hydrogen or hydronium ions, acids, bases, salts, metallic impurities due to residual catalyst, or species intended to be electronic dopants but which end up as mobile ionic species. Ionic

conduction occurs throughout the entire structural range, from polycrystalline to amorphous, and requires actual mass transport [28].

2. The second species are localized electronic excited states. These energy states although they can contribute to electron spin resonance signals if their spins are unpaired, are localized on a single molecular residue or repeat unit and hence cannot participate in conduction [29].

3. The third species is migratory localized ionic states, particularly anions. Although these states are truly ionic, the transport mechanism responsible for conduction is electronic [30, 31].

Conductivity (σ) is expressed in units of siemens (S) per centimeter. (A siemen is a reciprocal ohm) The electrical conductivities of the conducting polymer systems now range from that typical of insulators ($\sigma < 10^{-8}$ S/cm) to that typical of semiconductors ($\sigma = 10^{-7} - 10^{-1}$ S/cm) and conductors ($\sigma > 10^{2}$ S/cm. [32, 33, 34]

I.2.6 Thermal analysis of polymers

Thermal analysis can be used to characterize the physical and chemical properties of polymers under specific conditions.[35] The thermal parameters of a polymer, such as glass transition temperature (Tg), melting point (Tm) and crystalline point (Tc) can be determined using differential scanning calorimeter (DSC).[36]

The glass transition temperature is the most important characteristics of amorphous state in the polymer during its transition from solid to liquid.

When an amorphous glass polymer is heated, the kinetic energy of the molecules increases, as temperature is increased further, the polymer loses its glasslike properties and assumes those more commonly identified with a rubber.

The temperature at which this takes place is called glass transition temperature (Tg). If heating is continued, the polymer will lose its elastomeric properties, and the temperature at which this takes place is called melting temperature (Tm).[34]

The glass transition temperature of polymer thin films has important attention because of the importance thermal properties in the technological applications of thin films. [37]

The association of metal ions in polymer matrixes generates charge carrier ions and increases the rigidity of polymer chain up to moderately high metal salt concentration, resulting in a higher Tg. [38]

I.3 Transition metals

The three series of elements arising from the filling of the 3d, 4d and 5d shells, and situated in the periodic table following the alkaline earth metals, are commonly described as “transition elements”, though this term is sometimes also extended to include the lanthanide and actinide (or inner transition) elements.

These elements exhibit a number of characteristic properties which together distinguish them from other groups of elements:

1. They are lustrous and deformable and have high electrical and thermal conductivities.
2. Most of them display numerous oxidation states which vary by steps of 1 rather than 2 as is usually the case with those main-group elements which exhibit more than one oxidation state.
3. They have an unparalleled propensity for forming coordination compounds with Lewis bases.

I.3.1 Types of Ligand

Ligands are most conveniently classified according to the number of potential donor atoms which they contain and are known as uni-, bi-, ter-, quadri-, quinqi- and sexi-dentate accordingly as the number is 1, 2, 3,4,5 or 6. Bidentate ligands are frequently chelating ligands and, with the metal ion, produce chelate rings which in the case of the most commonly occurring bidentate ligands are 5- or 6-membered [39].

I.4 polymer metal complexes

Metal complexation is a process by which certain transition metal ions coordinate with organic functional groups like carbonyl, amine groups through ionic bonds, coordination bonds, and ion dipole interactions to form what we call complexes having many interesting properties and applications.

I.4.1 Application of metal polymer complexes

Metal complexation polymers are used in wastewater treatment for selective removal of toxic metal ions [40-43] and to improve the thermal properties of polymers [44-46]. An important application of polymer-metal complexes is in the area of catalysis. Catalytically active organic polymers can be obtained through the coordination of certain transition metal ions with functional groups on the polymers [47, 48]. Recently, metal complexed stimuli responsive polymer gels have been used to produce smart catalysts, which combine the advantages of homogeneous catalysis such as high activity and high selectivity with those of heterogeneous catalysis such as long life and easy separation, the catalytic function of polymer-metal complex depends on the structure of the complexes [49-51].

I.5 Aim of study

1. Metal complexation with organic functional groups of polyacrylamide through ionic bonds, coordination bonds, and ion dipole interaction to form organometallic hybrids.
2. To characterize the PAam-M^{+2} complexes using different methods FTIR, UV-Visible spectroscopy and DSC.
3. Creation of new material PAam-M^{+2}. This creation depends on various metal ions Fe^{+2}, Cu^{+2}, Co^{+2}, Ni^{+2} capable of complexation with PAam film.
4. To improve thermal and conductive properties of polyacrylamide.

CHAPTER TWO

EXPERIMENTAL

II. Experimental

II.1 Chemicals

Polyacrylamide (PAam, Mwt 5000,000), Copper (II) chloride dihydrate ($CuCl_2.2H_2O$), Iron (II) chloride tetrahydrate ($FeCl_2.4H_2O$), Cobalt (II) fluoride tetrahydrate ($CoF_2.4H_2O$), Nickel (II) sulfate hexahydrate ($NiSO_4.6H_2O$), Hydrochloric acid 32% by weight, Sodium hydroxide. All of the above chemicals were of analytical grade and were purchased from Sigma-Aldrich Co. All solutions were prepared in deionized water.

II.2 Instruments

1. Fourier transform infrared spectrophotometer (Testscan shimadzu FT-IR 8000 series).
2. A Perkin-Elmer lambda 5 UV-visible spectrophotometer.
3. Differential Scanning Calorimeter (DSC).
4. Two point probe system.
5. Atomic Force Microscope (AFM).

II.3 Procedure

II.3.1 Preparation of polyacrylamide film

To prepare PAam film 0.7104g of PAam was dissolved in 25ml deionized water, the solution was then poured into petridesh placed in an oven at 35^0C for 24h. Transparent film was obtained after evaporation of water.

II.3.2 Preparation of polyacrylamide – Metal film complexes

To prepare PAam-Metal complexes 0.7104g of PAam was dissolved in 25ml of deionized water, by gradual addition of metal solution to obtain the adequate concentrations of polyacrylamide - metal complexes, then the solutions were poured in petrideshs placed in oven at 35^0C for 24h. Transparent film was obtained. Different concentrations of PAam-Metal complexes are used to form of 2.5%, 5%, 7.5%, 10% and 25% (w/w) concentration as shown in Table2.1.

II.3.3 Preparation of PAam-Metal complexes for FTIR

About (5µL) a polyacrylamide-Metal complex solution was spread onto a silicon window then the window placed in oven at 35^0C for 24h. Water was completely evaporated with constant weight. Film of a few µm thicknesses was obtained.

II.3.4 Preparation of PAam-Metal complexes for conductivity measurements

To prepare the film of PAam-Metal complexes (5 µL) was added to mica substrate in oven for 24h at 35^0C to evaporate water.

II.3.5 Preparation of PAam-Metal complexes at different pHs

To prepare the film of PAam at different pHs 0.7104g of PAam was dissolved in 25ml of deionized water, then pH was adjusted by graduated addition of standard 0.1M NaOH and 0.1M HCl. using Jenway pH meter (3310) in the presence of buffer. Solutions of various pH (1.7-10.0) were prepared.

Table: 2.1 Explains the prepared PAam-Metal complexes.

Polymer – metal complexes		Concentrations of polymer - metal complexes Mass of PAam (gm) / Mass of Salts (gm)									
Polymer	**metal**	25%		10%		7.5%		5%		2.5%	
Polyacrylamide	**$NiSO_4.6H_2O$**	0.710	0.657	0.710	0.263	0.710	0.197	0.710	0.131	0.710	0.066
Polyacrylamide	**$CoF_2.4H_2O$**	0.710	0.422	0.710	0.169	0.710	0.126	0.710	0.084	0.710	0.042
Polyacrylamide	**$FeCl_2.4H_2O$**	0.710	0.497	0.710	0.199	0.710	0.149	0.710	0.099	0.710	0.048
Polyacrylamide	**$CuCl_2.2H_2O$**	0.710	0.426	0.710	0.170	0.710	0.127	0.710	0.085	0.710	0.042

CHAPTER THREE

RESULTS & DISCUSSION

III. Results and discussions

III.1 Analysis and Characterization of PAam and complexes using FTIR spectroscopy

Metal ion complexation of PAam functional groups were investigated towards Fe (II), Cu (II), Co (II) and Ni (II). The prepared complexes with 20-35µm thickness films were characterized using FTIR spectroscopy. **Figure 3.1** shows the FTIR spectrum of the PAam casting film on the Teflon surface, and **Table 3.1** gives the peak assignment of the FTIR spectrum of PAam. [52-54]

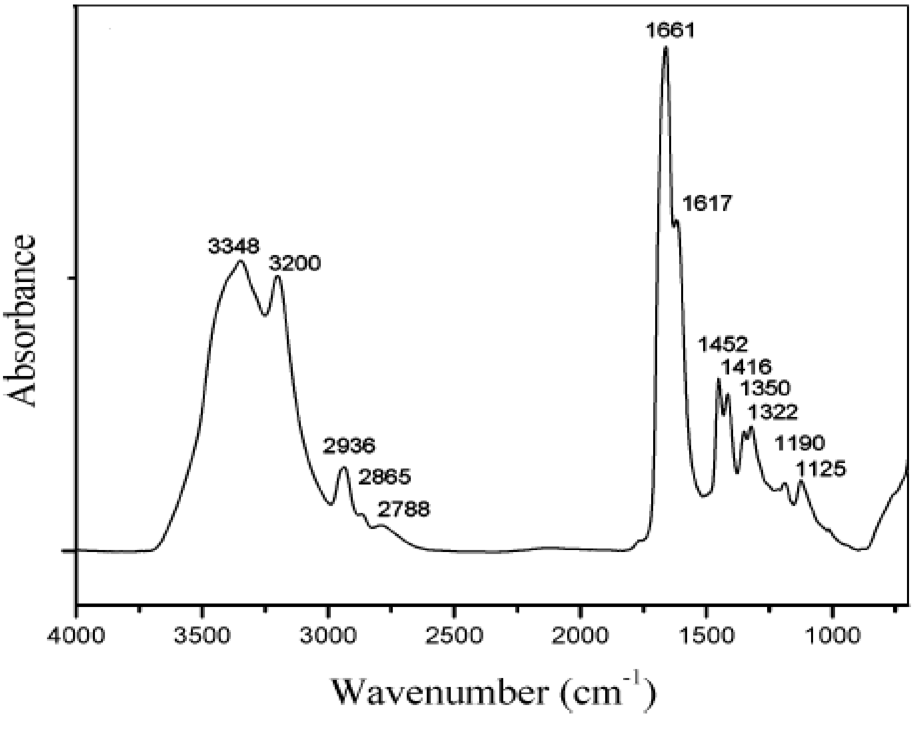


Fig. 3.1: FTIR spectrum for the PAam casting film on the Teflon surface

Table 3.1 Peak assignment of PAam film

peak position (cm-1)	**Assignment**
3348	N-H asy stretching of NH_2 (ν)
3200	N-H sy stretching of NH_2 (ν)
2936	C-H asy stretching of CH_2 (ν)
2866	C-H sy stretching of CH_2 (ν)
2788	C-H stretching of CH (ν)
1661	C=O stretching of CO (ν) , amide I band
1617	N-H bending of NH_2 (δ), amide II band
1452	C-H bending of CH_2 (δ)
1416	C-N stretching (ν), amide III band
1350	C-H wagging of CH_2 (wag), out of plane
1322	C-H bending of CH (δ)
1190	N-H wagging of NH_2 (wag)
1125	N-H rocking of NH_2 (r) in plane, C-C skeletal vibration

The characteristic peaks of polyacrylamide are:

ν_{sy} N-H transmittance band at 3201.6 cm^{-1}

ν_{asy} N-H transmittance band at 3348.2 cm^{-1}

The peaks at 1662.5 and 1620.1cm^{-1} are the two strong peaks which are the characteristic bands of the C=O stretching (ν), and N-H bending (δ) respectively. **Fig. 3.2**.

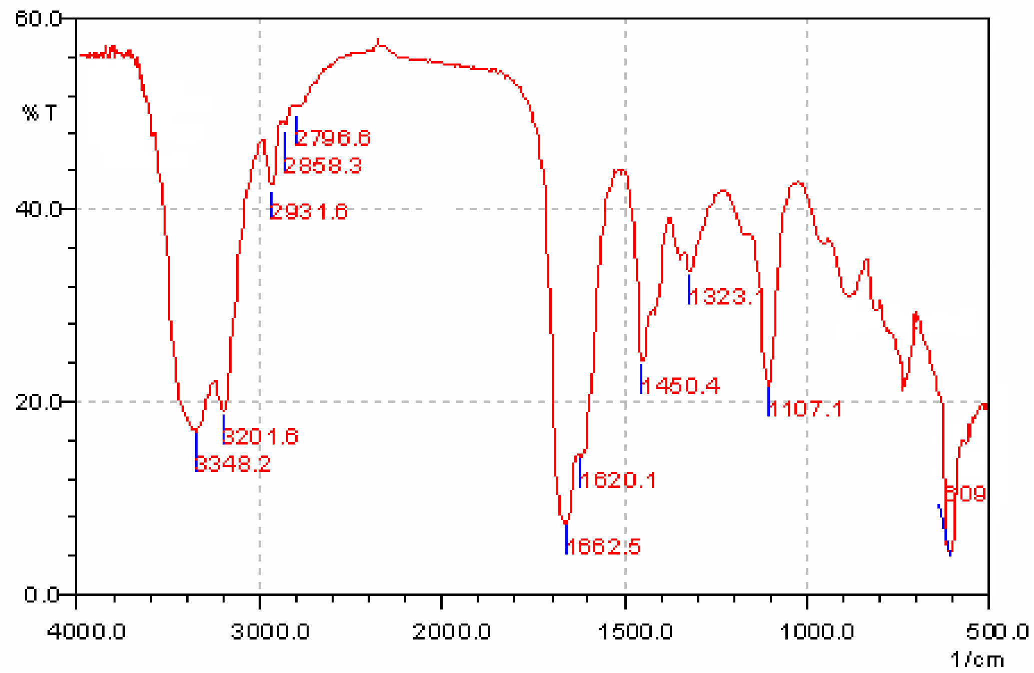


Fig. 3.2: FTIR spectrum of pure film polyacrylamide

The IR spectra of the PAam-Metal complexes show different bands at different metal ions.

III.1.1 Polyacrylamide – Fe^{+2} complexes

The FTIR spectra of polyacrylamide – Fe^{+2} complexes show intersting effect on the characteristic peaks of polyacrylamide specially of $\nu_{asy} NH_2$, N-H bending **(Table 3.2)** which exhibits at 3352.1cm^{-1}, 1616.2 cm^{-1} respectively.

Table 3.2: Characteristic peaks of PAam & PAam – Fe^{+2} complexes

Complexes	$\nu_{as} NH_2$	$\nu_s NH_2$	$\nu_s CH_2$	$\nu_{as} CH_2$	ν CH	ν (C = O)	**N-H bending**
Polyacrylamide	3348.2	3201.6	2931.6	2858.3	2796.6	1662.5	1620.1
P – Fe (2.5%)	3352.1	3201.6	2935.5	2866.0	2792.7	1662.5	1616.2
P – Fe (5%)	3352.1	3201.6	2939.3	-	2796.6	1662.5	1616.2
P – Fe (7.5%)	3352.1	3201.6	2935.5	2866.0	2804.3	1662.5	1616.2
P – Fe (10%)	3352.1	3201.6	2947.0	-	-	1666.4	1616.2
P – Fe (25%)	3352.1	3209.3	2958.6	-	-	1662.4	1612.4

From **table 3.2** the results show that (PAam) at concentration ranging from 2.5 up to 7.5% would bind only with NH_2 group to form the PAam – Fe^{+2} complexes. Whereas, a shift was noticed at higher concentration (above 10%) indicating that both groups (NH_2) and (C=O) are present as a result of bonding ligate to metal.

The FTIR spectrum of polyacrylamide with Fe^{+2} transition metal at different concentrations as mentioned in **Fig. 3.3**, **3.4**, **3.5**, **3.6** and **Fig. 3.7**.

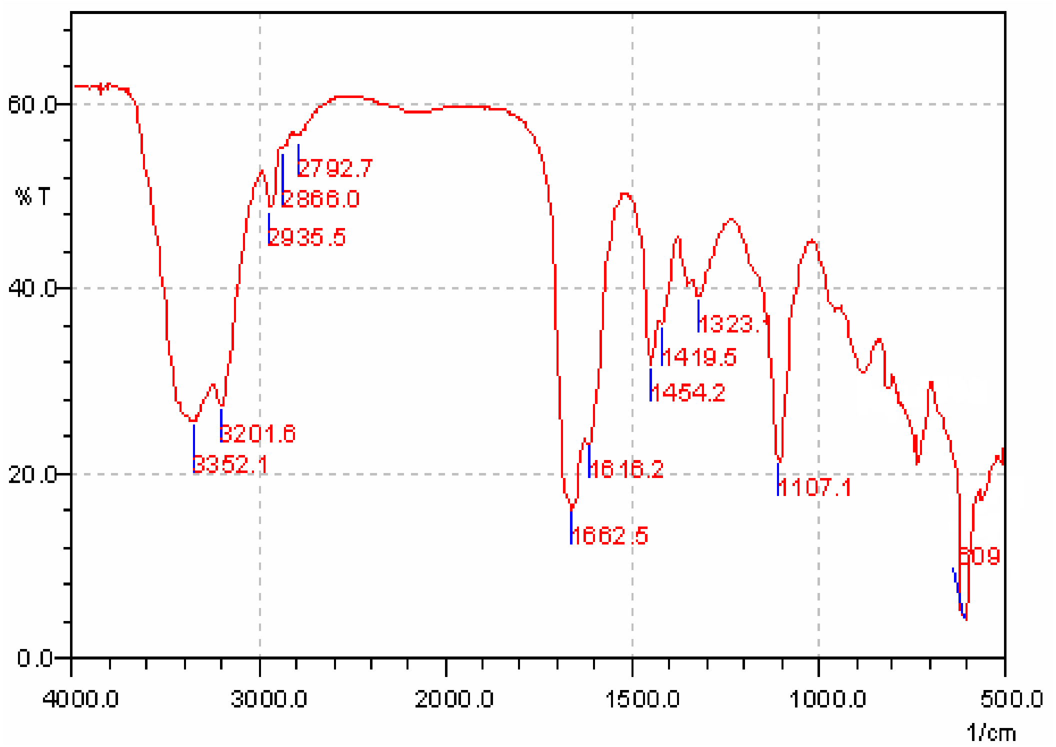


Fig. 3.3: FTIR spectrum of PAam- Fe^{+2} at 2.5% concentration

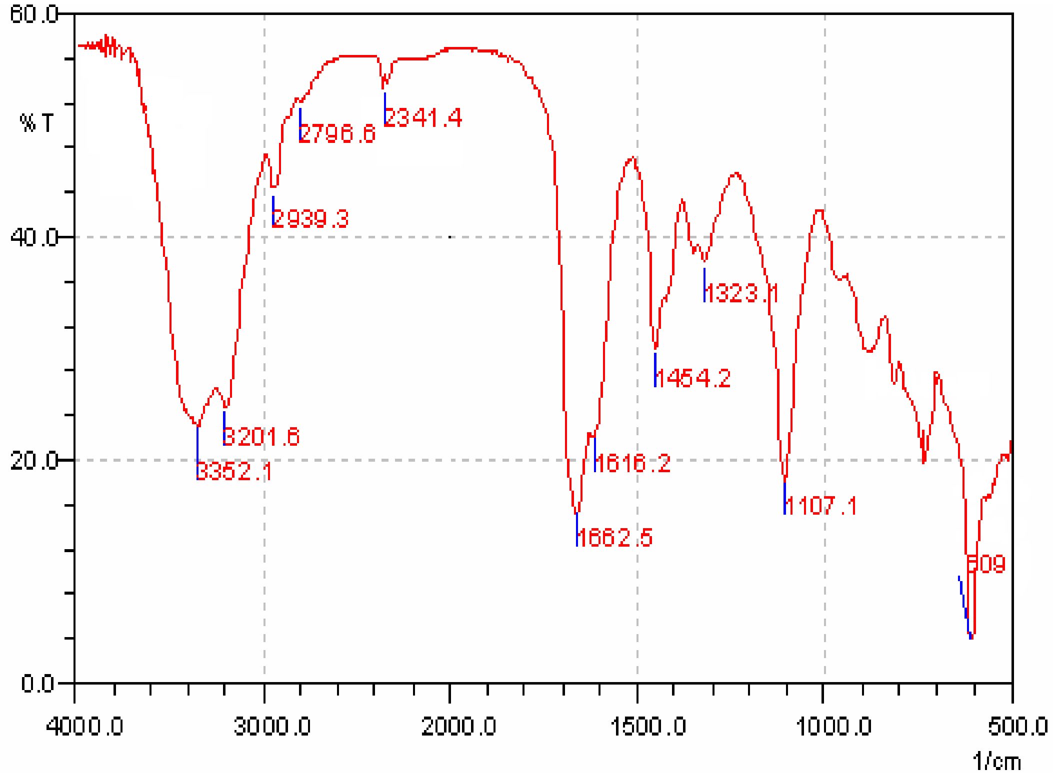


Fig. 3.4: FTIR spectrum of PAam- Fe^{+2} at 5% concentration

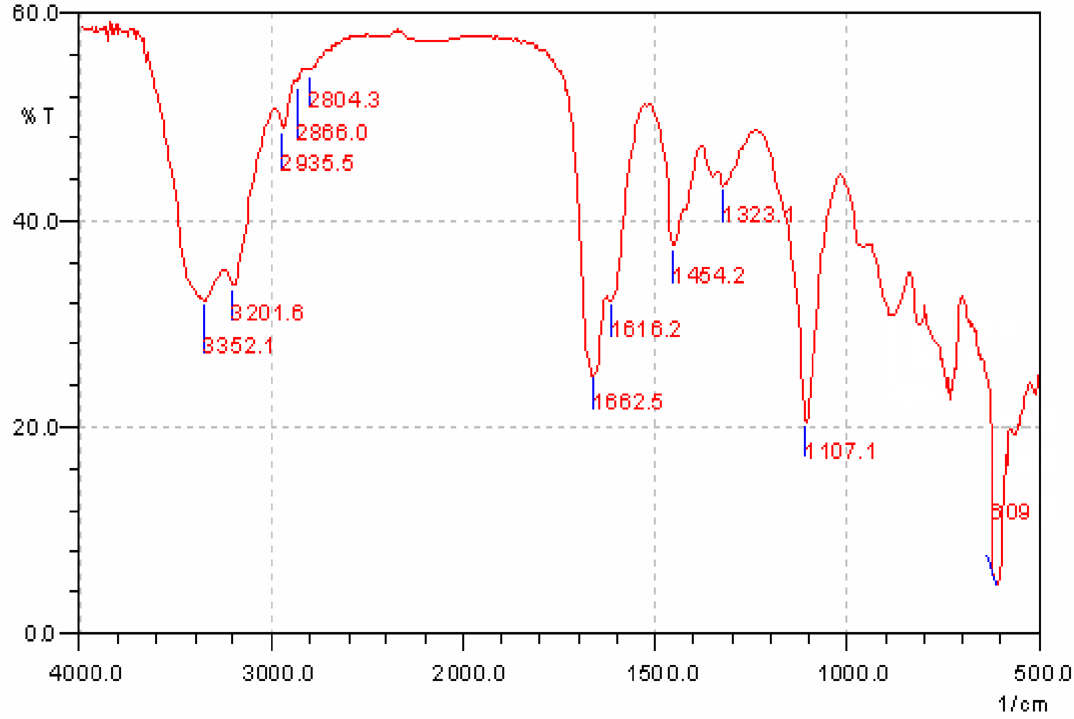


Fig. 3.5: FTIR spectrum of PAam- Fe^{+2} at 7.5% concentration

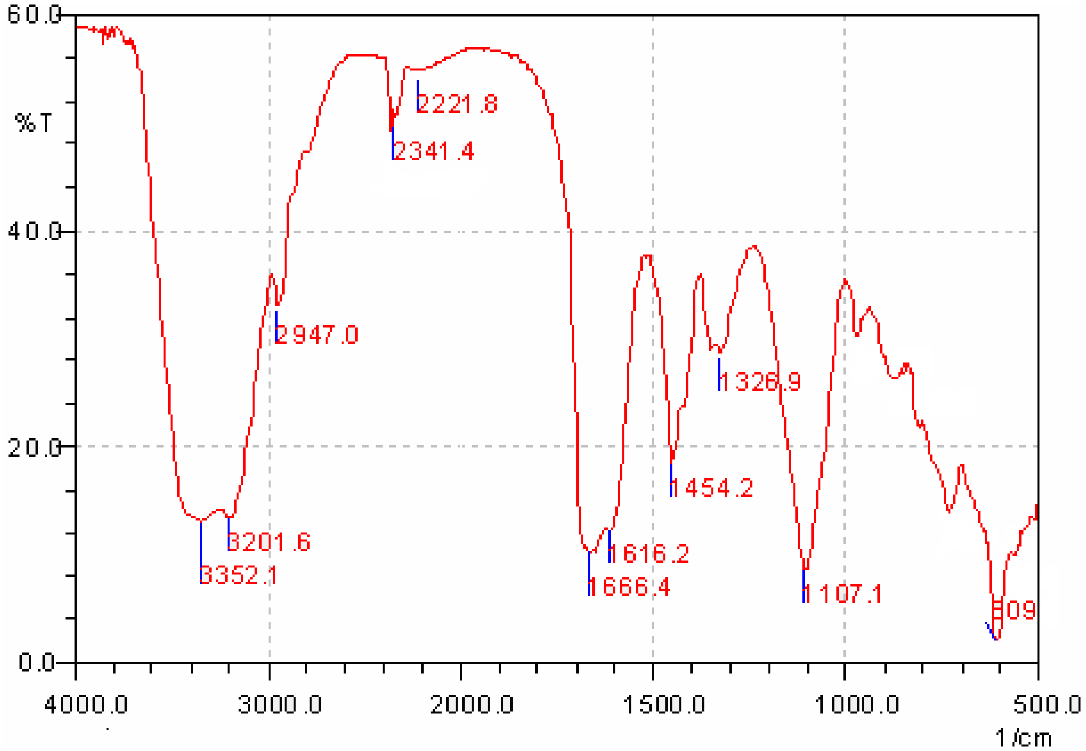


Fig. 3.6: FTIR spectrum of PAam- Fe^{+2} at 10% concentration

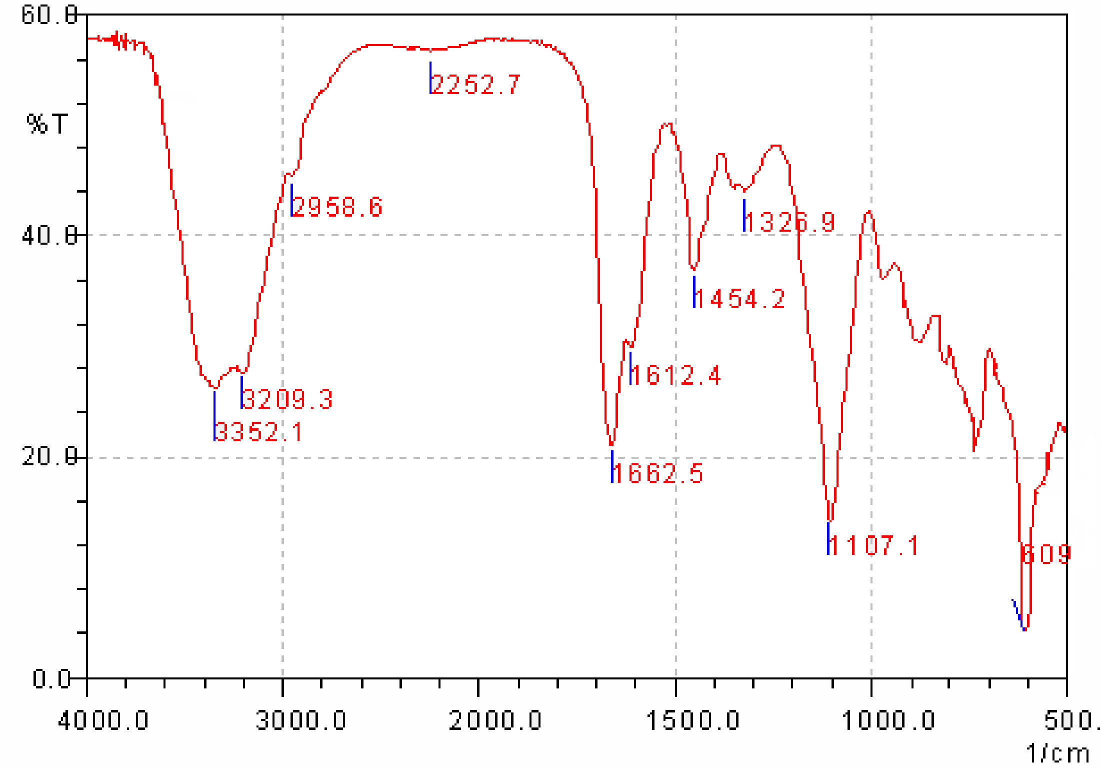


Fig. 3.7: FTIR spectrum of PAam- Fe^{+2} at 25% concentration

III.1.2 Polyacrylamide – Cu^{+2} complexes

The absorption of the carbonyl group in the polymer chain is shifted by 3.9cm^{-1} in presence of Cu^{+2} ions. While the amine group effects at 5%, 7.5%, and 10% concentration by 3.9 cm^{-1}, this peak shift means that the complexation occurs at both the carbonyl and amine group, but at 2.5%, 25% concentration, the amine group shows no change which may suggested that the coordination is monodentate type. The group N-H bending in the polymer chain is shifted by 3.9cm^{-1} at concentration 2.5%, 5%, 7.5%, and 10%, while at 25% by 7.7cm^{-1}.

Fig. 3.8 up to **Fig. 3.12** shows the FTIR spectrum of the PAam – Cu^{+2} complexes, and table 3.3 gives the peak assigment of the FTIR spectrum for all the prepared concentrations. It should be noticed that Cu^{+2} ion form complex with PAam from C=O side at 2.5, 25% concentration and from both C=O and NH$_2$ at 5, 10%.

Table 3.3: Characteristic peaks of PAam & PAam – Cu^{+2} complexes

Complexes	**ν_{as} NH$_2$**	**ν_s NH$_2$**	**ν_s CH$_2$**	**ν_{as} CH$_2$**	**ν CH**	**ν (C = O)**	**N-H bending**
Polyacrylamide	3348.2	3201.6	2931.6	2858.3	2796.6	1662.5	1620.1
P – Cu (2.5%)	3348.2	3201.6	2935.5	2862.2	2792.7	1666.4	1616.2
P – Cu (5%)	3352.1	3201.1	2939.3	2866.0	2796.6	1666.4	1616.2
P – Cu (7.5%)	3352.1	3197.8	2939.3	2804.3	-	1666.4	1616.2
P – Cu (10%)	3352.1	3201.6	2947.0	-	-	1666.4	1616.2
P – Cu (25%)	3348.2	3201.6	2950.9	-	-	1666.4	1612.4

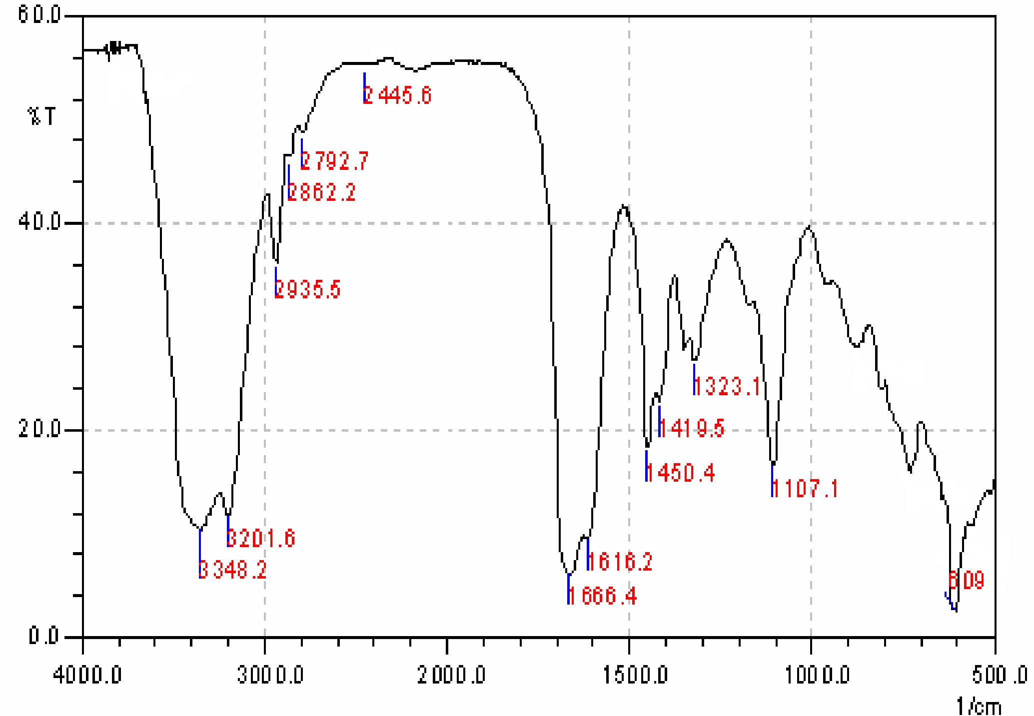


Fig. 3.8: FTIR spectrum of PAam- Cu^{+2} at 2.5% concentration

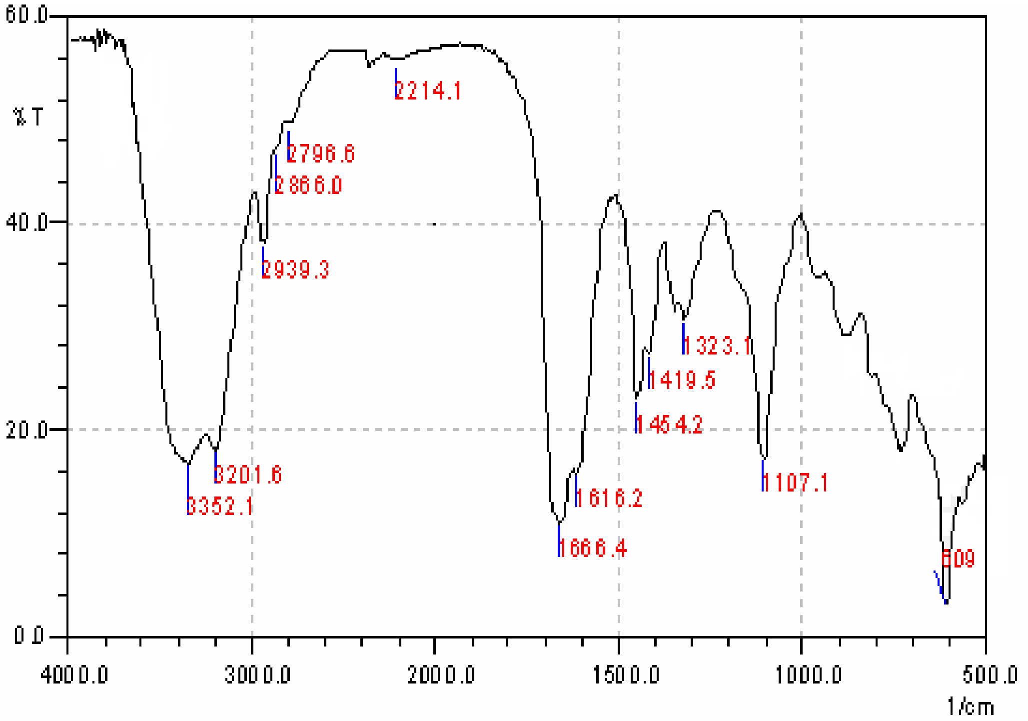


Fig. 3.9: FTIR spectrum of PAam- Cu^{+2} at 5% concentration

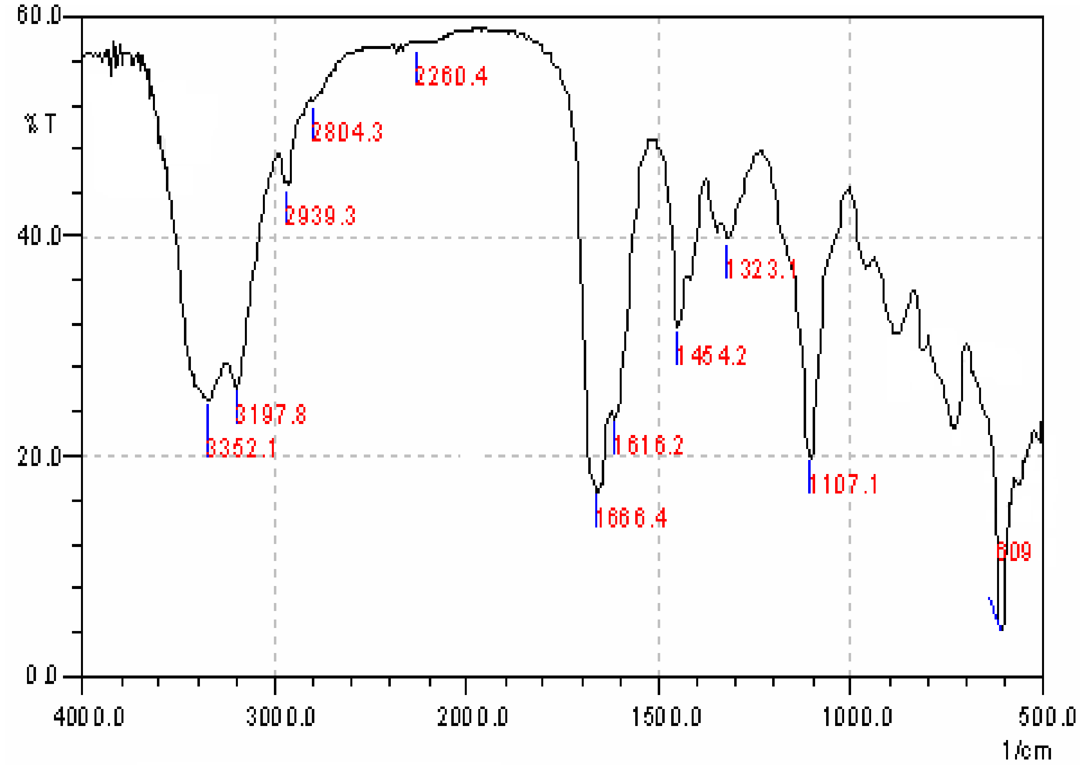


Fig. 3.10: FTIR spectrum of PAam- Cu^{+2} at 7.5% concentration

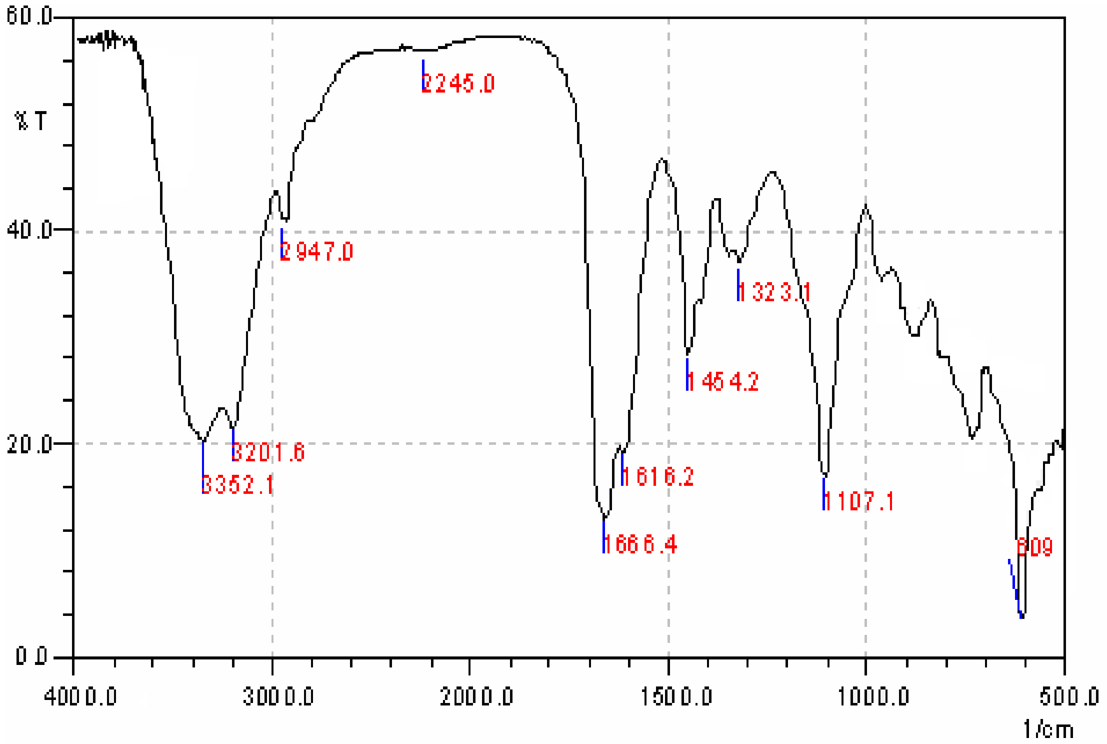


Fig. 3.11: FTIR spectrum of PAam- Cu^{+2} at 10% concentration

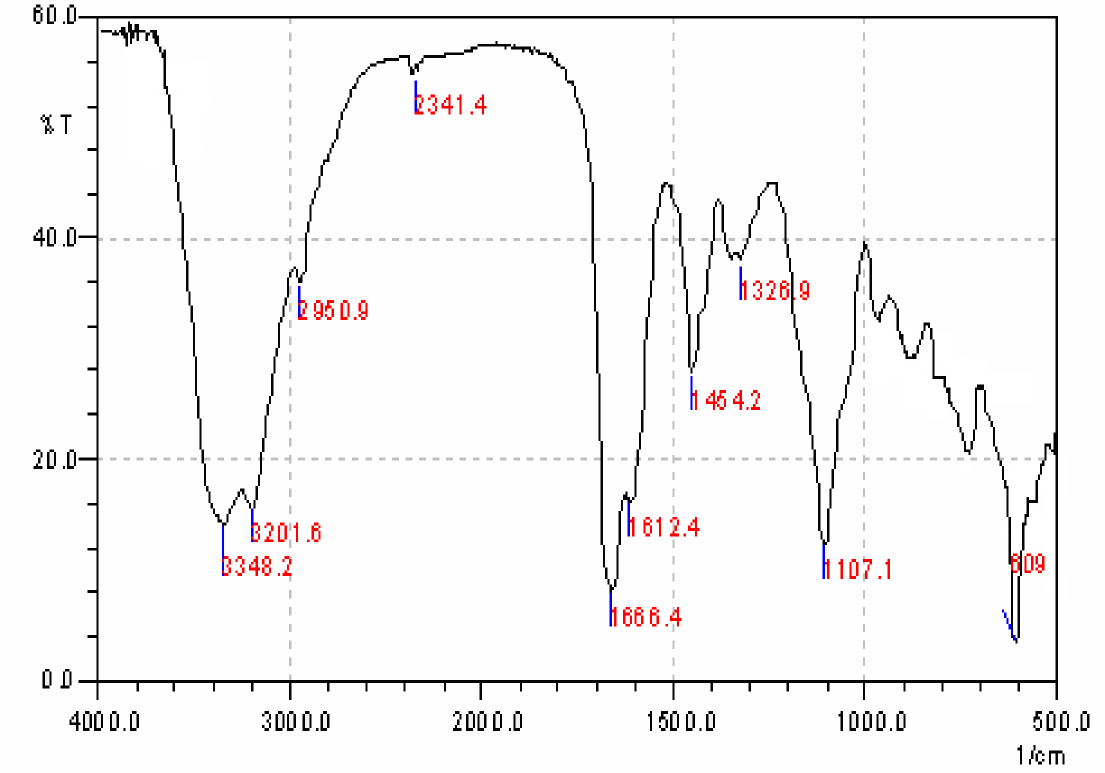


Fig.3.12: FTIR spectrum of PAam- Cu^{+2} at 25% concentration

III.1.3 Polyacrylamide – Co^{+2} complexes

The characteristic peaks of the complexation of Co^{+2} ions with the polymer chain at different concentrations 2.5%, 5%, 7.5% and 10% is shown in **table 3.4**. This is indicated either by mono or bidentate according to the effects on amine (symmetry), carbonyl and N-H bending absorption bands. While the other two strong characteristic bands of the ν_{asy} NH_2 and ν(C = O) at 3348.2 and 1662.5 cm^{-1} for PAam shifted to 3340 and 1658 cm^{-1} at 25% concentration respectively, which indicate the chelating of Co^{+2} to the polymer.

Table 3.4: Characteristic peaks of PAam & PAam-Co^{+2} complexes

Complexes	**ν_{as} NH_2**	**ν_s NH_2**	**ν_s CH_2**	**ν_{as} CH_2**	**ν CH**	**ν (C = O)**	**N-H bending**
Polyacrylamide	3348.2	3201.6	2931.6	2858.3	2796.6	1662.5	1620.1
P – Co (2.5%)	3348.2	3197.8	2935.5	2858.3	2788.9	1662.5	1616.2
P – Co (5%)	3348.2	3197.8	2939.3	2866.0	2788.9	1666.4	1616.2
P – Co (7.5%)	3348.2	3197.8	2939.3	2866.0	2792.7	1662.4	1616.2
P – Co (10%)	3348.2	3197.8	2947.0	-	2792.7	1666.4	1616.2
P – Co (25%)	3340.5	3209.3	2950.9	-	2792.7	1658.7	-

The IR spectrum of polyacrylamide with Co^{+2} transition metal at different concentrations is shown in **Fig. 3.13**, **3.14**, **3.15**, **3.16** and **Fig. 3.17**.

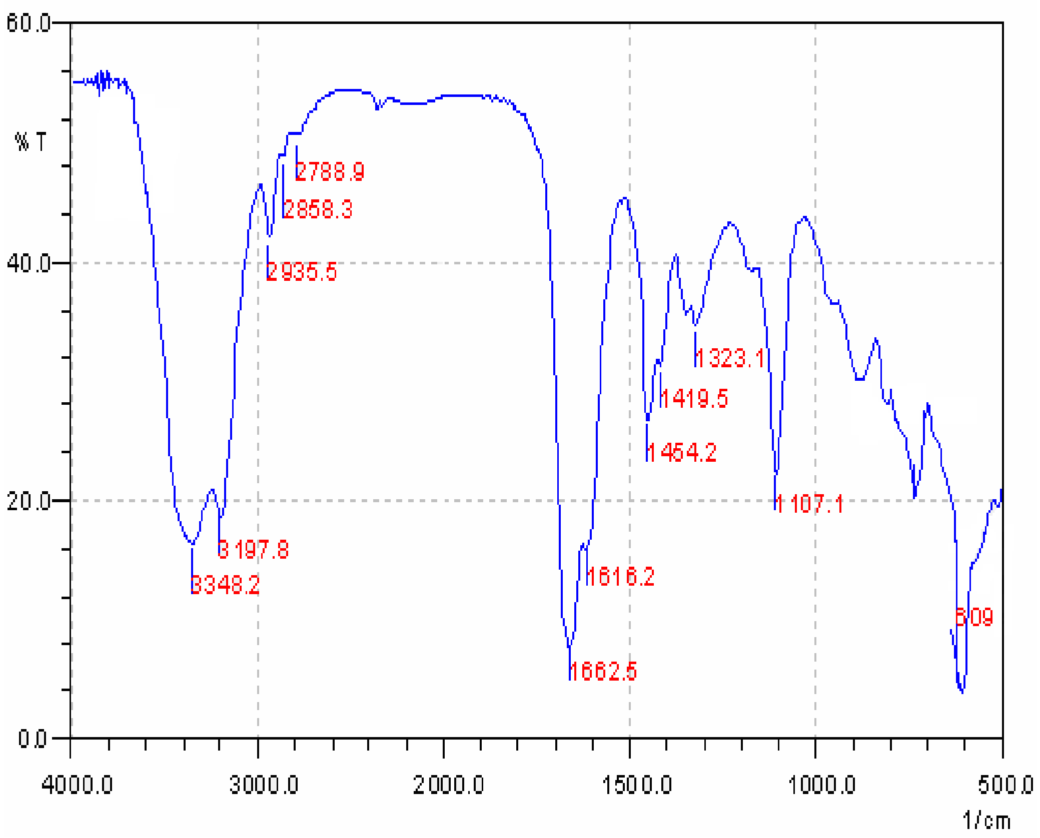


Fig. 3.13: FTIR spectrum of PAam- Co^{+2} at 2.5% concentration

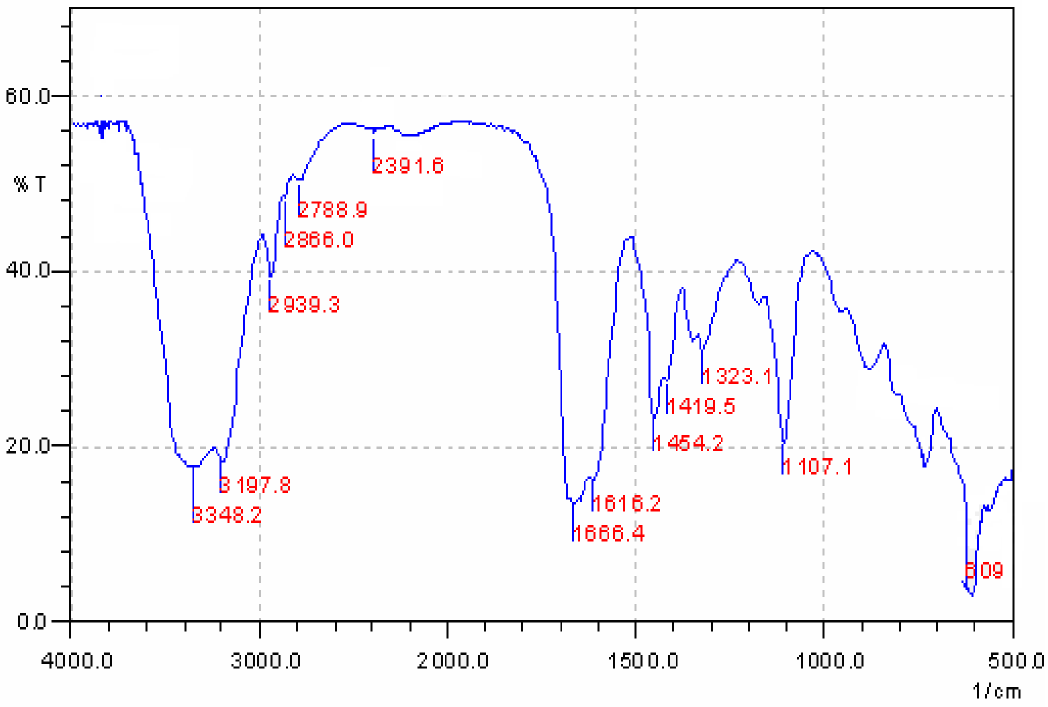


Fig. 3.14: FTIR spectrum of PAam- Co^{+2} at 5% concentration

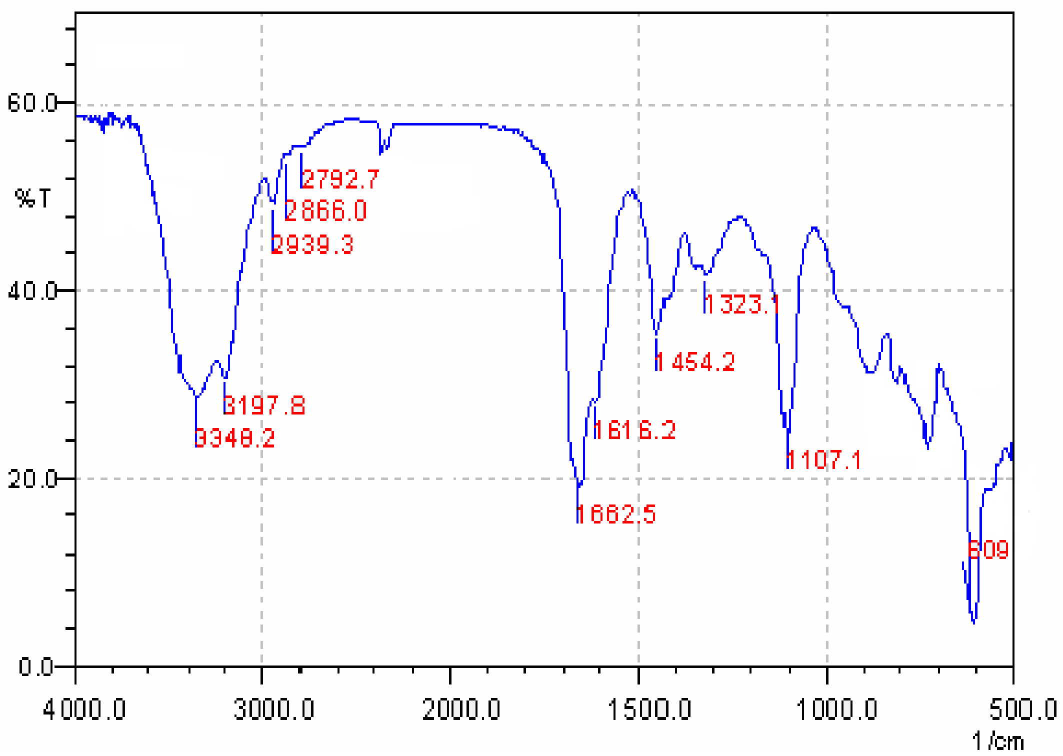


Fig. 3.15: FTIR spectrum of PAam- Co^{+2} at 7.5% concentration

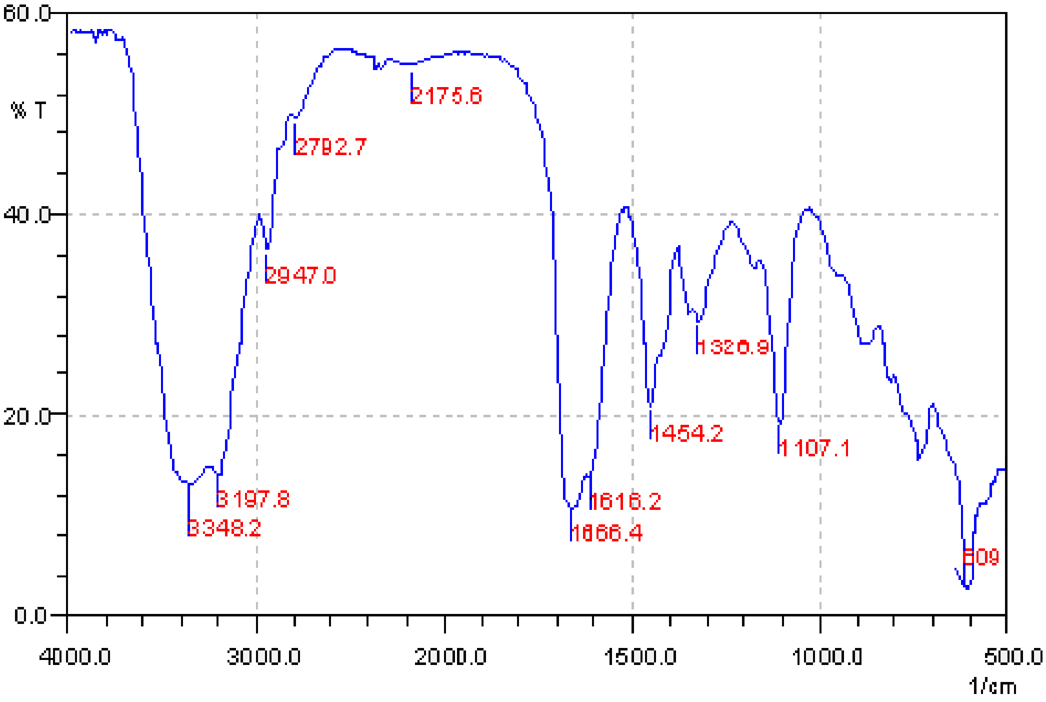


Fig. 3.16: FTIR spectrum of PAam- Co^{+2} at 10% concentration

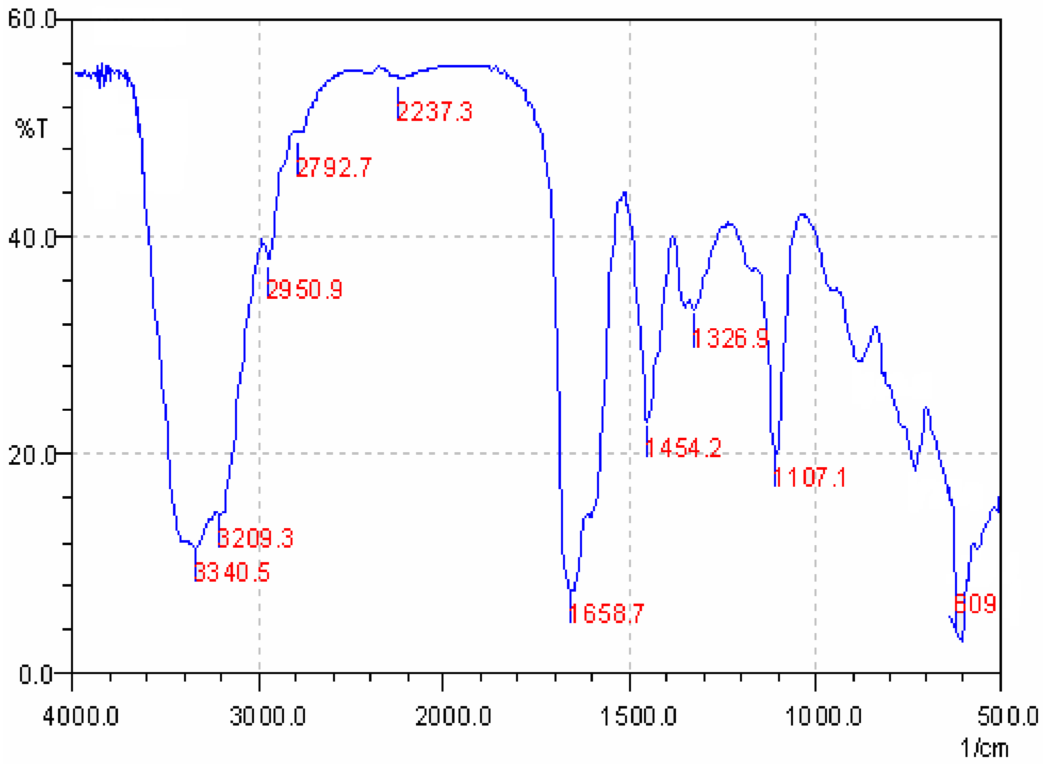


Fig. 3.17: FTIR spectrum of PAam- Co^{+2} at 25% concentration

III.2 Complexation of PAam – Metal in acidic and basic conditions

The hydrolysis of polyacrylamide in acidic and basic conditions occurs randomly, and complete hydrolysis established under specific conditions especially at high temperature and normal pH [14]. In **Fig. 3.18** and **Fig.3.19** FTIR show the hydrolysis of PAam under acidic (pH 1.7) and basic (pH 10) conditions respectively to produce randomly polyacrylamide-co-acrylic acid. The amine group in the polymer chain reduced to hydroxyl group in the case of hydrolysis, this behavior occurs because the absorbance of amine and carbonyl groups still no significant a change. We expected that the complete hydrolysis of polyacrylamide to acrylic acid occurs under specific pH and temperature conditions.

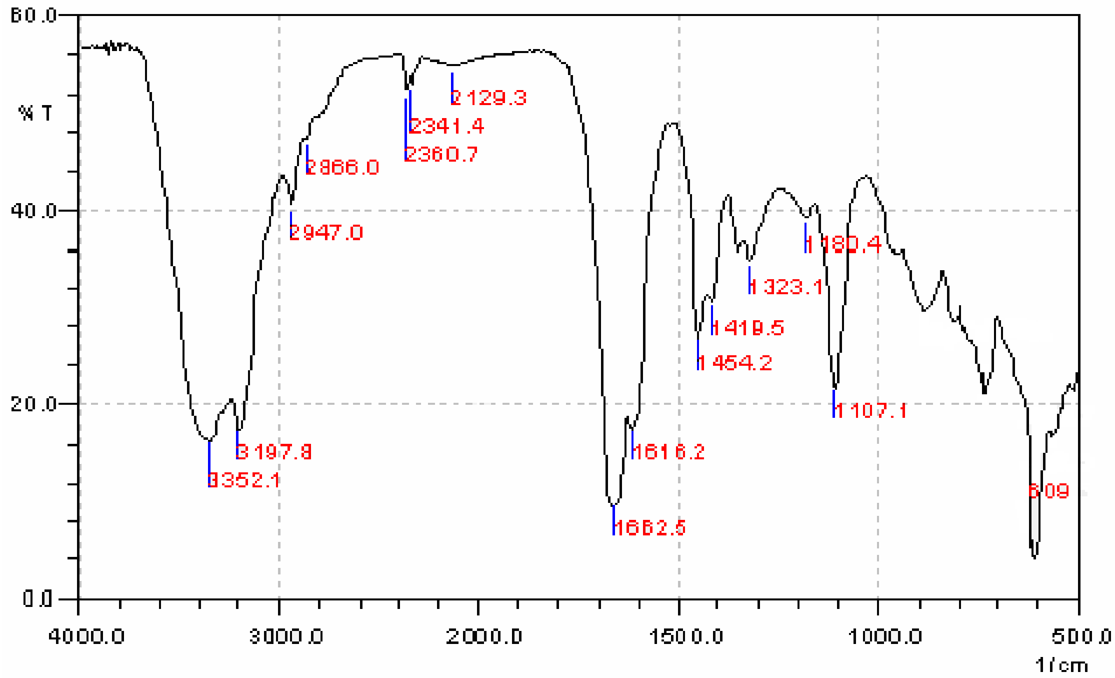


Fig. 3.18: FTIR spectrum of PAam in acidic condition (pH = 1.7)

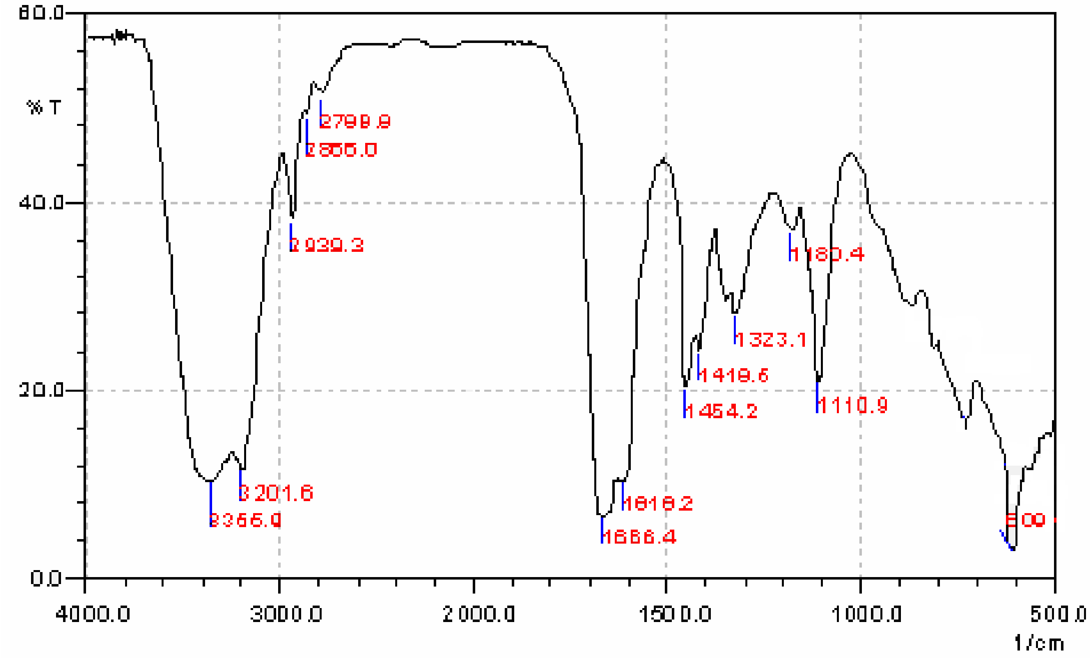


Fig. 3.19: FTIR spectrum of PAam in basic condition (pH = 10.0)

III.3 Analysis and characterization of PAam and complexes using DSC

The DSC measures the power (heat energy per unit time) differential between a small weighed sample of polymer (ea. 10 mg) in a sealed aluminum pan reference to an empty pan in order to maintain a zero temperature differential between the reference and the sample during programmed heating and cooling temperature scans. The technique is most often used for characterizing the Tg, Tm and Tc. The technique can also be used for studying the kinetics of chemical reactions, like oxidation and decomposition. The conversion of a measured heat of fusion can be converted to a percent crystallinity provided, of course, the heat of fusion for the 100% crystalline polymer is known.[35]

In our study, DSC was used for characterizing the Tg, Tm and Tc. A special heating and cooling programs were used for evaluating Tc as shown in **table 3.5**.

Table 3.5: Special program for evaluating Tc

Ramp	20^0C
Thermal equil.	1 mints
Jump	-40^0C
Ramp	20^0C to 250^0C (1st heating)
Ramp	20^0C to -40^0C (Cooling)
Ramp	To 250^0C (2nd heating)

III.3.1 Analysis of PAam

The thermogram of pure PAam is shown in **Fig. 3.20**, the glass transition temperature and melting point of PAam at 161.4^{0}C, 237^{0}C respectively.

III.3.2 Analysis of PAam – Cu^{+2} 5% concentration

The thermal behavior of the complex PAam-Cu^{+2} at (5%) is shown in **Fig.3.21**. The glass transition temperature and melting temperature of this complex appears at 168.8^{0}C and 248.5^{0}C respectively. These two transitions are shifted from the transitions of polyacrylamide which accounts for a decrease in flexibility of the chain segments caused by complexation.

III.3.3 Analysis of PAam – Co^{+2} 5% concentration

The glass transition temperature of PAam-Co^{+2} at 5% polymer to metal appears at 166.2^{0}C, and the melting temperature appears at 250.8^{0}C. More shift in the case of Co^{+2} and the main reason for the degree of increase in Tg is due to the degree of association between the polymer and metal ion as shown in **Fig.3.22**.

III.3.4 Analysis of PAam – Ni^{+2} 5% concentration

The Tg and Tm of PAam-Ni^{+2} (5%) at 167.8^{0}C and 255^{0}C respectively as shown in **Fig. 3.23**.

The glass transition temperature and melting point of PAam and PAam Cu^{+2}, Co^{+2}, Ni^{+2} complexes are shown in **table 3.4**.

On the basis of the above arguments, metals with more favorable association strength must have a larger drive to be more rigid.

The variations of Tg and Tm of PAam and PAam-M^{+2} is presented in **table 3.6.**

Table 3.6: Tg, Tm of PAam and PAam Cu^{+2}, Co^{+2}, Ni^{+2} complexes.

Temperature **Complexes**	**Tg(^{0}C)**	**Tm(^{0}C)**
Polyacrylamide	161.4	237.0
Polyacrylamide – Cu^{+2} (5%)	168.8	248.5
Polyacrylamide – Co^{+2} (5%)	166.2	250.8
Polyacrylamide – Ni^{+2} (5%)	167.8	255.0

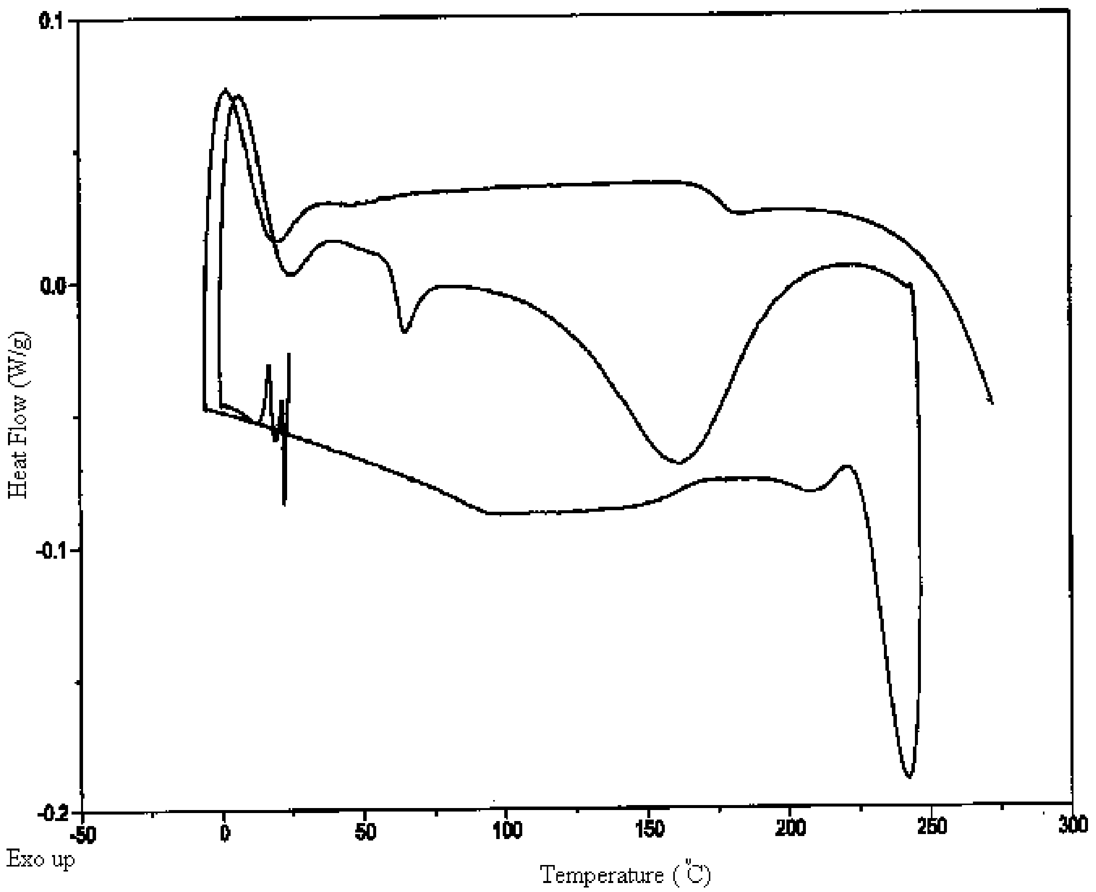


Fig. 3.20: DSC thermogram of pure film polyacrylamide

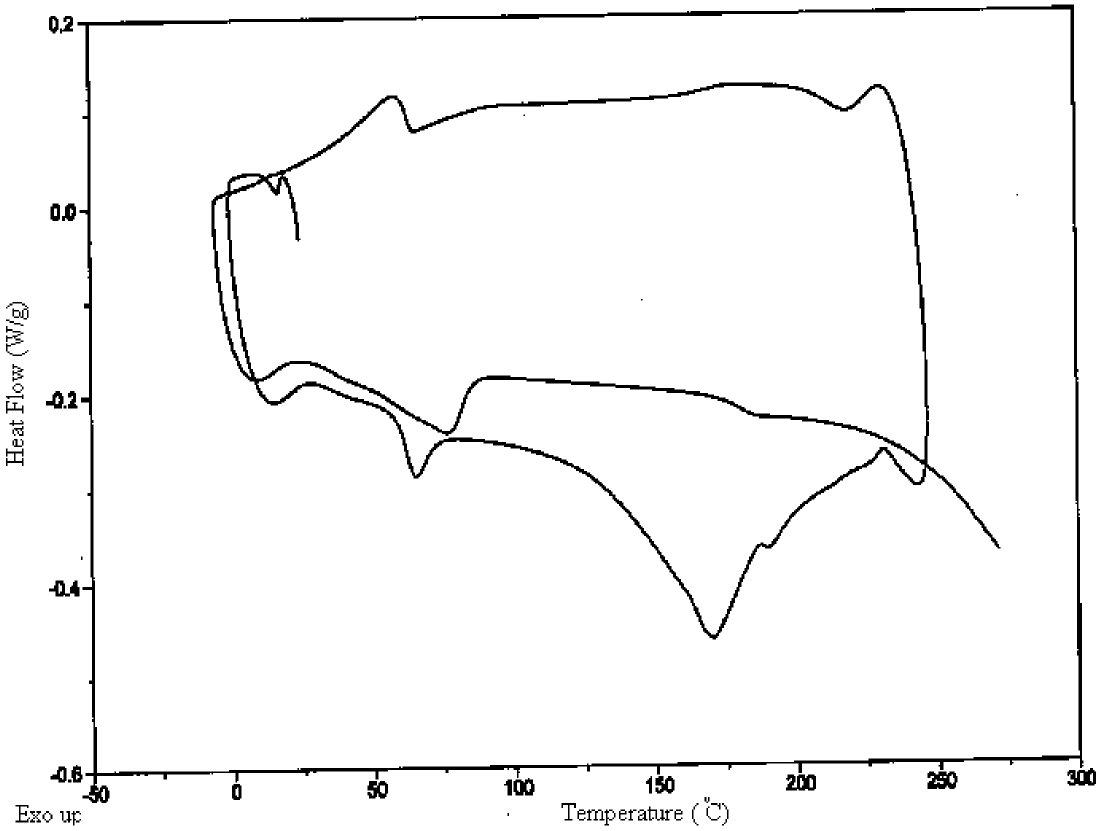


Fig. 3.21: DSC thermogram of PAam-Cu^{+2} at 5% concentration

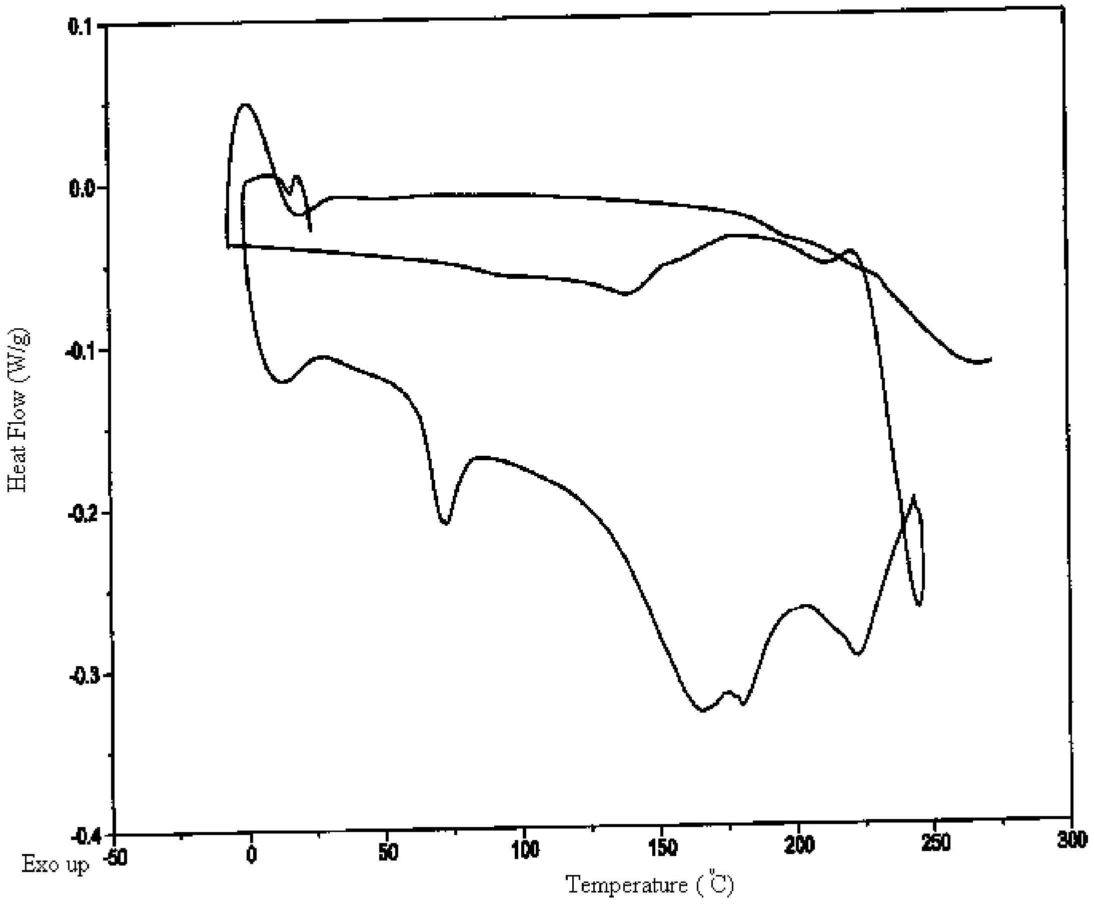


Fig 3.22: DSC thermogram of PAam-Co^{+2} at 5% concentration

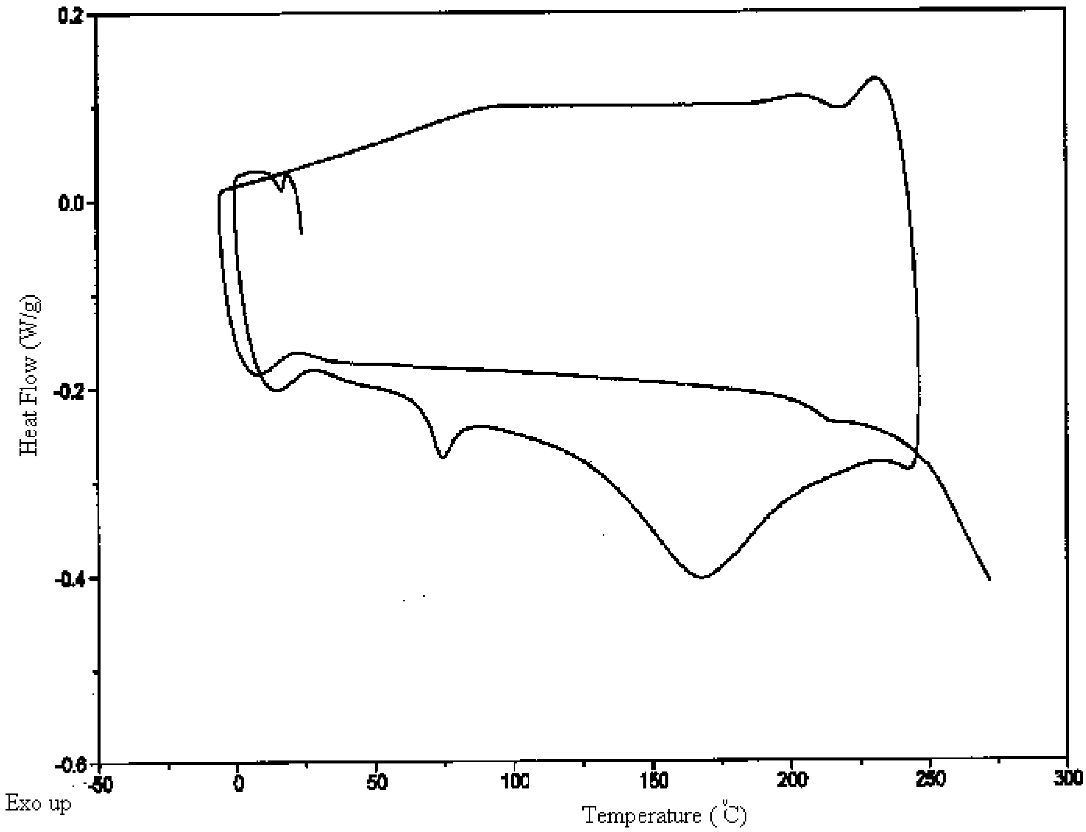


Fig. 3.23: DSC thermogram of PAam-Ni^{+2} at 5% concentration

III.4 Analysis of polyacrylamide and complexes using UV visible spectroscopy

The UV-visible spectroscopy study of all films was obtained at 70-80μm film thickness. The wavelength was measured in the range of 200-800nm. In order to investigate the PAam-M^{+2} complexation by UV-visible spectroscopy, UV-vis spectra of PAam and free ions was carried for comparison.

III.4.1 Analysis of PAam-Ni^{+2} complexes

The UV-visible spectrum of PAam film shows only one characteristic band at λ_{max} =230nm as shown in **Fig. 3.23**. In the case of Ni^{+2} solution there was no considerable change in the position of the characteristic band of the polymer at 230nm, however a new band was observed at λ_{max} = 285nm for 5 and 10% PAam-Ni^{+2} (**Fig. 3.26** and **Fig. 3.27**) due to the complexation. This band is completely different than the main absorption maxima bands of free Ni^{+2} that appears at λ_{max} 393.2nm and 721.4nm as shown in **Fig. 3.25**. Also the intensity of polyacrylamide film peak decrease to 1.55 and 1.88 for 10% and 5% respectively.

III.4.2 Analysis of PAam Co^{+2} complexes

UV-Vis spectrum of PAam-Co^{+2} (10%) complex film shows a new characteristic band at λ_{max} = 285nm due to the complexation, (**Fig. 3.29**) the main bands of Co^{+2} solution appears at 196nm and 510nm (**Fig. 3.28**), the intensity of these bands decrease by the complexation with Co^{+2} ions.

III.4.3 Analysis of PAam-Cu^{+2} complexes

The spectrum of free Cu^{+2} ions solution is represented in (**Fig. 3.30**). The main band appears at 197nm. The characteristic band of PAam-Cu^{+2} (10%) at 276nm according to the complexation (**Fig. 3.31**), this band is an important band which is not observed in both of PAam and Cu^{+2} ions solution spectra.

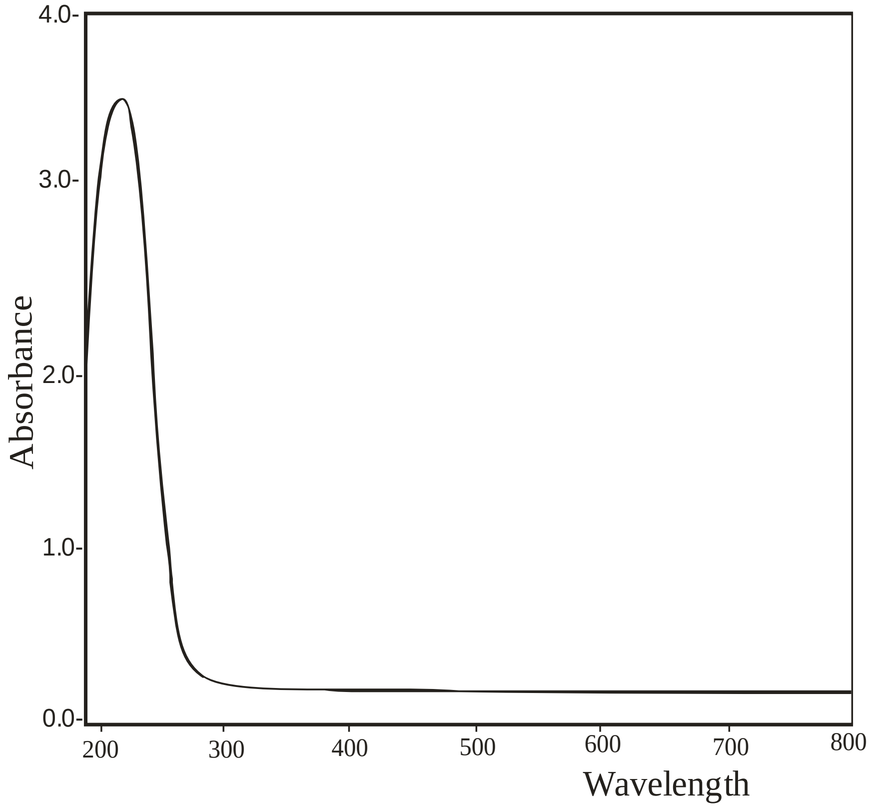


Fig. 3.24: UV-spectra of Pure PAam

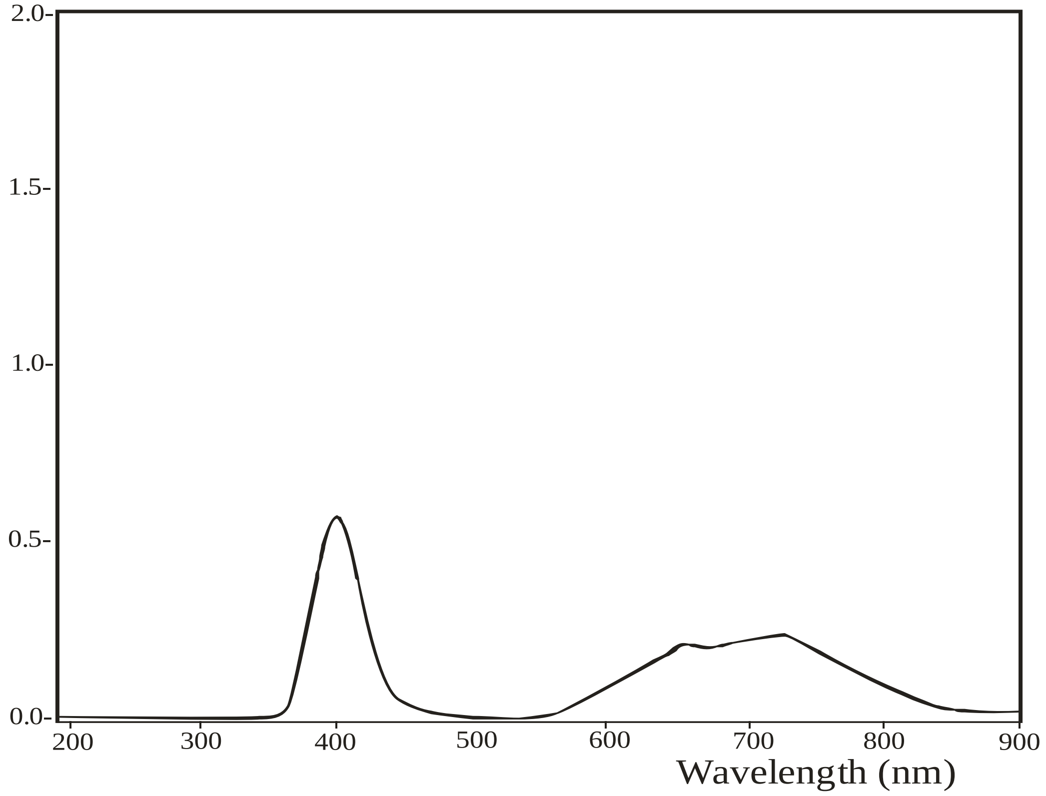


Fig. 3.25: UV-spectra of Ni^{+2} solutions

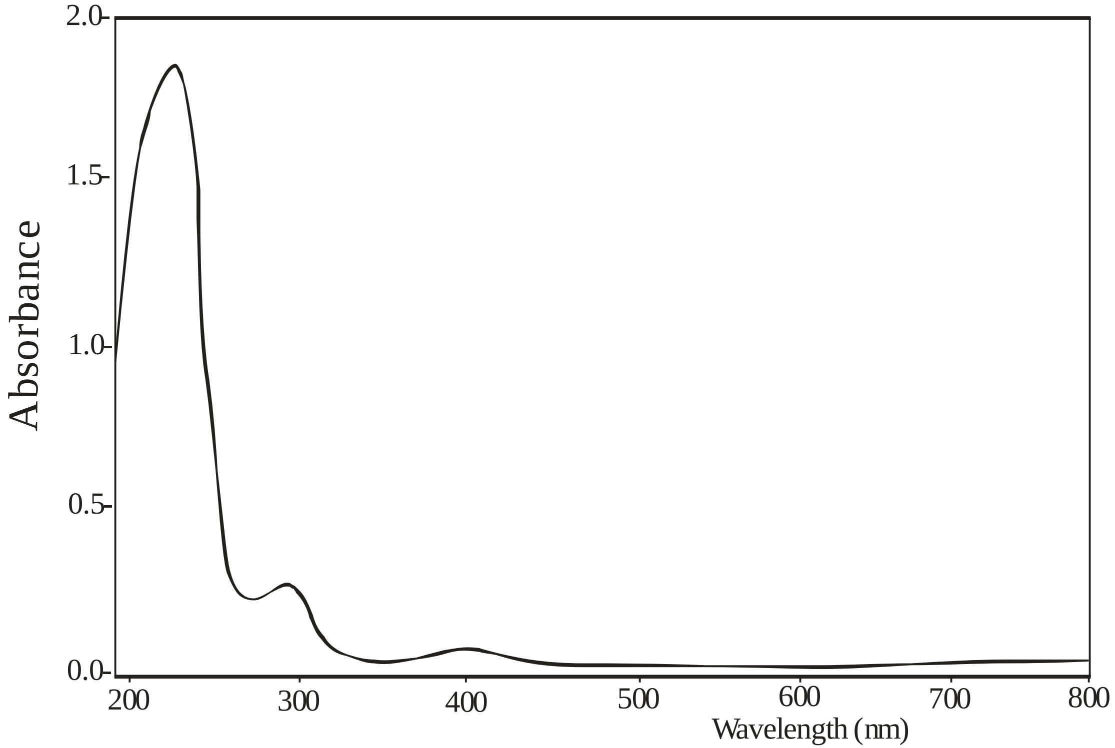


Fig. 3.26: UV-spectra of PAam-Ni^{+2} (5 %)

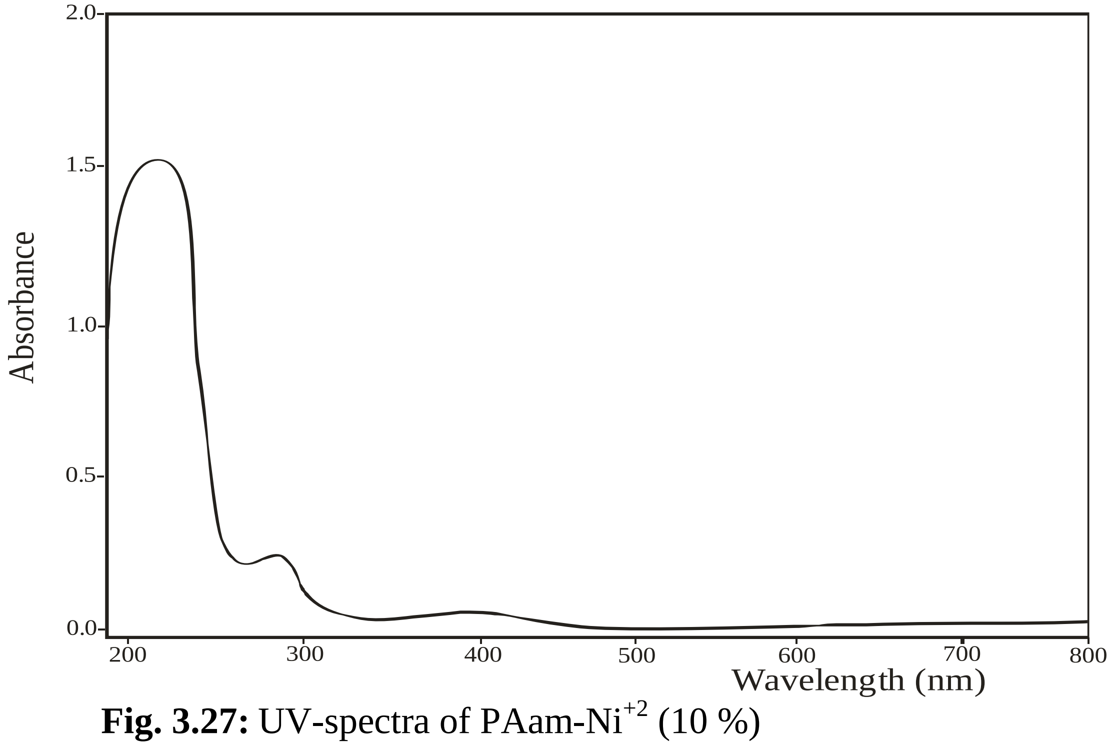


Fig. 3.27: UV-spectra of PAam-Ni^{+2} (10 %)

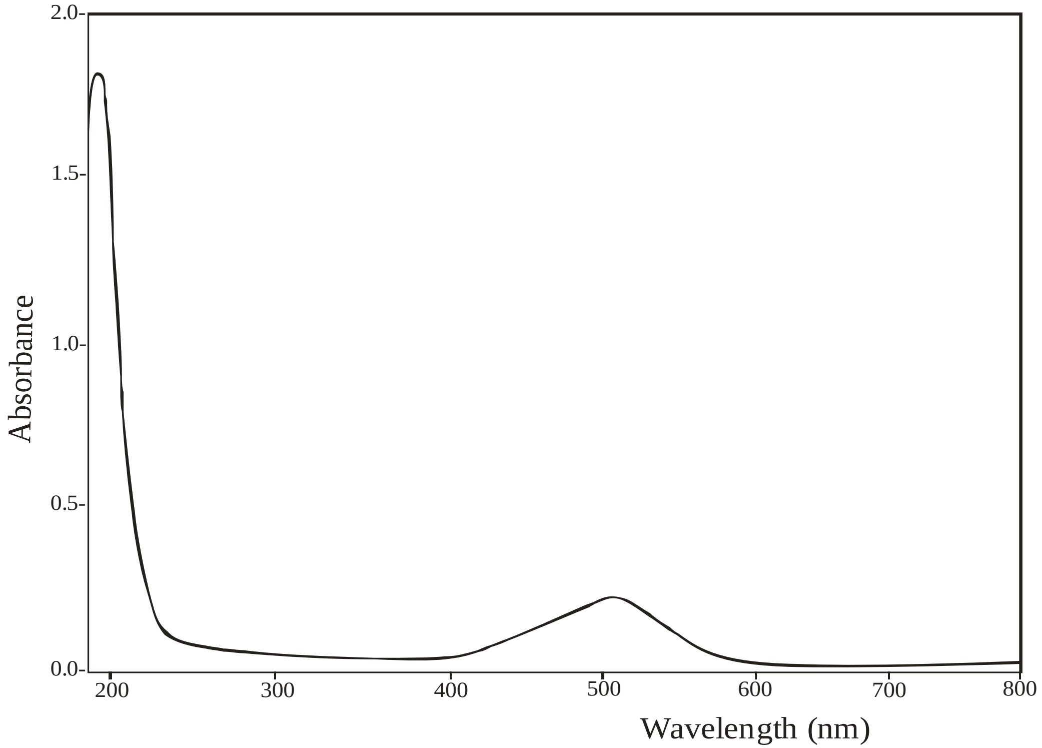


Fig. 3.28: UV-spectra of Co^{+2} solutions

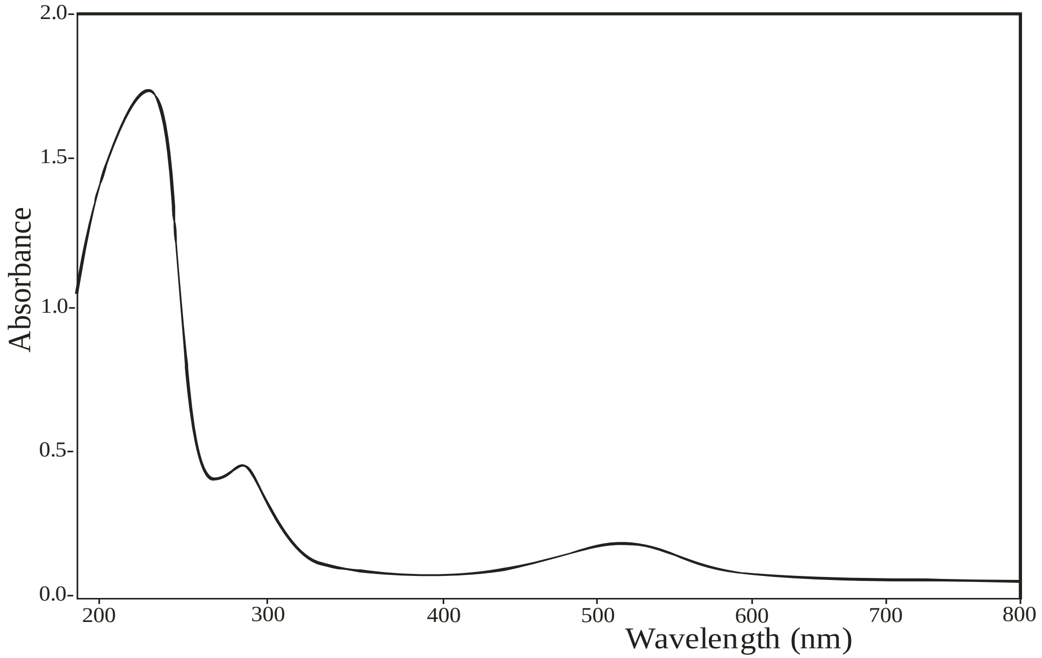


Fig. 3.29: UV-spectra of PAam-Co^{+2} (10 %)

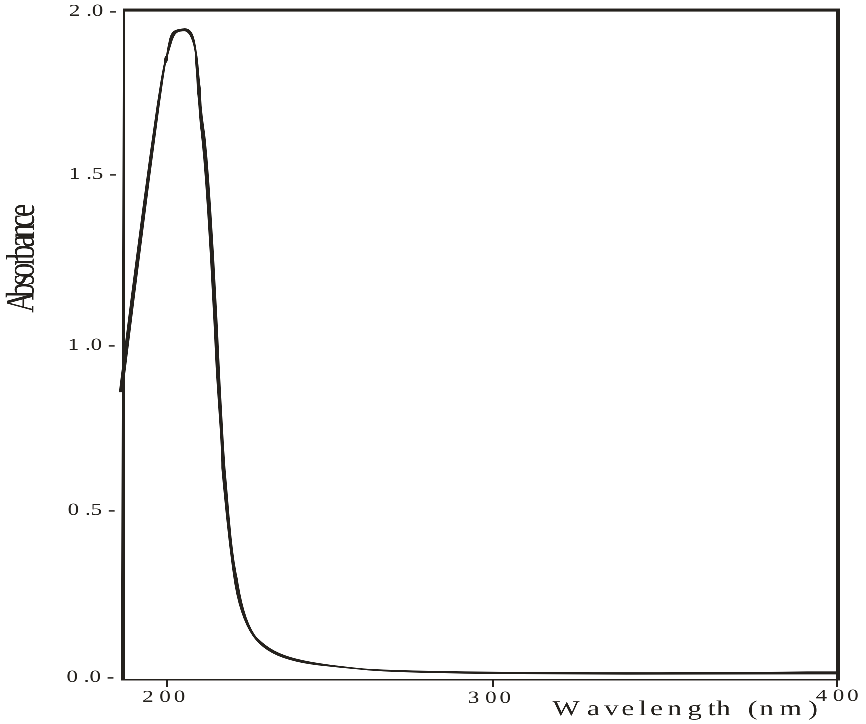


Fig. 3.30: UV-spectra of Cu^{+2} solutions

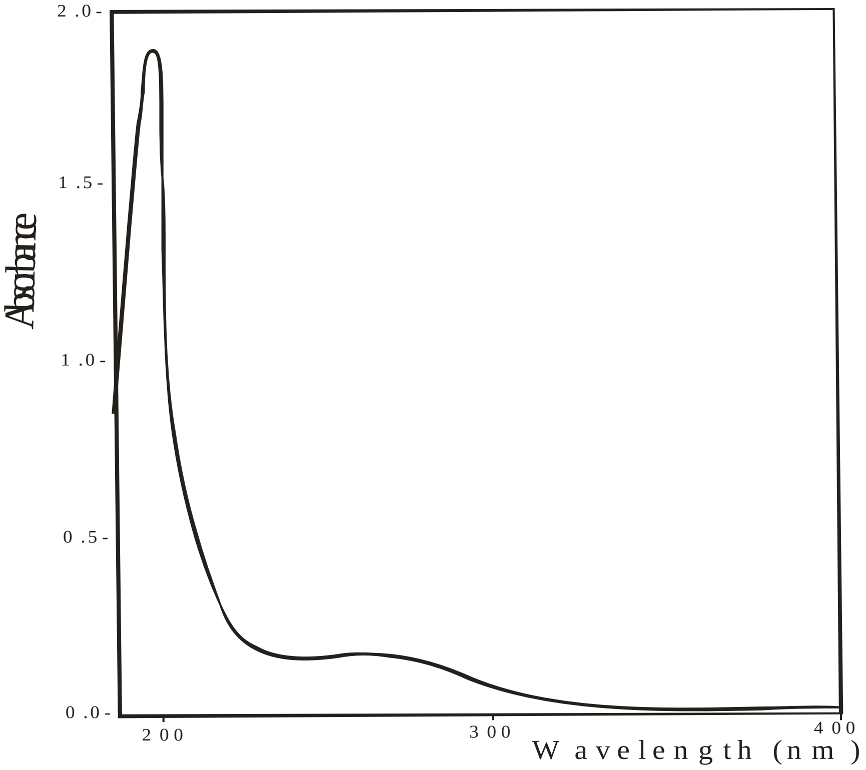


Fig. 3.31: UV-spectra of $PAamCu^{+2}$ (10 %)

III.5 Electrical conductivity of PAam and PAam-Ni^{+2}complexes

The Current-Voltage (I-V) characteristic curves of PAam and PAam-Ni^{+2} were measured using two point probe system; the probes were moved across the sample, applying a voltage across the surface, measuring the resultant current.

The (I-V) curve of polyacrylamide is shown in **Fig. 3.32**, three dimensional films where formed. The surface conductivity was calculated depending on the relation: $\sigma = I/2\pi sV$ mhos cm^{-1}, since I is the resultant current; s the distance between the electrodes (0.2cm); σ is the surface conductivity; V is the voltage.

Surface conductivity (σ) = slope (I-V) curve/$2\pi s$ =$5.278*10^{-11}/2\pi*0.2$cm = 0.042nScm^{-1}. According to the calculation, polyacrylamide is classified as insulator.

The current-voltage of PAam-Ni^{+2} 2.5% is shown in **Fig. 3.33**. The surface conductivity of PAam was improved using Ni^{+2} at (2.5%) concentration. For this case, the surface conductivity of PAam-Ni^{+2} (2.5%) was calculated according to relation $\sigma = I/2\pi sV$ which is increased significantly, it is equal to 10.76nScm^{-1}.

The electrical resistivity of PAam-Ni^{+2} up to 25% concentration where calculated using the relation $R = \rho L/A$, since one dimensional rods were formed. R is the resistance; ρ is the resistivity and L, A are the length

(15 μm) and the cross sectional area (r = 0.5 μm) of the rod formed respectively. The current- Voltage curve (**Fig. 3.34**) shows the resistance (R) equal to $0.73*10^8\Omega$ and so by calculation, the resistivity (ρ) equals to 0.6 Ω cm, and the electrical conductivity of PAam-Ni^{+2}complex (25%) equals to 1/ρ = 1/0.6 = 1.66 Scm^{-1}.According to the calculation the PAam-Ni^{+2} (25%) complex is classified as semiconductor with a voltage gap of 0.5V.

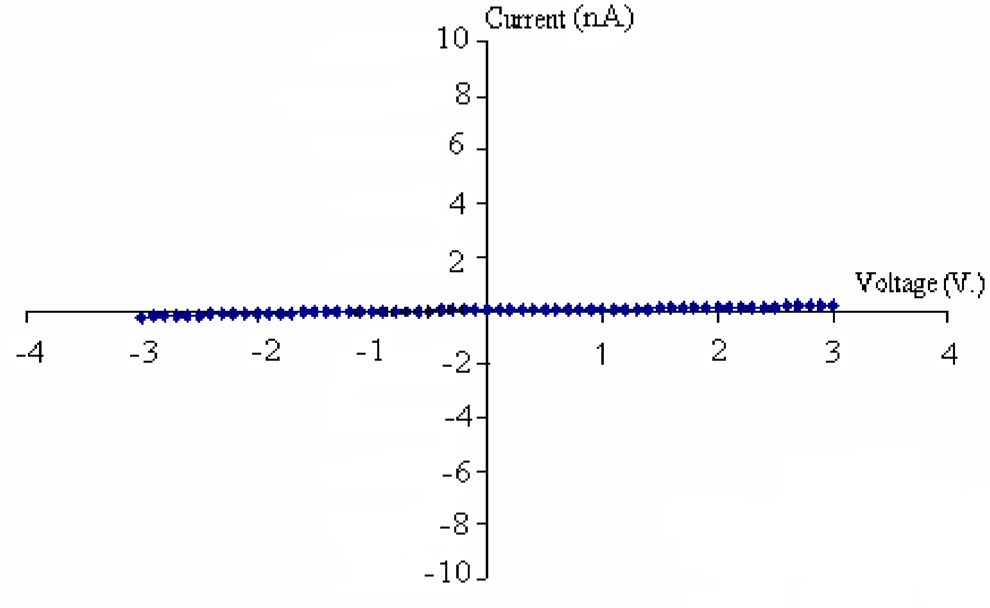


Fig. 3.32: Current-Voltage Curve of PAam

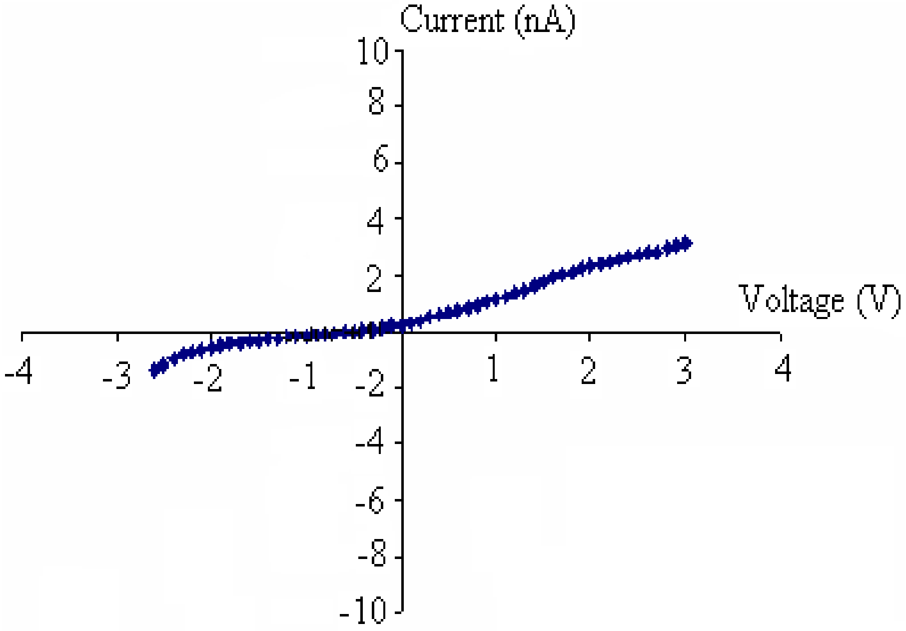


Fig. 3.33: Current-Voltage Curve of PAam-Ni^{+2} complex 2.5%

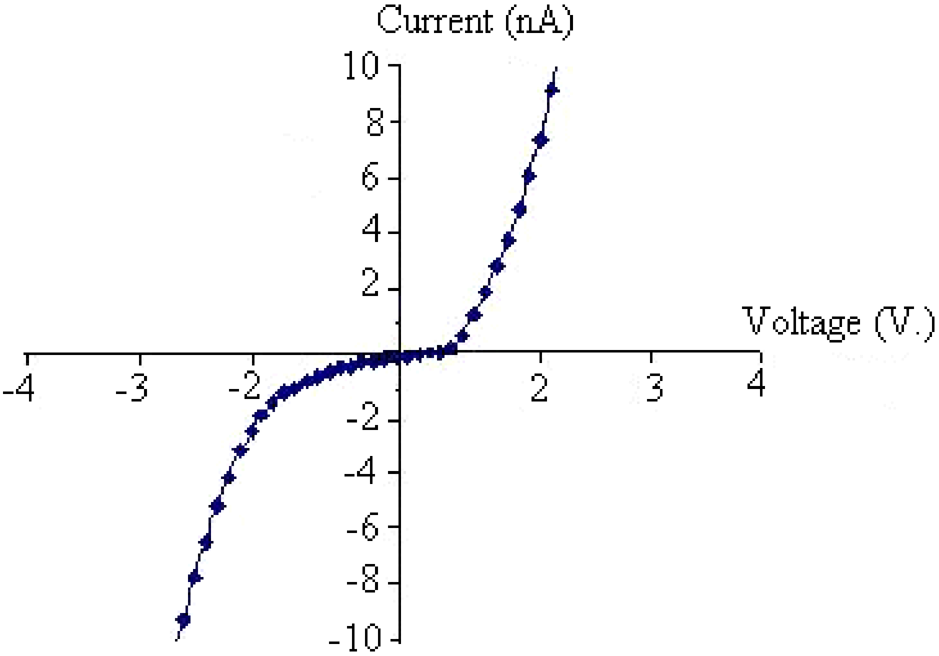


Fig. 3.34: Current-Voltage Curve of PAam-Ni^{+2} complex 25%

III.6 Morphological characterization of PAam and PAam-Ni^{+2} complexes using Atomic Force Microscopy.

Atomic force microscopy (AFM) is an important technique due to its ability to image and characterize the structures in biological and chemical systems. The images of AFM depend on the size, shape, and terminal functionality of the probe tips used for imaging. [55] AFM probes consist of microfabricated silicon or silicon nitride cantilevers with integrated pyramidal tips. [56]

Major objectives of this study have been (i) to determine how metal ions (Ni^{+2}) affects the surface reactivity of PAam, and (ii) to characterize the growth of metal ions on PAam surface. The main components of this effort are surface structure, surface chemistry, and surface electronic properties.

AFM was used to characterize the surface of the prepared samples. The AFM image of polyacrylamide is shown in **Fig. 3.35**, from the cross section, we can see that the roughness is a bout 0.5μm. The image of PAam-Ni^{+2} (2.5%) is shown in **Fig.3.36**, the roughness is 0.5 μm. Different surprising results, instead of three dimension film, one dimensional rods were formed when 25% PAam-Ni^{+2} complex is prepared as shown in **Figure 3.37**. The rods were about 1 μm in diameter and 15 μm long.

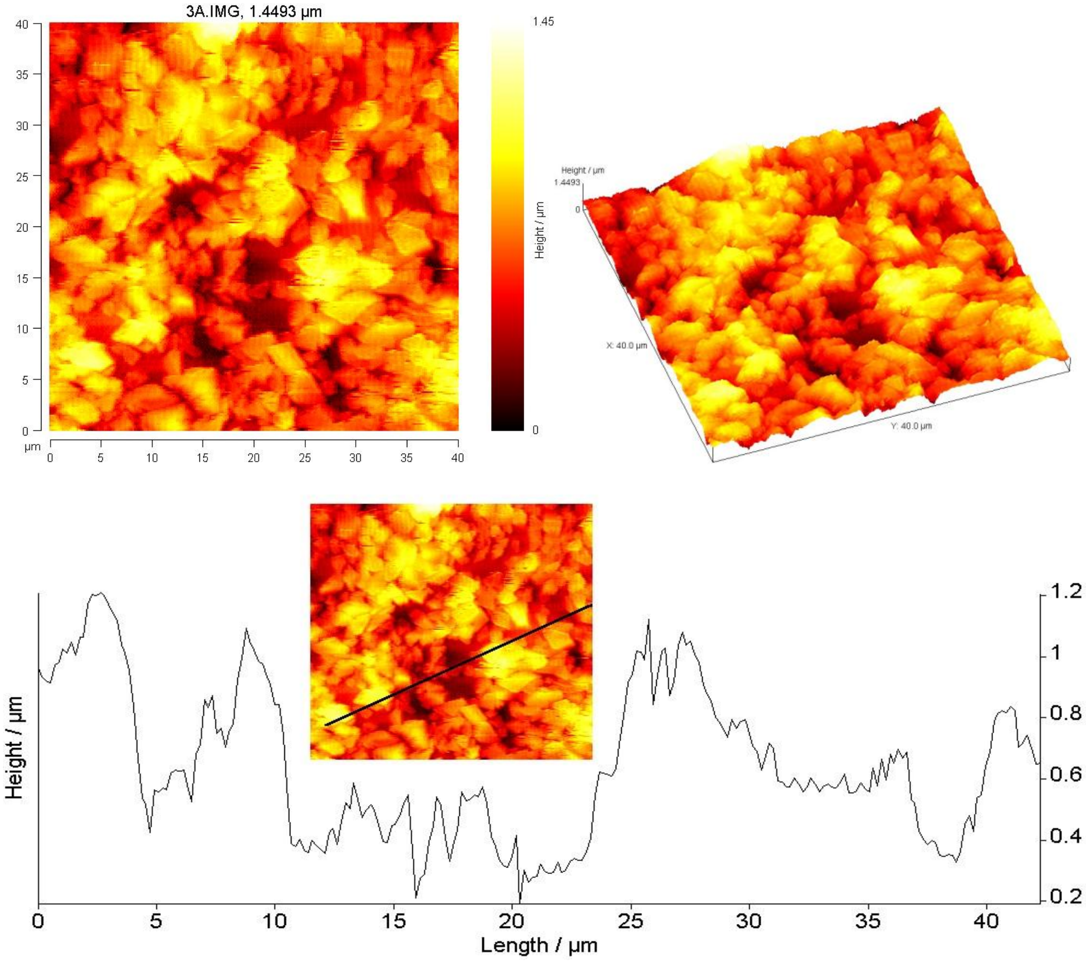


Figure 3.35: AFM image of PAam

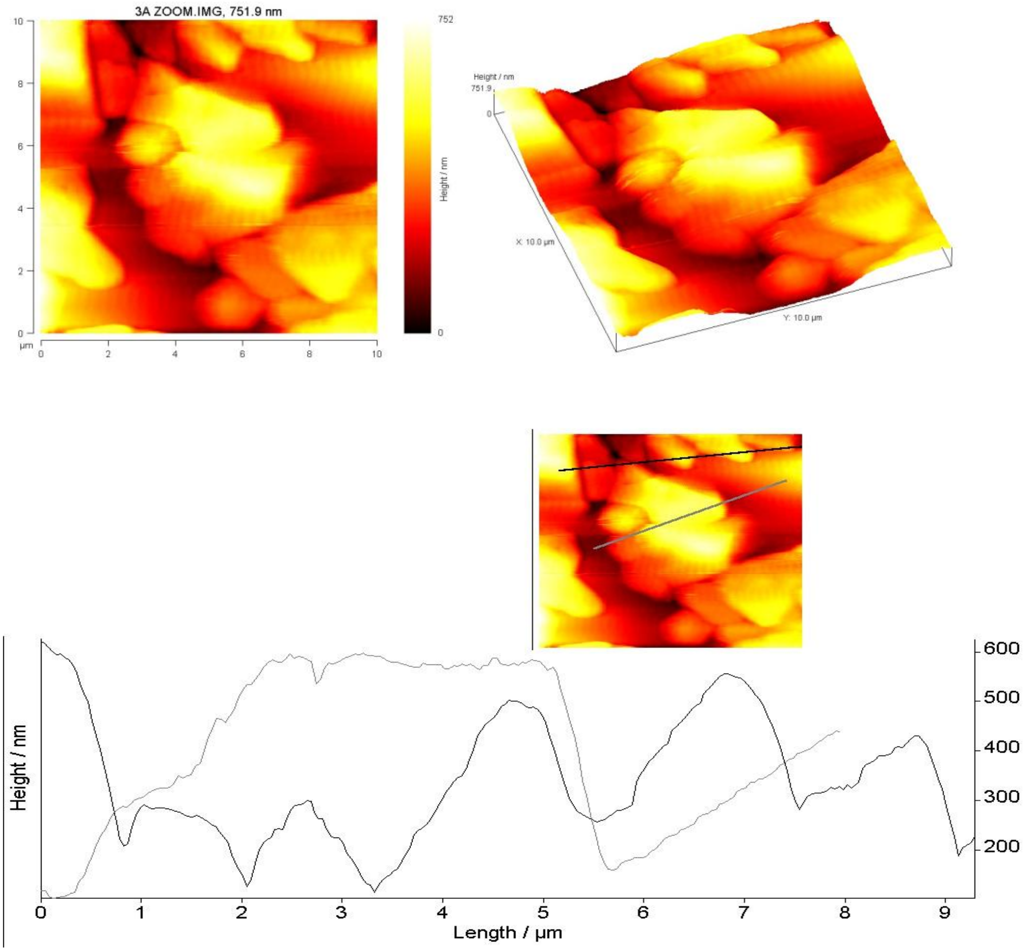


Figure 3.36: AFM image of PAam-Ni^{+2} complex film 2.5%.

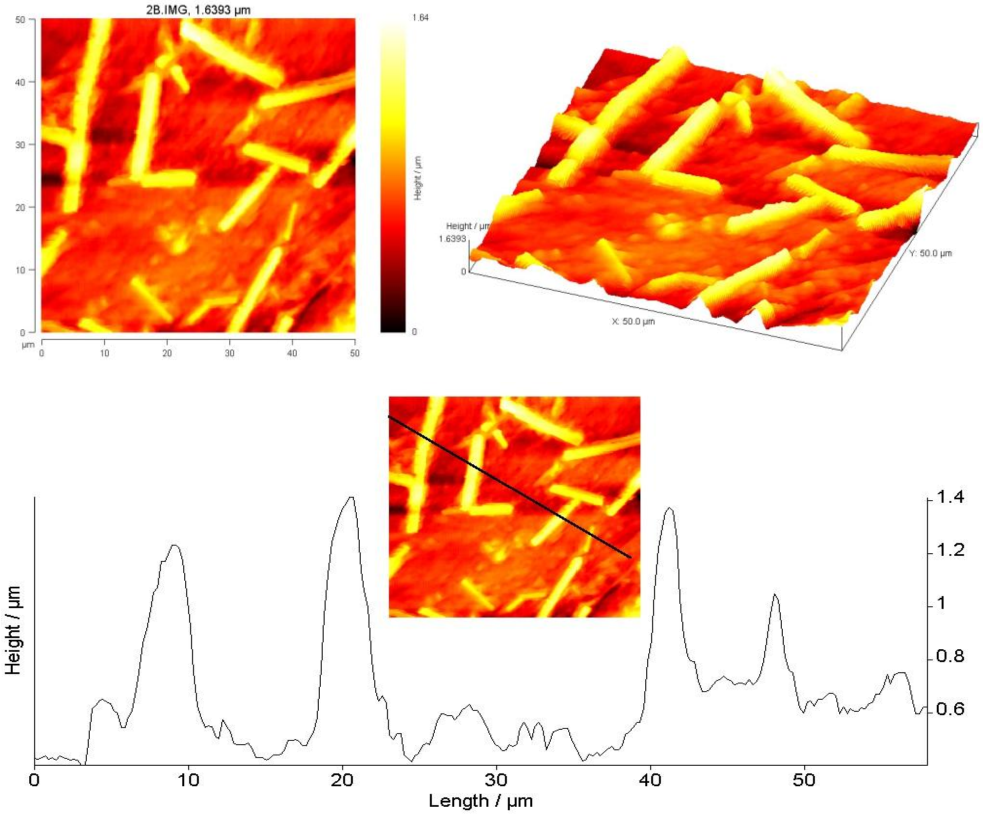


Figure 3.37: AFM image of PAam-Ni^{+2} complexes film 25%.

CHAPTER FOUR

CONCLUSION

We have investigated the complexation of hydrophilic side group in PAam with metal ions using FTIR, UV-visible spectroscopy and DSC techniques. The PAam – M^{+2} complexes have specific transmittance that is completely different from the pure polymer, this behavior related to the metal ions association in the polymer chain. The UV-visible spectroscopy and DSC analysis characterized the association of M^{+2} at the backbone of PAam by showing different transitions at different concentration ratios.

The thermal parameters of PAam-M^{+2} such as glass transition temperature (Tg) or the melting point (Tm), were determined by DSC. The Tg of PAam appears at 161.4^0C, while the Tg of PAam-Cu^{+2}, PAam-Co^{+2} and PAam-Ni^{+2} were observed at 168.8 ^{0}C, 166.2^0C and 167.8^0C respectively. The melting temperatures (Tm) of PAam appear at 161.4^0C. The melting temperatures (Tm) of these complexes were observed at 248.5^0C, 250.8^0C and 255^0C respectively.

The electrical conductivity of PAam improved mainly in the presence of M^{+2}, the PAam behavior is insulator, while it showed a semiconductor like behavior when M^{+2} is associated in the polymer chain. AFM studies confirmed these findings by studying the surface features of PAam and PAam-Ni^{+2} complex films. The results were shown photographically.

Our study shows that these films may have an important application in various industries.

REFERENCES

[1] Sax, N. I., *Dangerous Prop. Ind. Mater.* **1991**, 11 (1), 2.

[2] World Health Organization. *Environ. Health Criteria* **1985**, 49, 1.

[3] Williams, D. C. *Functional Monomers: Their Preparation, Polymerization and Application* **1973** Yocum, New York.

[4] Collins, J. J.; Swaen, G. M. H.; Marsh, G. M.; Caporossi, J. C.; Jucas, L. J. *J. Occup. Med.* **1989**, 31 (7), 614.

[5] Tanaka, T. *Phys. ReV. Lett.* **1978**, *40*, 820.

[6] Hideaki, S. Edward, W. *J. Am. Chem. Soc.* **2001**, *123,* 12877-12885

[7] Marcus J. Caulfield, Greg G. Some Aspects of the Properties and Degradation of Polyacrylamides *Chem. Rev.* **2002**, 102, 3067-3083

[8] Dutra, E. R.; Mano, V.; Machado, J. C. *Polym.Degrad. Stab.* **2000**, 67 (3), 491.

[9] Grassie, N.; McNeill, I. C. *Eur. Polym.* J. **1978**, 14 (11), 931.

[10] Van Dyke, J. D.; Kasperski, K. L. J. Polym. Sci.,**1993**, 31 (7), 1807.

[11] Toth, I.; Szepvolgyi, J.; Jakab, E.; Szabo, P.; Szekely, T. *Thermochim.*
Acta **1990**, 170, 155.

[12] Zurakowska-Orszagh, J.; Busz, W.; Soerjosoeharto, K. *Bull. Polym. Sci.* **1977**, 25 (11), 845.

[13] Leung, W. M.; Axelson, D. E.; Van Dyke, J. D. *J. Polym. Sci.,***1987**, 25 (7), 1825.

[14] Thomas, W.; Wang, D. W. Encyclopedia of Polymer Science and Engineering **1985** Mark, H. F., Bikales, N. M, New York.

[15] Ilavsky, M.; Hrouz, J.; Stejskal, J.; Bouchal, K. Macromolecules **1984**, 17, 2868.

[16] Zurimendi, J. A.; Guerrero, S. J.; Leon, V. *Polymer* **1984**, *25* (4), 999.

[17] Sykes, P. A Guide Book to Mechanism in Organic Chemistry**1986**, 6th edition, Longman Scientific & Technical. London.

[18] Ingold, C. K. *Structure and Mechanism in Organic Chemistry*; Cornell University Press: Ithaca, NY, **1953**.

[19] Kulicke, W. M.; Kniewske, R.; Klein, J. *Prog. Polym. Sci.* **1982,** *8*, 373-468.

[20] Taylor, K. C.; Burke, R. A.; Nasr-El-Din, H. A.; Schramm, L. L. *J. Pet. Sci.Eng.* **1998**, *21*, 129-139.

[21] Lu, J. H.; Wu, L. *J. Agric. Food Chem.* **2001**, *49*, 4177-4182.

[22] Taylor, K. C.; Nasr-El-Din, H. A. *J. Pet. Sci. Eng.* **1994,** *12*, 9-23.

[23] www.http://nobelprize.org/chemistry/educational

[24] Feast, W.J., Tsibouklis, J., Pouwer, K.L., Gronendaal, L. and Meijer, E.W.*Polymer* **37** (**1996**) 5017.

[25] L.B. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, and J.R. Reynolds
Adv. Mater. 12(7) (2000) 481.

[26] Neil W. Ashcroft and N. David Mermin, Solid state physics. Holt-Saunders, **1976**.

[27] Ramakrishna, M. Bull. Mater. Sci.,**2002**, 25, 403–406

[28] Blythe, A. R., Electrical Properties of Polymers, Cambridge Solid State. Cambridge, England,**1979**.

[29] Pohl, H. J. Polym. Sci. Sym. **1967**, 13.

[30] Vlanski J. et al., Poly. Plast. Tech. Eng. **1982**, 17(2), 139.

[31] J. Mort and G. Pfister, Poly. Plast. Tech. Eng. **1970**, l2, 89.

[32] Kohlman, R. J., Epstein, A.J. Handbook of Physical Properties of Polymers, **1996**, J.E. Mark, AIP.

[33] Kohlman, R. J., Epstein, A.J. Handbook of Conducting Polymers, **1997**, *Marcel Dekker, Inc.*, New York.

[34]Malcolm P. Stevens. *Polymer Chemistry* **1999**, 3rd edition, Oxford University, New York.

[35] Cheremisinoff, N, P. Polymer Characterization Laboratory Techniques and Analysis.**1996**, Westwood, New Jersey.

[36] Twombly B, Shepard D. *Instrum. Sci. Technol*. **1994**; 22, 259.

[37] Allara, D. L; Atre, S.V.; Parikh, A. N. *Polymer Surfaces and Interfaces II*; John Wiley & Sons: Chichester, **1993**.

[38] Jong H. K; Byoung, R. M; Jongok, W.*J. Phys. Chem. B* **2003**, 107, 5901-5905.

[39] Greenwood N. N., Earnshaw A., C*hemistry of the Elements* **1997**, 2nd edition, Butterworth-Heinemann UK .

[40]Tanaka, T.; Wang, C.; Pande, V.; Grosberg, A. Yu.; English, A.; Masamune, S.; Gold, H.; Levy, R.; King, K. *Faraday Discuss*. **1996**, *102*, 201.

[41] Rivas, B. L.; Maturana, H A.; Molina. M. J.; Gomej-Anton, M. R.; Rosa, M.; Pierola, I. F. *J. Appl. Polym. Sci.* **1998**, *67*, 1109.

[42] Tiera, M. J.; De Oliveira, V. A.; Burrows, H. D.; Da Graca Miguel, M.; Neumann, M. G. *Colloid Polym. Sci***. 1998**, *276*, 206.

[43] Thompson, J. A.; Jarvinen, G. *Filter.* **1999**, 36, 28.

[44]Siyam, T.; Ashour, A. H.; Youssef, H. A. *Polym. Int.* **1999**, 48, 799.

[45]Bekturov, E. A.; Mammutbekov, G. K. *Macromol. Chem. Phys*. **1997**, 198, 81.

[46]Jose, L.; Pillai, V. N. R. *Macromol. Chem. Phys*. **1996**, 197, 2089.

[47]Naoki, T. *Shokubai* **1998,** 40, 536.

[48]Yakura, N.; Kashiwada, T.; Hirai, H. *Kobunshi Ronbunshu* **1998**, 55, 415.

[49] Bergbreiter, D. E.; Case, B. L.; Liu Y.S.; Caraway, J. W. *Macromolecues* **1998**, 31, 6053.

[50] Case, B. L.; Franchina, J G.; Liu, Y.-S.; Bergbreiter, D. E. *Chem. Ind.* **1998**, 75, 403.

[51] Bergbreiter, D. E. *Catal. Today* **1998**, *42*, 389.

[52] Hocking, M. B.; Klimchuk, K. A.; Lowen, S. *J. Polym. Sci.,Part A*: *Polym. Chem.* **2001**, 39, 1960-1977.

[53] Gupta, M. K.; Bansil, R. *J. Polym. Sci., Polym. Phys. Ed.***1981**, 19, 353-360.

[54] Kulicke, W.-M.; Siesler, H. W. *J. Polym. Sci., Polym. Phys.Ed.* **1982**, 20, 553-556.

[55] Bustamante, C., Rivetti, C. Keller D, J. Curr. Opin. Struct. Biol. **1997**, 7, 709-716.

[56] Shao, Z., Mou, J., Czajkowsky, J., Yang, J. Yuan, J.Adv. Phys. **1996**, 45, 1-86.