SYNTHESIS OF MODIFIED CONDUCTING POLYMERS AND STUDY OF THEIR WATER PURIFICATION CAPABILITY

BY

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Submitted in partial fulfilment of the requirements for the degree of Master of philosophy (M.Phil.) in Chemistry

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Dedicated

To
My beloved

Father; Kalipada Das
&
Mother; Laxmi Rani Das

Declaration

I declare that the content in my M.Phil. thesis entitled ***"Synthesis of modified conducting polymers and study of their water purification capability"*** *is original and accurate to the best of my knowledge. I also declare that the materials contained in my research work have not been previously published or written by any person for any degree or diploma.*

M. Phil. Student

(Chinmoy Kumar Das)

CERTIFICATE

This is to certify that the research work embodying in this thesis has been carried out under my supervision. The work presented herein is original. This thesis has not been submitted elsewhere for the award of any other degree or diploma in any University.

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Certification of Thesis work

A Thesis on

"Synthesis of modified conducting polymers and study of their water purification capability"

By

Chinmoy Kumar Das

has been accepted by the following panel of examiners as satisfactory in partial fulfillment for the degree of Master of philosophy in Chemistry and certified that the student demonstrated a satisfactory knowledge on the field covered by this thesis in an oral examination held on June 29, 2008.

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Chinmoy Kumar Das

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Abstract

Perpetration, characterization and water purification capability of modified conducting polymers have been described. Synthesis of polyaniline (PANI), polyaniline-silica (PANI-silica), polyaniline-stearate (PANI-stearate), polyaniline-sodium dodecyl sulfate (PANI-SDS) and polyaniline-ethylene diamine tetraacetic acid (PANI-EDTA) were carried out at pH 3.1 and at room temperature in aqueous medium by in situ oxidative chemical polymerization process. These composites have been characterized by a wide range of experimental techniques including density analysis, optical microscopy, infra-red spectroscopy, UV-visible spectroscopy and adsorption capability.

Elemental analysis for silica content indicate that the chemically synthesized PANI-silica composite contain as high as about 11 % silica in the matrix. At the same time it was seen that only 3.9 % EDTA were impregnated in to the polymer matrix and has been confirmed by the complexometric titration. It was seen that the density of PANI-silica composite is higher than that of the bulk polymer. On the other hand, the densities of PANI-stearate, PANI-SDS and PANI-EDTA are smaller than that of the PANI matrix.

Optical microscopic view provided very important and visualized information about the bulk polymer and the synthesized composite materials. The presences of white spots into the composites clearly indicate the incorporation of foreign particles into the polymer matrix.

Infra-red spectroscopic studies yield useful qualitative information on PANI, PANI-silica, PANI-stearate, PANI-SDS and PANI-EDTA composites. From the spectra, the band characteristics of PANI and other PANI based composite materials confirm the formation of the respective polymer and the composites. IR spectra observed for the studied sample exhibited the appropriate adsorption bands those are attributable to both polymer and the composite component.

Typical DTA and TGA analysis for the bulk PANI, PANI-silica, PANI-stearate, PANI-SDS and PANI-EDTA composite materials provide the useful information about the formation composites and the characteristic thermal properties. Both from the DTA and TGA analyses it was seen that bulk PANI and composite materials have strong affinity to water molecules, i.e., moisture that was about 40% of the total mass. Distinguishable weight loss at different phases with temperature shown in TGA clearly ascribable to the formation of composite materials. DTA also give the comparable data in favour of formation of composites and also the probable reaction involve in the experiment.

Surface area measurements show that the PANI-silica composite have much higher than that of the bulk polymer. The incorporation of fine silica particles into the polymer might lead to this increased surface area. Adsorption of Mn^{2+} and As^{3+}ions on the PANI-silica matrix has been found to occur. At the same time PANI-stearate and PANI-SDS composite materials could be used as the trap for the Mn^{2+} and As^{3+}ions present in the water sample. On the other hand PANI-EDTA composite could adsorb only Mn^{2+} ion from aqueous medium.

Chapter 1: Introduction

1.1 Conducting Polymers

The interest in the field of organic semiconductors originated from the suggestion that the transfer of π electrons from molecule to molecule may play an important role in fundamental physical processes of living organisms. Very small but measurable electrical conduction was reported for anthracene in 1906. Single crystals of purified anthracene and other condensed aromatic ring systems formed interesting objects of preliminary study of the fundamental behavior of some charge carriers in such systems, even though such molecular crystals showing some degree of electrical conductivity would be prominently brittle, low melting and easily soluble. It obviously follows that a high polymeric system obtained in a semiconducting or conducting form would combine the interesting electrical property of molecular crystals of condensed polynuclear aromatic compounds with the useful range of mechanical (strength, modulus, rigidity, etc.) and thermal (melting/softening point or heat distortion temperature) properties and good corrosion resistance.

The common synthetic polymers are electrical insulators in general. A conducting polymer would, however, be a much desired product for use as corona shield or as a separate layer in an insulation system in film/sheet form to prevent corona discharge and for providing a conducting surface for electroplating non-conductors or for use in printed circuit boards, electronic devices, photovoltaic devices, solar cells, batteries, etc.

Highly conducting polymers for use as high quality conducting coatings, strong films or filaments are in the process of development. A practical and more obvious approach involves incorporation of metallic powders, flakes or other conductive fillers such as graphite powder or conducting carbon blacks into common plastics or rubbers. However, such filled conducting compositions have their own limitations. Despite infusion of conductivity due to the incorporation of the conducting filler particles, the prominent insulation or resistance character of the matrix polymer generates heat during passage of electricity. Accumulation of heat and consequent rise in temperature and thermal expansion cause the conducting filler particles in such filled polymer systems move further apart, thereby leading to a dropping trend in conductivity with time of passage of electricity. As for synthesis of inherently conducting polymers, there are developing trends in two directions (i) synthesis of conjugated polymers and (ii) preparation of polymeric charge transfer complexes.

The first approach is based on the fact that electron delocalization favorably occurs as a molecular system becomes more conjugated. Likewise, in charge-transfer complexes, a partial electron transfer occurs from the donor site to the acceptor site of the molecule; a good example is a crystalline complex of quinoline with tetracyanoquinodimethane, having a room temperature conductivity of the order of only 1s cm^{-1} (or $ohm^{-1}cm^{-1}$) and a temperature dependence corresponding to an activation energy of 0.1 eV. By complexation of this nature, a conductivity level in the upper side of the semiconducting range is readily achieved for an organic high polymeric system.

Polymeric charge-transfer complexes of this kind are attractive for their use in electronic engineering as they are commonly endowed with good range of mechanical and thermal properties with the advantage that they could be processed into such useful shapes as cohesive films, sheets, discs, rings and thin wires.

The scattering of conduction electrons causes the electrical resistance of metals when they collide with ion cores during flow under a potential gradient, thus contributing to a heating effect. The displacement of the cores from their positions arises from their thermal motion. The thermal motion of the ion cores decreases with lowering of temperature with consequent lowering in the resistance character or increase in the conductivity level.

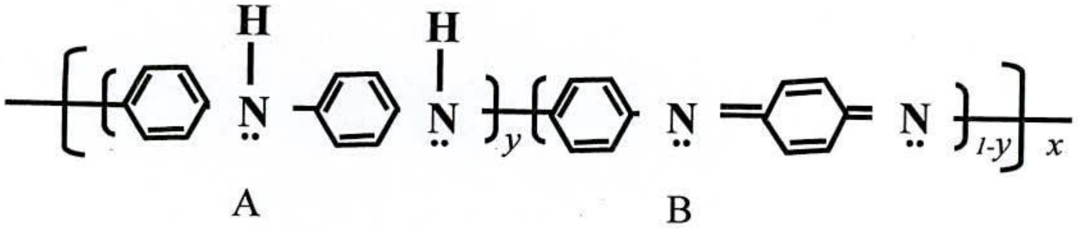
The resistivity of the semiconducting materials on the other hand decreases with rise in temperature because of the fact that with higher thermal excitation more electrons are released from interatomic bonds and the applied electric field enables the released electrons in higher numbers more through the mass giving rise to increased electronic conduction with rise in temperature. Even though, conducting polymers having ion-exchanging capacity during charging and discharging process have been reported [1-2]. It was found that the conducting polymers exchange both anions and cations depending on the polymerizations conditions, the type and size of the counterions incorporated during the polymerizations process as well as on the ions present in the electrolyte solution. This ion-exchange property of conducting polymers has revealed its new window of many practical applications and leads us to synthesize conducting polymer-based composites

Inherently conducting polymers, also commonly known as synthetic metals, somehow possess the electrical, electronic, magnetic and optical properties of a metal while also exhibiting [3] the physical and mechanical properties, rheological features and processabilities associated with a conventional polymer. The applicability of the concept of "doping" is the unifying theme that distinguishes the inherently conducting polymers from all others. Addition of electron donors or acceptors causes doping that results in dramatic electronic and magnetic changes in the Inherently conducting polymers along with increase in conductivity to or approaching the metallic range.

Doping is reversible; removal of dopant or dedoping produces the original low conducting, semiconducting or insulating (base) polymer usually without degradation of the polymer backbone. Some Inherently conducting polymer are Polyacetylene , Polydiacetylenes, Poly(p-phenylene Sulphide) and PANI.

1.2 Polyaniline is the most prominent inherently conducting polymer

The most important inherently conducting polymer from the view point of low cost and high application potential is polyaniline. It has drawn the attention of many workers in recent years in respect of synthesis by chemical and electrochemical means. Its non-redox doping character is also an added attraction. PANI's relatively low cost, ease of synthesis in easily process able dispersion forms and satisfactory environmental stability are also some advantageous features.



The base form of PANI has the general formula consisting of reduced (A) and oxidized (B) repeat units [4-6]. The average oxidation state, (1 - y) may vary from zero (to give the completely reduced polymer characterized only by the repeat unit A) to 0.5 (to give the "half oxidized" polymer characterized by 1: 1 alternating sequences of A and B) to one (to give y = 0 and the completely oxidized polymer characterized by the repeat unit B only). For the presence of 1:1 alternating sequence of A and B repeat units in PANI, the polymer is called emeraldine base. The imine nitrogen atoms can be protonated in full or in part to give the respective salts, the degree of protonation being dependent on the oxidation state and pH of the aqueous acid used.

The partly protonated emeraldine hydrochloride salt is prepared readily in the form of a black-green precipitate by polymerizations of aniline by oxidative coupling in aqueous acid media (like HCl) by such oxidizing agents as $(NH_4)_2 S_2O_8$, H_2O_2, Cr^{6+}-complexes/salts etc. It can also be prepared electrochemically from aniline.

Soluble PANI can be obtained by solution polymerization of aniline in N-methyl pyrrolidone and in aqueous acidic solution [7-10] using the support of a water soluble polymer such as poly(vinyl alcohol) methyl cellulose, carboxy methyl cellulose, polyacrylic acid, polyacrylamide, poly(vinyl pyrrolidone) etc. PANI has application potentials in electromagnetic interference shielding, as gas sensors, in gas separation, as electrodes in rechargeable batteries and in static charge dissipation. On the basis of above numerous applications PANI has been chosen to prepare composite materials where PANI provides the main backbone-structure.

The most familiar composites are those composed of one or more types of constituents dispersed in a matrix. For example, reinforced concrete consists of a stone and sand aggregate and steel rods (fibers) embedded in a matrix of cement. Recently, organic polymer inorganic oxide composites have been prepared by embedding the inorganic oxides into the polymer matrix [11]. For example, silica/titanium oxides have been embedded into the PANI or polypyrrole (PP) bulk.

There are two major reasons for the revived interest in composite materials. One is that the increasing demands for better performance in many product areas, especially in the aerospace, nuclear energy and aircraft fields is taxing to the limit our conventional mono-lithic materials. The second reason- the most important for the long run is that the composites concept provides scientists with a promising approach to designing, rather than selecting, materials to meet the specific requirements of an application.

On an increasing demand, composites are used as starting materials for many compounds, for instance, a highly electrically conducting plastic by introducing copper in the right form (only 4 % vol is needed) with poly (vinylchloride). The wings of aircraft are made of graphite fiber in a woven from in an epoxy resin. It is molded to shape in an autoclave. A set of parallel fibers in a matrix is very anisotropic solid, which can be used to very good effect in certain devices in computer. Metal matrix composites are being developed because the metal as matrix, say Al or Mg for low temperature applications or Ti for the high temperatures, has advantages over thermosetting resins. The principle of compositing materials is also used in a very sophisticated way in microelectronics. One of the important applications of polymer composite as conducting polymer as electrodes in the rechargeable batteries. In such applications, use is made for the electro-chemical reversibility of the polymers acting as electrodes [12]. The use of thermoplastic, linear chain, polymers as the matrix phase promises to satisfy the criteria which we have defined as necessary for advanced structural composites to become major general materials [13].

1.3 Composites

The word composite, as technically defined, means a macroscopic combination of two or more distinct materials having an identifiable interface between them, but more pointedly, the definition is confined to only such materials as would contain a fibrous or particulate reinforcement supported by a binder or matrix material. The discontinuous phase constituted of the fibre or particulate reinforcement is commonly stiffer and stronger than the continuous (matrix) phase. In most cases, a substantial volume fraction (> 10%) of the discontinuous phase is necessary just to achieve significant reinforcement. The difference between a composite and a filled system lies in the fact that while in a composite the discontinuous phase imparts significant mechanical reinforcement, it only plays the role of a loading agent or diluent without property enhancement or reinforcement in what is called a filled system. Fillers may, however, impart many advantages such as fire/flame retardancy, shrinkage control, improved thermal/electrical conductivity and above all cost benefit. One may also have composites where the stiff components may constitute the major, continuous phase such as the rubber modified (toughened) plastics.

Composites, in general, and fibre reinforced plastics or glass fibre reinforced plastics in particular, have been developed out of sheer necessity imposed by the stringent requirements of modern technology. The demand of the automotive and particularly of the aerospace community prompted developments in reinforced composites which combine light weight and high strength of Aluminium and Al-alloys and excel them in respect of chemical resistance, corrosion/weather resistance and dent resistance (good recovery of deformation). Composites are in growing demand from architects and construction engineers in the transport, sports, aerospace, defence, building and many other sectors. Composites have been developed because no homogeneous structural material could offer all the desired attributes for a given application.

As materials of construction in automotive and aerospace sectors, plastics are undoubtedly growing in acceptance. Even then, in engineering status, simple plastics still find their place at or near the bottom; but they hold high potential for a much brighter future through material development in the form of fibre reinforced plastics composites. In many cases, there are clear objections to use of plastics on consideration of demands on thermal and aging resistance and lack of confidence centering limitations in a desired balance of thermal and mechanical properties. The best way to overcome these limitations and constraints to enable plastics to not only complete with or even overshadow light metals and alloys in stress and safety-sensitive engineering applications is to make composites [14] through fibre reinforcement of prospective polymers coupled with judicious cross-linking of the polymer matrix.

The polymer controls the chemical, thermal and often the electrical performance of composites or the matrix material while the mechanical performance within the polymer's ultimate temperature capability is dictated by effectiveness of the reinforcement. Each polymer has basic attributes that no amount of incorporation of reinforcing or other additives of different dose levels and varieties can disguise; no plastic can reliably function even briefly at a temperature above the softening or heat distortion temperature of the base polymer. However, the heat distortion temperature and mechanical (tensile) strength of selected polymers may be substantially enhanced through judicious incorporation of a reinforcing fibre such as glass fibre and by cross-linking. With appropriate support and fibre reinforcement, the polymer or the matrix material enables us to partly realise the inherent high strength and stiffness of the reinforcing fibre material. The principal benefits of fibre reinforcements are: improved resistance to hot deformation, lowering or avoidance of low temperature embrittlement, higher strength modulus, rigidity and stiffness, improved creep resistance and hence improved dimensional stability.

The discovery of light-weight, strong and stiff carbon fibres in the mid 1960s proved to be a turning point in the development of high performance plastic composites offering serious threats to the light alloys in their traditional use as materials of construction in the aerospace sectors. A chain of further developments in strong stiff, light weight synthetic fibres, particularly the aromatic polyamide popularly known as aramid fibres and by the trade name Kevler, and also developments in aromatic resins and other engineering polymers (as matrix materials) suitable for use in the design of high performance fibre reinforced plastics composites followed in the wake of developments of carbone fibres (short fibres and continuous filaments) [15]. With the developments in high performance aromatic polymers, the old division between the functional and processing potentials of thermoplastics and thermosets is getting blurred progressively. Thermosets, however, commonly exhibit lower shrinkage, improved chemical resistance and thermal performance, while thermoplastics give advantages in higher outputs, better design of parts over and above their recycling potential.

Amorphous thermoplastics such as poly(phenylene oxide), polycarbonate etc. are valued for low shrinkage and good impact behaviour, even though their fatigue resistance is rated low and on fibre reinforcement, they offer low or limited benefits; crystalline polymers on the other hand exhibit higher shrinkage and are dimensionally affected more on heating but they are characterized by substantial improvements in heat distortion temperature and tensile/flexural strength on fibre reinforcements.

A composite is viewed as a laminate if the reinforcing fibres are arranged in layered fashion such as in the form of webs, fabrics or mats, mixing of the matrix resin with randomly oriented short fibres, allows the resin fibre mix or the dough to be injection moulded or compression moulded with or without the presence of a particulate filler and such dough-like short fibre resin mixes are commonly known as dough moulding compound. Short fibres are not necessarily randomly arranged. Maximum strength and stiffness are obtained when continuous fibres/filaments are aligned parallel to the applied load. Such unidirectionally aligned fibres in resin matrix, can be most efficiently achieved by such methods as pultrusion (combining pulling with extrusion).

1.4 Synthesis of PANI based composites

Two techniques are known for synthesizing composites materials :

i) Chemical synthesis and

ii) Electrochemiocal synthesis

A widely used chemical process is the oxidative polymerisation. Various oxidizion agents are used in this process such as potasium dichromate, ammonium persulphate, ferric chloride, hydrogen peroxide etc [16-18]. A colloidal solution is used for the polymerization. During dispersion polymerization [19], a monomer, soluble in the reaction medium is converted into polymer which is insoluble under those conditions. Aggregation of growing insoluble polymer chains results in macroscopic precipitation of the polymer. If, however, a steric stabilizer is present in the system, the precipitation may be prevented and a dispersion of polymer particles, typically of submicrometer to micrometer size, is produced instead [20]. The steric stabilizer is usually polymer soluble in the reaction medium. It becomes either physically adsorbed or chemically grafted onto the precipitating polymer. The resulting "hairy" particles are colloidally stable [21,22] and they do not aggregate.

Conventional chemical polymerization techniques have been successfully applied by various research groups for the preparation of sterically stabilized particles of electrically conducting polymers such Polypyrrole and PANI [23]. A wide range of polymer composites e.g. poly(oxyethylene) [24,25], poly (vinyl alcohol-co-vinyl acetate) [26], proteins [27] have been reported by various research groups.

In the electrochemical oxidizing the monomer electrochemically in a dispersion of silica forms procedure silica-composites. Several techniques viz. potentiostatic, galvanostatic and potential sweep-techniques such as cyclic voltammetry are used for electrochemical polymerization of aromatic compounds. In potentiostatic technique a constant potential is applied to the working electrode, which is sufficient to oxidize the monomers to be polymerized on the electrode. In galvanostatic process, a constant current density is maintained to polymerize the monomers while film thickness can be controlled in the similar way as for potentiostatic technique. On the other hand, cyclic voltammetry involves sweeping the potential between potential limits at a known sweep rate. On reaching the final potential limit, the sweep is reversed at the same scan rate to the initial potential and the sweep may be halted, again reversed, or alternatively continued further. In such experiments cell current is recorded as a function of the applied potential. Polymerization process is carried out in a single compartment cell containing three electrodes viz. working, counter and reference electrodes. Most commonly used working and counter electrodes are usually platinum while the calomel electrode is used widely as reference. The potential of the working electrode is controlled versus the reference electrode, using a potentiostat. The electrochemical preparation of conducting polymers draw back to early attempts of Dall' olio and coworkers [28] who obtained "pyrrole black" on electrochemical oxidation of pyrrole in aqueous sulphuric acid as an insoluble precipitate on a platinum electrode.

Chemical method has some advantages over electrochemical method. The products which are formed as thin layer on the electrode surface, needed to be separated from time to time. Thus, the process is annoying and also time consuming. Moreover, the electrodes and other electrochemical apparatus are highly expensive. In this work, the studied samples were synthesized chemically. Silica, Stearate paricles, Sodium dodecylbenzene sulfonate and Ethylene Diamine Tetraacetic Acid were impregnated into the polymer matrix through in-situ chemical polymerization.

1.5 Optical Microscopy

In comparison to a biological microscope, the optical one differ in the manner by which the specimen is illuminated. In optical microscope, a horizontal beam of light from some light source is reflected by means of plane-glass reflector, downward through the microscope objective onto the surface of the specimen. Some of the incident light reflacted from the specimen surface will be mignified in passing through the lower lens system, the objective and will continue upward through the plane-glass reflector and be mignified again by the upper lens system, the eyepiece. The initial magnifying power of the objective eyepiece is used at the proper tube length, the total magnification is equal to the product of the magnification of the objective and the eyepiece.

The maximum magnification obtained with the optical microscope is about 2000X. The main limitation is the wavelength of visible light, which limits the resolution of fine detail in the optical specimen. The magnification may be extended somewhat by the use of shorter-wave length radiation, such as ultraviolet radiation, but the sample preparation techique is more involved. The specimen is polished and etched following normal metallogrographic practice before taking photograph. In the optical microscope the image is brought into focus by changing the lens spacing.

1.6 Infra-red (IR) spectroscopy

Emission or absorption spectra arise when molecules undergo transition between quantum states corresponding to two different internal energies. The energy difference ΔE between the states is related to the frequency of the radiation emitted or absorption by the quantum relation

$$\Delta E = h\upsilon$$

where h = planck's constant, υ = frequency.

Infrared frequencies have the wave length range from 1 μm to 50 μm are associated with molecular vibration and vibration-rotation spectra. Detection of chemical groups and bonding are done by the typical spectra.

In polymers the IR absorption spectrum is often surprisingly simple, if one considers the numbers of atoms involved. This simplicity results first from the fact that many of the normal vibrations have almost the same frequency and therefore appear in the spectrum as one absorption band and, second, from the strict selection rules that prevent many of the vibrations from causing absorptions.

The energy of most molecular vibrations corresponds to that infrared region of the electromagnetic spectrum. Molecular vibrations may be dected and measured either in an infrared spectrum or indirectly in a Raman spectrum. The most useful vibrations, from the point of view of the Organic chemist, occur in the narrower range of 2.5-16 μm (1 $\mu m=10^{-4}$ cm) which most infrared spectrometers cover. The position of an absorption band in the spectrum may be expressed in micron (μm), or very commonly and throughout this paper in terms of the reciprocal of the wavelength, cm^{-1}. The usual range of an IR is therefore, between 4000 cm^{-1} at the high frequency end and 625 cm^{-1} at the low frequency end.

Functional groups have vibration frequencies characteristics of that functional group. Within well defined regions of this range; these are summarized in figs 3.2 and from the subject matter of these topics. We will, however, postpone discussion of the region in which samples are prepared and spectra taken. The fact that many functional groups can be identified by their characteristic vibration frequencies makes the infrared spectrum the simplest, most rapid, and often most reliable means for assigning a compound to its class.

In attempting to deduce structural information about an unknown compound from its infrared spectrum, our approach should be to look for the presence or absence of absorptions having the frequencies characteristics of certain functional grouping [29].

Absorption in the infrared results in vibrational excitation of bonds, different types of bonds require differing amount of energy for vibrational excitations. In an infrared spectrum, the region 1500-4000 cm^{-1} is useful for determination of functional groups, while the region beyond this is the fingerprint region (1400 to 600 cm^{-1}). Polar groups usually exhibit stronger peaks in the infrared spectrum than nonpolar groups. The absorption position of $-NH_2$ (a double peak), $-COOH$ and $>C=O$ are particularly distinctive [30].

1.7 Ultraviolet and visible spectra

The ultraviolet and visible (UV) spectra of organic compounds are associated with transitions between electronic energy levels. The transitions are generally between a bonding or lone-pair orbital and an unfilled non-bonding or anti-bonding orbital. The wavelength of the absorption is then a measure of the separation of the energy levels of the orbitals concerned. The highest energy separation is found when electrons in б-bonds are excited, giving rise to absorption in the 120-200 nm (1 nm = 10^{-9}cm = 10 Å = 1 mμ) range. This range, known as the vacuum ultraviolet, since air must be excluded from the instrument, is both difficult to measure and relatively uninformative. Above 200 nm, however, excitation of electrons from p-orbital and d-orbital and π-orbital, and particularly, π -conjugated systems, gives rise to readily measured and informative spectra.

UV spectrophotometeric applications are numerous. The techniques may be applied to many of the organic chromophoric groups as well as many inorganic species. For example, ultraviolet spectrophotometry has been used for monitoring more than 60 metal ions in HCl which have been previously separated by liquid Chromatography. It has been applied to the analysis of drugs and pharmaceutical products such as antihistamines, to steroid phosphates in cosmetic creams and emulsions, as well as to cholesterol in milk fat and blood. Automated procedures are now utilized for analysis in clinical samples, food products, vitamins, cast iron, steels, and alloys. Many non-absorbing species may be indirectly determined by first converting to an absorbing species.

The procedures are sensitive in the 10^{-4} to 10^{-7} M concentration range, are moderately selective, and have a relative error of 1% to 4%. This relative error may be reduced by special techniques. In many cases the sample may be recovered for subsequent study.

(i) Detection of Conjugation; the ultraviolet spectrum is not used primarily to show the presence of individual functional groups but rather to show their mutual relationship. The chief relationship is regarding conjugation such as

(a) Conjugation between two or more carbon-carbon double (or triple) bonds

(-C=C-C=C-)

(b) Conjugation between carbon-carbon and carbon-oxygen double bonds

(-C=C-C=O)

(c) Conjugation between double bonds and an aromatic ring and even the presence of aromatic ring itself. (-C=C-C=)

UV spectrum can also reveal the number and location of substituents attached to the carbons of the conjugated system.

(ii) Detection of the Geometrical Isomers; The geometric isomers can be identified by u.v. spectroscopy as the trans isomers exhibit λ_{max} at slightly lower wavelengths and have larger extinction coefficients than the cis-isomers. For example trans stilbene C_6H_5-CH=CH-C_6H_5 show λ_{max} 294. (€=24,000) and cis isomer has λ_{max} 278 (€=9350).

(iii) Qualitative Analysis and Purification Control; It is also used in qualitative analysis and purification control in dye stuffs and pharmaceutical industries. For identification of compounds containing unbonded electrons (π-electron) or those with conjugated double bond system (π-electron) a comparison is done by comparing the absorption spectrum with the spectra of known compounds.

In UV absorption spectrum the absorption curve in influenced by the whole molecule as well as by particular groups containing, the absorbing electrons. This makes it difficult to identify a particular group so this method is not as useful as the N.M.R. method. For purification control the presence of impurities can be done by UV spectroscopy, which is considered as the best method for such detection. This method is considered superior to other methods because the bands due to impurities are very intense. In manufacture of nylon it is desirable, that the starting materials are very pure and the purity of these materials could be checked by UV spectroscopy. This helps in getting a product of high quality.

iv) Quantitative analysis: This method could be used for quantitative determination of those compounds which absorb UV radiations. Quantitative determination is based on Beer's law and Lambert's law.

1.8 Thermal Analysis

The thermal properties of polymers are conveniently studied by employing such techniques as Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry.

The DTA technique usually allows detection of thermal response and effects accompanying chemical or physical changes in a material sample when it is heated or cooled in a programmed manner through a zone of transition or reaction. It allows measurements of glass transition temperature (T_g), the crystallization temperature (T_{cr}), crystalline melting point (T_m) and the temperatures of thermal/oxidative degradation, cross-linking or other reactions.

In practice, the material sample and a thermally inert reference material held in the respective holder of the DTA cell are heated or cooled in a programmed manner. Any physical or chemical change in the test sample at a specific temperature, which is a characteristic feature of the material under study, is usually associated with a thermal transition leading to an enhanced difference of temperature, ΔT between the test and reference materials held in the same furnace chamber. ΔT is recorded as a function of temperature, T. For no thermal transitions in the test sample, ΔT remains nearly constant. In DTA, the correlation between ΔT and energy changes over a specific transition or reaction is unknown, thus making the conversion of endotherm or exotherm peak areas to energies uncertain. However, the technique is applicable to virtually all polymers and many other material systems, giving mostly qualitative information about thermal effects with clear indications of transition temperatures, but it is normally unsuitable for quantitative measurements of such parameters as heat capacity, heat of fusion or heat of crystalline polymers or change in specific heat at the glass transition for amorphous polymers, which are readily employing Differential Scanning Calorimetry.

Thermo Gravimetric Analysis (TGA) is a useful analytical technique for recording weight loss of a test sample as a function of temperature which may then be used for an understanding of the chemical nature of the polymer. Coupled with analysis of the volatiles and residue, TGA provides information about stability and decomposition of the material in an inert atmosphere or in air or oxygen, and about moisture content and other volatiles and plasticizer content, ash content, extent of cure of cross-linked polymers; in suitable cases, the analysis enables identification of polymers taking help of characteristic thermograms. The test sample is placed in a furnace while it remains suspended from one arm of a precision balance. TGA thermograms are obtained by recording change in the weight of the test sample as it is held at a constant high temperature or it is dynamically heated in a programmed manner. A curve may be drawn to represent weight loss of the sample as a function of temperature or else in a differential form showing weight change with time as a function of temperature.

1.9 Adsorption Study

When a solid is dipped into a solution, adsorption takes place on the surface of the solid for the same reasons which cause adsorption in gas-solid system. There is, however, the presence of the solvent which may modify the adsorption. If the solute is a strong electrolyte, the cation and the anion are not likely to be equally adsorbed, particularly at low concentration. In general, one of the ions, depending on the nature of the adsorbent and concentration, is preferentially adsorbed and the particles will acquire electric charge. In the present section adsorption of non-electrolytes or weak electrolytes will be considered. It is observed that at constant temperature the amount of adsorption depends on the concentration of the solute, the higher the concentration the greater the adsorption. The general pattern of the isotherm as long as physical adsorption takes place, is the same as in gas-solid system shown in Fig. 1.1

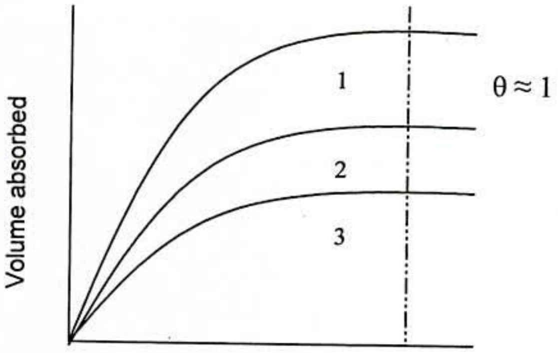


Fig 1.1: Schematic representation of isotherms at different temperatures 1,2,3 are increasing order of temperatures

Deviations occur, as in gas-solid systems, due to multilayer formation or penetration through the surface. As a matter of fact, the basic principles and mechanism in all adsorption processes are the same; the magnitude varies from system to system. In solution there is the probability of adsorption of the solvent molecules also. If the solute is adsorbed more than the solvent we get the usual positive adsorption and the solute concentration becomes less in the bulk of the solution. But if the solvent is more adsorbed than the solute then the solution becomes more concentrated with respect to the solute.

Freundlich Isotherm

The extent of adsorption from solution is related to concentration by an empirical expression known as Freundlich isotherm

$$\frac{x}{m} = \mathrm{K}\mathrm{C}^{n}$$

Where x, is the amount of the solute adsorbed by *m* gms of the solid, C, the concentration and *n* and K are constants. This equation can be converted to a linear form by taking logarithms

$$\log\frac{x}{m} = \log \mathrm{K} + \mathrm{n} \log \mathrm{C}$$

A plot of log $\frac{x}{m}$ *vs.* log C should give a straight line of slope n.

Many systems show agreement with this equation over limited range of concentrations although the significance of *n is* not understood; moreover, no useful or significant information can be obtained except establishing an empirical relation.

Langmuir's Isotherm

Langmuir's theory of unimolecular layer can be extended in an exactly analogous manner to adsorption from solutions. The workable form is at once obtained by putting C in place of P and *x* in place of *v*, a quite justifiable procedure.

$$\frac{C}{x/m}=\frac{C}{k1}+\frac{1}{k2}$$

The linear equation then becomes so that a plot of $\frac{C}{x/m}$ *vs.* C gives a straight line, k_1 and k_2 being constant. Just as the equation is obeyed by many systems so also there are many cases which deviate from it. The deviation principally arises out of multilayer formation.

Adsorption is a surface phenomenon. Adsorption may be defined as a process in which the concentration of a chemical species is greater on the surface than in the bulk resulting from in elastic collision suffered by molecules on the surface. The species that is adsorbed is called adsorbate and the material of the surface is called adsorbent. Adsorption strictly refers to accumulation of adsorbate on the surface only due to residual field of force.

The adsorption surface is generally a solid or liquid. Surface of solids or liquids have certain properties and characteristics that make them different from the bulk of matter. Although there is no chemical distinction between the molecules or atoms on the surface and the molecules or atoms in the bulk, energy considerations lead to quite dissimilar properties.

When two immiscible and chemically non reactive phases are brought into contact with each other, adsorption is a common observation which means that the concentration of one phase is greater at the interface than the bulk. This occurs due to unsaturation of the surface atoms. Most studies of adsorption from solution have been concerned with equilibrium conditions and predominantly with the adsorption isotherm. In almost all studies of adsorption by solids from solution which results from adsorption. Generally two types of adsorptions have been distinguished :

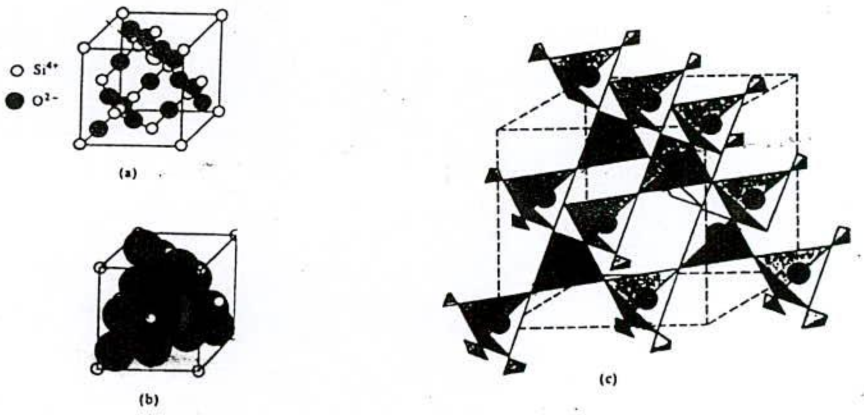
(a) Physical adsorption (Physisorption) and

(b) chemical adsorption (chemisorption).

Physical adsorption results purely from physical forces like vander waals forces and chemical adsorption is due to formation of chemical bonds.

1.10 Silicon dioxide

The most important ceramic compound is silica or silicon dioxide (SiO_2). Widely available in raw materials in the earth's crust, this material by itself and in chemical combination with other ceramic oxides (forming silicates) represents a large fraction of the ceramic materials available to engineers. For this reason, the structure of SiO_2 is important. In fact, there is not a single structure to describe, but many (under different conditions of temperature and pressure). For a representative example, Fig. 1.2 shows the cristobalite (SiO_2) structure.



Structure: Cristobalite (SiO_2 type)
Bravais Lattice: fcc
Ions/unit cell: 8 Si^{4+} and 16 O^{-2}

Fig. 1.2 : Unit cell of SiO_2: a) ion position, b) full size ions connectivity of SiO_4^{-4} tetrahedra

There are 24 ions (eight Si^{4+} and 16 O^{-2}) per unit cell. In spite of the large unit cell needed to describe this structure, it is perhaps the simplest of the various crystallographic forms SiO_2. The general feature of all SiO_2 structure is the same a continuous connected network of SiO_4^{-4} tetrahedra. Although the basic SiO_4^{-4} tetrahedra are present in all SiO_2 crystal structures, the arrangement of connected tetrahedra changes [31].

Silicon dioxide is an acidic oxide. It is very inert. General silica is a freshly powder but colloidal silica which is called ludox is semi-liquid. Silica is surface active substance. It has high surface area. A Feng *et al.* studied on water adsorption and desorption kinetics on SiO_2 insulation [32]. They studied it by thermo-gravimetrically, FTIR spectrometrically. J Laszlo *et al.* studied monosized SiO_2 base micro spheres for chromatographic separations [33].

Again silica can be used as catalyst for ammonium decomposition and can be used as catalyst for the manufacturing of olefin polymers containing transition metal compounds and ionic compounds. Again it can be used catalyst for catalytic cracking of polystyrene. Recently silica is used for preparation of colloidal-composites with PANI.

1.11 Metal Stearate

Metallic salts of fatty acids are molecules attached readily to both polar molecules and non-polar molecules. The long hydrocarbon chains are non-polar or hydrophobic repelled by water and the salt end molecules are ionic or hydrophilic and water soluble. The lipophilic carbon chains infiltrate and destroy the lipoprotein matrix of the insect's cell membranes. Food grade soap salts are used also as general purpose food additives. Aluminum, calcium, magnesium, lead, zinc or other metals are used in place of sodium or potassium for soaps to be used in industry. Metallic salts of fatty acids are fused as stabilizer and plasticizer. They are used as flatting and sanding agents in lacquers, coatings & inks. They can be applied in tablet manufacturing. They are used as drying lubricants and dusting agents for rubbers. They are used as catalysts in chemical synthesis and emulsifiers for emulsion polymerization of synthetic rubber and resin which can be approved for use in food contact applications. They are used as waterproofing additives and ointments.

Ionic surfactants which contain hydrophobic hydrocarbon group connected with one or several hydrophilic groups dissociate into a positively charged cation and a negatively charged anion in an aqueous solution. If the head is negatively charged to carry the surface active properties, it is called anionic surfactant, whereas a positively charged head is the carrier of the surface active properties in cationic surfactants. Typically cationic surfactants are based on the nitrogen atom carrying the cationic charge such as amine and quaternary ammonium product.

Cationic surfactant is considered to be poor cleaners but it contributes to the fabric softening, the disinfecting properties, and the grease-water interfacial tension reducing. Cationic surfactants include quaternary ammonium compounds, amines (primary, secondary, tertiary, diamines, polyamines, amine salts), imidazoline compounds and esterquats.

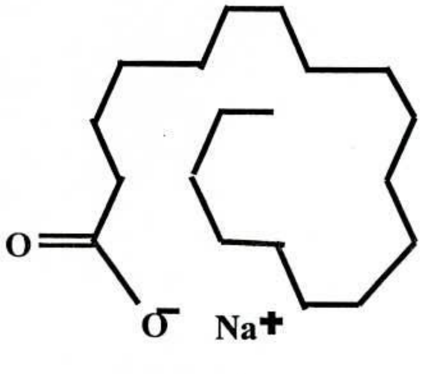


Fig. 1.3 : Structure of Sodium Stearate

Anionic surfactant is the widely used type of surface-active agent for laundry detergents, liquid cleaners and shampoos due to excellent cleaning properties particularly effective at oily soil cleaning and oil/clay soil suspension. Anionic surfactants are deactivated in many hard water. To prevent deactivation, builders should be dosed. Anionic surfactant is used as a emulsifier in cosmetics, tooth paste, cream, shampoo, and acrylic binder. Common soap is an anionic surfactant. Carboxylate, sulfate, sulfonate and phosphate are the polar groups in anionic surfactants. Anionic surfactants include alkyl benzene sulfonate, fatty acid salts, sodium lauryl sulfate, alkyl sulfate salts, sodium lauryl ether sulfate, alphaolefin sulfonates, phosphate esters, sulphosuccinates alkyl phenol ether sulfates and isothionates.

1.12 Sodium Dodecyl Sulfate

Sodium Dodecyl Sulfate (SDS) ($C_{12}H_{25}SO_4Na$) is an anionic surfactant that is used in household products such as toothpastes, shampoos, shaving foams, some dissolvable aspirins, fiber therapy caplets, and bubble baths for its thickening effect and its ability to create a lather.

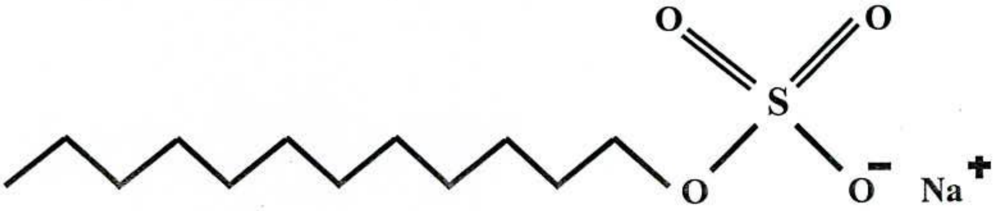


Fig. 1.4 : Structure of Sodium Dodecyl Sulfate

The molecule has a tail of 12 carbon atoms, attached to a sulfate group, giving the molecule the amphiphilic properties required of a detergent. It is prepared by esterification of sulfuric acid with dodecanol (lauryl alcohol, $C_{12}H_{25}OH$) followed by neutralization with sodium carbonate. It is used in both industrially produced and home-made cosmetics. Like all detergent surfactants (including soaps), it removes oils from the skin, and can cause skin and eye irritation. SDS can be converted by ethoxylation to sodium laureth sulfate (also called sodium lauryl ether sulfate), which is less harsh on the skin, probably because it is not as much of a protein denaturant as is the unethoxylated substance. It is probably the most researched anionic surfactant compound. It has recently found application as a surfactant in gas hydrate or methane hydrate formation reactions, increasing the rate of formation as much as 700 times.

1.13 Ethylene Diamine Tetraacetic Acid

Ethylene Diamine Tetraacetic Acid (EDTA) is a popular acronym for the chemical compound refers to the chelating agent with the formula

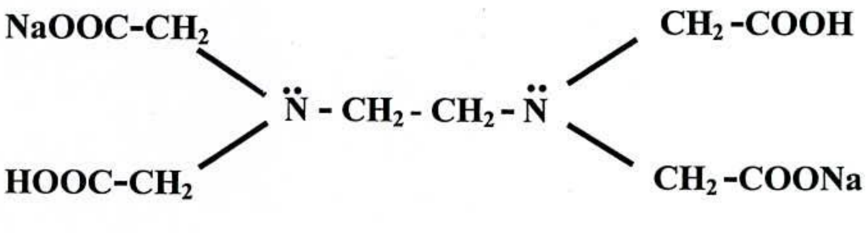


Fig. 1.5 : Structure of Sodium Ethylene Diamine Tetraacetic Acid

This amino acid is widely used to sequester di- and trivalent metal ions. EDTA binds to metals via four carboxylate and two amine groups. EDTA forms specially strong complexes with Mn(II), As(III), Cu(II), Fe(III), and Co(III). Recalcitrant chelating agents such as EDTA are an environmental concern predominantly because of their persistence and strong metal chelating properties. The presence of chelating agents in high concentrations in waste waters and surface waters has the potential to remobilize heavy metals from river sediments and treated sludges, although low and environmentally relevant concentrations seem to have only a very minor influence on metal solubility. Elevated concentrations of chelating agents enhance the transport of metals (e.g. Zn, Cd, Ni, Cr, Cu, Pb, and Fe) in soils, and enhance the undesired transport of radioactive metals away from disposal sites. Low concentrations of chelating agents may either stimulate or decrease plankton or algae growth, while high concentrations always inhibit activity. Chelating agents are nontoxic to many forms of life on acute exposure; the effects of longer-term low-level exposure are unknown. EDTA at elevated concentrations is toxic to bacteria due to chelation of metals in the outer membrane. EDTA ingestion at high concentrations by mammals changes excretion of metals and can affect cell membrane permeability.

EDTA is uses as Industrial cleaning: complexation of Ca $^{2+}$ and Mg $^{2+}$ ions, binding of heave metals. Detergents: complexation of Ca^{2+} and Mg^{2+} (reduction of water hardness). Photography: use of Fe (III)/EDTA as oxidizing agent. Pulp and paper industry: complexation of heavy metals during chlorine-free bleaching, stabilization of hydrogen peroxide. Textile industry: complexation of heavy metals, bleach stabilizer. Agrochemicals: Fe, Zn and Cu fertilizer, especially in calcareous soils. Hydroponics: Iron-EDTA is used to solubilize iron in nutrient solutions.

1.14 Review of the literature

Research on composite particles has become a wide and interdisciplinary field of science during the last decade. Recently, there has been increasing interest in organic-inorganic hybrid materials. Toki *et al* [34] have described the preparation of poly (vinyl pyrolidine) silica hybrids via sol-gel chemistry. Both Yoshinaga *et al* [35] and Wei *et al* [36,37] have reported systems in which an organic polymer is chemically grafted to silica while Zimmermann *et al* [38] have shown that PbS-gelatin composites can exhibit remarkably high refractive indices. There have also been various papers describing the preparation of composite materials, which contain conducting polymers. Wung *et al* [39] have reported on the preparation and characterization of poly (p-phenylene vinylene)-silica composites and Kramer *et al* [40] have synthesized PANI glasses by the in situ chemical polymerization of aniline. Yoneyama's group [41,42] have incorporated a range of inorganic oxides into electrochemically synthesized thin films of Polypyrrol and PANI.

Kanatzidis *et al* [43] and other workers have prepared a range of materials in which a conducting polymer is intercalated within an inorganic host matrix. Mayor *et al* [44] reported the preparation of polymer protected palladium particles and investigated the catalytic activity of the metal polymer system towards the hydrogenation of cyclohexene as a model reaction. Polypyrrole-tin (iv) systems have been characterized in terms of their particle size, chemical composition, d.c. electrical conductivity and surface composition [45, 46].

Many researches was carried out on composite materials. A. R. Bunsell has described the fibres for metallic and ceramic composites [47]. T. S. Raman *et al.* has carried out a research on advanced fibre reinforced composites. They used many techniques such as Dielectrometry, FT-IR spectoscopy, Ion graphing and Luminescence [48]. The development of composite materials can help to prepare high temperature materials. R Metselaar *et al.* have developed the composite materials which can serve a number of purposes such as to protect the electrodes from the corrosive combustion atmosphere at temperature upto 1450°C [49]. In 1964, W.A. little synthesized a superconductor at room temperature with backbone with large polarizable side groups which led the discovery of new organic compounds with high electrical conductivity [50]. In the early 1980 exitement ran high when several prototype devices based on conductive polymers, such as rechargeable batteries and current rectifying p-n junction diodes [51] were announced. Among the many polymers known to be conductive, PANI, poly(acetylene), Polypyrrol and poly(thiophene), have been studied most intensively [52-58] A dependence of the electrical strength on thickness, area and volume of dieleric is demonstrated for poly (propylene) film by S. Cygan and J. R. Laghari [59]. It was found that the electric strength of polymer film decreases with volume. It was shown that the function of electric strength is not simply dependent on the volume as obtained from theory of extreme values but that an increase of the volume by increasing the thickness of the dielectric is much more significant than same increase of the dielectric volume caused by an increase in area.

D.K. Das Gupta *et al.* synthesized polymer ceramic composites by introducing the ceramic particles into the polymer matrix [60]. They explained the electrical and dielectric properties of this composite. M. Davies *et al.* explained the polyethersulphone and its fracture behaviour polyethersulphone has properties similar to many traditional engineering thermoplastics at room temperature. However, the degradation of these properties with increasing temperature is considerably more gradual [61]. Poly(dimethylsilozane)/SiO_2 and SiO_2/TiO_2 composites have been successfully prepared using a sol-gel process by J. Wen and J.E.Mark [62]. The hydrolysis and sol-gel transition reaction of the poly(dimethyl siloxane)/SiO_2 system have been studied by nuclear magnetic resonance, gel permeation chromatography, solvent extraction and shear modulus tests.

In the past few years, considerable research has been devoted to the development of novel processable forms of relatively air stable conducting polymers such as Polypyrrole and PANI [63]. One approach is the preparation of colloidal dispersions of such materials. Most workers have focused in dispersion polymerization techniques as the preferred method of synthesizing conducting polymers colloids. For example, Toki *et al.* have described the preparation of polyvinyl (pyrrolidone) / silica hybrids via sol-gel chemistry [64]. S. Maeda, R. Corradi, and S. P. Armes have described the synthesis and characterization Polypyrrole/silica microparticles [65]. Wung *et al.* have reported the preparation and characterization of poly(phenylene-vinylene)-silica composites [66]. Kramer *et al.* have synthesized PANI glasses by the in situ chemical polymerization of aniline [67].

More recently, Armes *et al.* reported the synthesis of colloidal nanocomposites of conducting polymer using small inorganic oxide particles as a particulate dispersant. They studied on PANI/silica, Polypyrrole/silica nanocomposites. They studied adsorption of DNA on this composites [68-72]. J. Jinsoo measured the microwave dielectric constant of PANI and studied its application to Electro Magnetic Interference Shielding [73]. R. B. Daniel *et al.* studied the polymer electroluminescent devices with PANI electrodes [74]. X. H. Quan *et al.* studied the

"Electrically conductive PANI-Poly(butadiene-co-styrene-co-2-vinylpyridine) latex composites and their properties [75]. T. Afshad studied conducting Polypyrrole and PANI based chemical sensors [76]. K. A. Striebel *et al.* studied the Novel Nanodisperse composite cathode for Rechargeable Lithium/polymer Batteries and the applications [77]. F. Leroux *et al.* studied the electrochemical Li Insertion into conductive polymer/V_2O_5 nanocomposites. They used PP and PANI as a conductive polymer [78]. K. Ramachandran *et al.* studied the electrochemical characterization of a PP-montmorillonite nanocomposites [79]. M. Hepel prepared Polypyrrole films and studied the electrocatalytical oxidation of methanol at finely dispersed platinum nanoparticles [80].

In recent years, the ion-exchange behaviour during charging and discharging processes of conducting polymers, e.g. PP, has been widely studied [81-92]. It was found that the conducting polymers exchange both anions and cations depending on the polymerisation conditions [81, 82], the type and size of the counterions incorporated during the polymerisation process [81-92] as well as on the ions present in the electrolyte solution [86-92], the polymer thickness [91] and the ageing of the polymer [92]. PP synthesised in solutions with small counterions, e.g. Cl^-, ClO_4^-, NO_3^-, mainly exhibits anion-exchanger behaviour due to the high mobility of these ions in the polymer matrix, but under certain conditions cation exchange was also found to take place in such systems [81, 82, 91, 92]. Cation exchange was primarily found to take place on PP modified with large counterions, e.g. polyvinylsulfonate, polystyrenesulfonate, due to the immobility of these ions in the polymer matrix [82-90, 92].

1.15 Plan of the present work

PANI-Poly(propylene) composites were prepared by oxidative polymerization of aniline in biaxially stretched poly(propylene) microporous films with ammonium peroxydisulfate as the oxidant by C. Zhao *et al.* [93]. A continuous permeation diffusion polymerization process was used in order to incorporate more PANI in the composite. Planes, Jerome *et al.* prepared PANI and determined the A.C. conducting properties of conducting polymers blends based on PANI [94]. S. A. Mallick *et al.* bioleached Cu from chalcopyrite ores coated with PANI film [95]. C. G. Innocenzo *et al.* used Cu dispersed into PANI films as an amperometric sensor in alkaline solution of amino acids and polyhydric compounds [96]. In 1979, Diaz *et al.* produced the first flexible, stable PANI film with high conductivity (100 Scm^{-1}). The substance was polymerized on a Pt-electrode by anodic oxidation in acetonitrile [97]. Thus the aim of our present work is to synthesis of conducting polymer-based composites. Large anionic counterions will be impregnated into the modified polymer matrix as cation-exchanger expecting that these ion-exchangers might have advantage compared to the conventional ion-exchangers in removing the undesired metal ions present in the natural water.

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Chapter 2: Experimental

2.1 Materials and Instruments

Reagents:

a. Aniline (Merck, AR. Grade) double distilled

b. Ammonium Peroxodisulphate (Merck, Mumbai)

c. Silica gel G (Merck, Mumbai)

d. Stearic acid (Merck, Germany)

e. Sodium Dodecyl Sulfate (Merck, Germany)

f. Ethylene Diamine Tetraacetic Acid (Merck, Mumbai)

Appartes:

a) Centrifuge Machine, Hittch, ZENTRIFUGEN, Germany.

b) IR-470, Shimadzu, Japan.

c) UV-Thermo Scientific, Type Helios Gama, England.

d) SWIFTMASTER II, Swift Instruments, Inc, Japan.

e) Shaker Model URN-480 Gemms Industrial Corporation, Made in Taiwan.

f) UV-Spectrophotometer DR/2500 HACH, USA.

g) Atomic Absorption Spectrophotometer, Perkin. Elmer (Precisely) Analyst-200, USA.

h) Hot Air Sterilizer Gemms Industrial Corporation, Made in Taiwan.

i) Electric Blanca – A & D Companies Limited.

2.2.1 Preparation of polyaniline-silica composites

The synthetic procedure for preparing PANI-silica described by the early workers [1-3] was employed in the present work with necessary modification. It is described below: Aqueous silicate solution was made by dissolving 7.5g of sodium silicate (commonly known as water glass) in 800 cm^3 of double-distilled water in a 1.0 dm^3 beaker. This solution was then filtered using Whatman filter paper.

pH of the solution (nearly 3) was adjusted to desired values by adding HCl solution. Then 3.2 g of ammonium persulphate was added as oxidant and the temperature was maintained constant at room temperature and a stirrer. 1.0 cm^3 distilled aniline was then injected using a 5 cm^3 syringe and it was seen that the reaction mixture turned into deep green colloidal mixture within few seconds. The reaction mixture was stirred well for a two hours and left over night for completion the reaction. The colloidal mixture was then centrifuged at 4500 rpm by a centrifuge machine (***Hittch***, ZENTRIFUGEN, Germany) for 30 minutes. The resulting dark green sediment was redispersed in double-distilled water and stirred well. The centrifugation-redispersion cycle was repeated several times in order to remove free silica particles and other soluble bi-products from the synthesized PANI-silica composites. A schematic representation for the preparation of PANI-silica composite is shown in Fig. 2.1. PANI-silica composite thus obtained was dried at 70°C under vacuum.

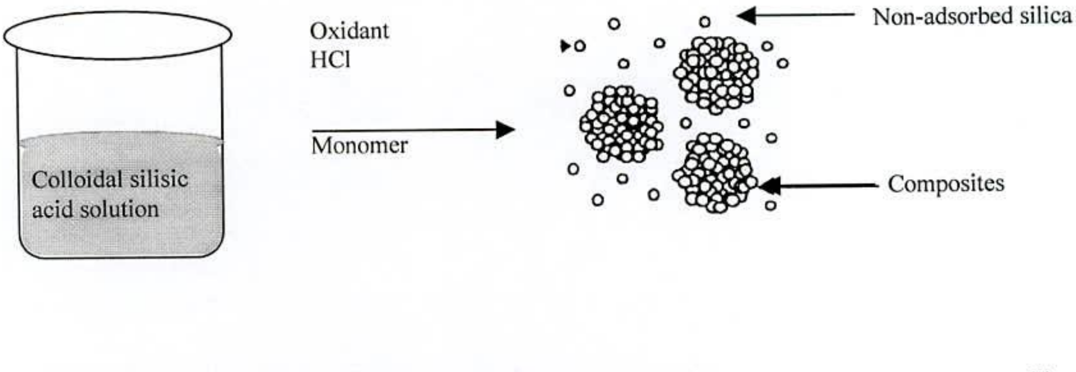

Fig. 2.1 Schematic representation of the formation of organic polymer silica composites

2.2.2 Preparation of polyaniline-Stearate composites

Aqueous stearate solution was made by dissolving 5.0 g of sodium stearate in 800 cm^3 of double-distilled water in a 1.0 dm^3 beaker. This solution was then filtered using Whatman filter paper.

pH of the solution was adjusted at 3.0 values by adding HCl solution. Then 3.2g of ammonium persulphate was added as oxidant and the temperature was maintained constant at room temperature and a stirrer. 1.0 cm^3 aniline was then injected using a 5 cm^3 syringe and it was seen that the reaction mixture turned into deep green colloidal mixture within few seconds. The reaction mixture was stirred well for two hours and left over night for completion of the reaction. The colloidal mixture was then centrifuged at 4500 rpm by a centrifuge machine for 30 minutes. The resulting dark green sediment was redispersed in double-distilled water and stirred well. The centrifugation-redispersion cycle was repeated several times in order to remove free sodium stearate particles and other soluble bi-products from the synthesized PANI/ Streate composites. Finally it was dried under vacuum at 70°C and was stored for further investigation.

2.2.3 Preparation of polyaniline-SDS composites

Aqueous Sodium dodecyl sulfate solution was made by dissolving 2.0 g of Sodium dodecyl sulfate in 800 cm^3 of double-distilled water in a 1.0 dm^3 beaker.

pH of the solution was adjusted at 3.0 values by adding HCl solution. Then 3.2g of ammonium persulphate was added as oxidant and the temperature was maintained constant at room temperature and a stirrer. 1.0 cm^3 aniline was then injected using a 5 cm^3 syringe and it was seen that the reaction mixture turned into deep green colloidal mixture within few seconds. The reaction mixture was stirred well for two hours and left over night for completion of the reaction. The colloidal mixture was then centrifuged at 4500 rpm by a centrifuge machine for 30 minutes. The resulting dark green sediment was redispersed in double-distilled water and stirred well. The centrifugation-redispersion cycle was repeated several times in order to remove free Sodium dodecyl sulfate particles and other soluble bi-products from the synthesized PANI-SDS composites. Finally it was dried under vacuum at 70°C and was stored for further investigation.

2.2.4 Preparation of polyaniline-EDTA composites

Aqueous Ethylene Diamine Tetraacetic Acid (EDTA) solution was made by dissolving 4.0 g of EDTA in 800 cm^3 of double-distilled water in a 1.0 dm^3 beaker. pH of the solution was adjusted at 3.1 values by adding HCl solution. Then 3.2g of ammonium persulphate was added as oxidant and the temperature was maintained constant at room temperature and a stirrer. 1.0 cm^3 aniline was then injected using a 5 cm^3 syringe and it was seen that the reaction mixture turned into deep green colloidal mixture within few seconds. The reaction mixture was stirred well for two hours and left over night for completion of the reaction. The colloidal mixture was then centrifuged at 4500 rpm by a centrifuge machine for 30 minutes. The resulting dark green sediment was redispersed in double-distilled water and stirred well. The centrifugation-redispersion cycle was repeated several times in order to remove free EDTA and other soluble bi-products from the synthesized PANI-EDTA composites. Finally it was dried under vacuum at 70°C and was stored for further investigation.

2.3 Analysis for silica content

PANI-silica was analyzed for their silica content. This was done by the well known hydrofluorization method [4]. About 1 g of the sample was taken in a platinum crucible to which 10 cm^3 of HF solution and 1 cm^3 of sulphuric acid solution (1:1) were added. The crucible with lid was placed on a sand bath for evaporation of silica as SiF_4, taking care to avoid loss by spattering. The crucible was cooled, the sides of the crucible washed down with water and 2 cm^3 of HF solution was again added carefully and the contents were evaporated to dryness. The residue was heated on a hot plate until the fumes of sulphuric acid were evolved no longer and then heated in a furnace at 120°C ± 20°C for 15 minutes. The crucible with the residue was then cooled in a desiccator and weighed. The operation of heating, cooling and weighing were continued until a constant weight was obtained. Each sample was analysed at least thrice and the reported result is the average of the performed runs. The percentage of silica content was calculated as follows:

$$\% \, SiO_2 = \frac{W_2 - W_3}{W_2 - W_1} \times 100$$

where, W_1 = mass of the platinum crucible with lid.

W_2 = mass of the platinum crucible with lid plus sample (initially taken)

W_3 = mass of the platinum crucible with lid plus sample (after ignition).

2.4 Infra-red spectroscopy

Infra-red (IR) spectra of all the composite materials were recorded on a IR spectrophotometer (IR-470, Shimadzu, Japan) in the region of 4000-400 cm^{-1}. IR spectra for the solid composites were obtained by mixing and grinding a small amount of the composite materials with dry and pure KBr. Thorough mixing and grinding of the solids were accomplished in an agate mortar. The powder mixture thus obtained was then compressed in a metal holder under a pressure of 8-10 tons to make a pellet. The pellet was then placed in the path of the IR beam in the spectrometer for measurements. Results of IR measurement of various composite samples was described in section 3.2.

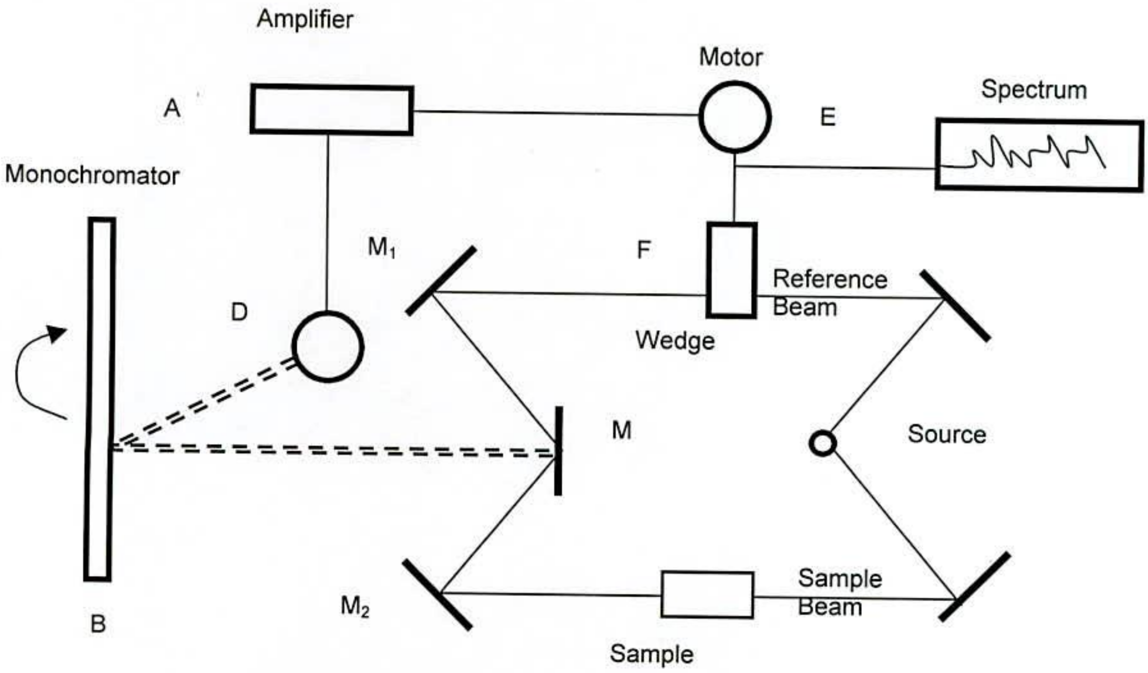

Fig. 2.2 A block diagram of an IR spectrophotometer

2.5 UV-VIS spectral analysis

A double beam spectrophotometer (UV-160A Shimadzu, Japan) attached with a synchronized recorder was employed for the UV-VIS spectral analysis of the various samples prepared chemically. About 1.0 mg of the chemically prepared samples were dissolved in DMF. The sample solution was diluted with DMF to a visual extent in such a way that the optical density did not exceed 2. DMF was used as reference solvent in this experiment.

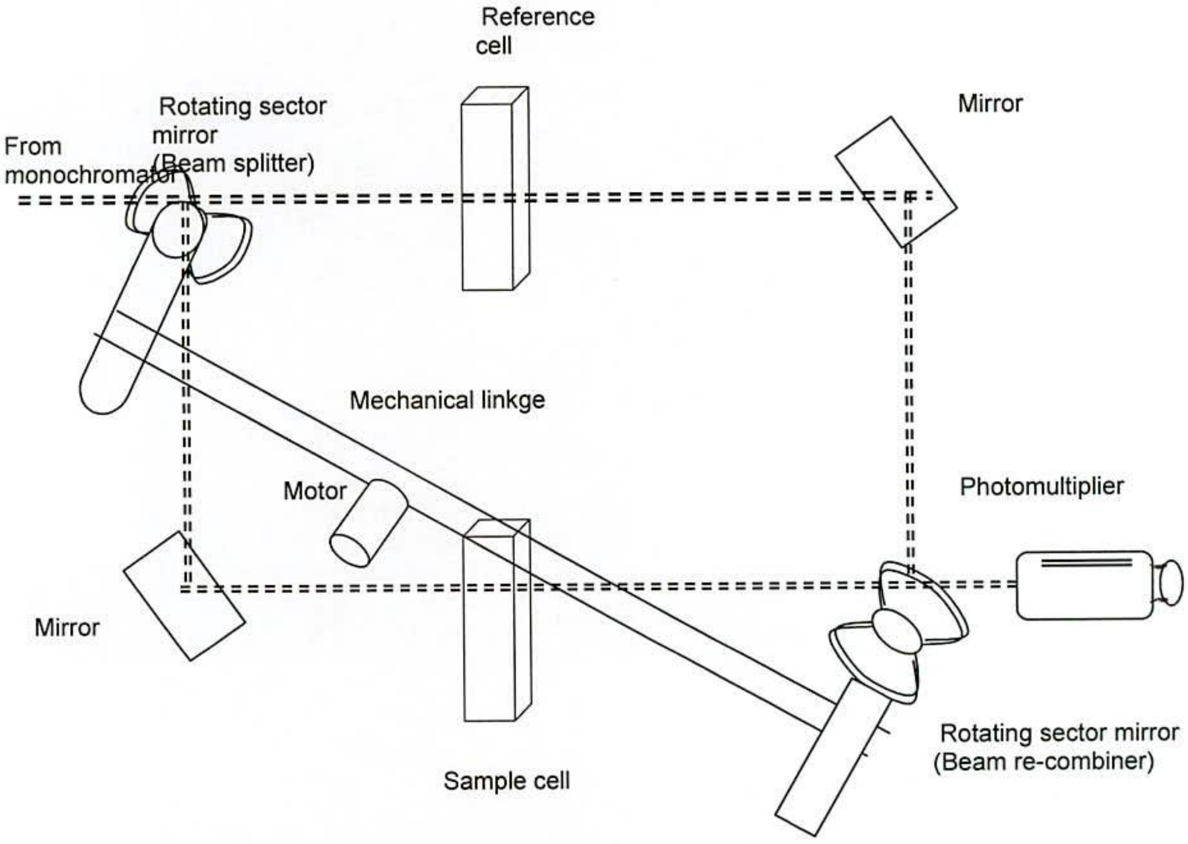

Fig. 2.3 A block diagram of an UV-Vis spectrophotometer

2.6 Optical microscopic analysis

Optical microscopic analysis for the chemically synthesized PANI, PANI/Composites (Silica, Stearate, SDS, EDTA), was performed. For this purpose, samples were compressed to rigid pellets for analysis. Prior to take the micrographs, all the pellet samples were polished to have a clear and representative view of the samples microstructure. Polishing was accomplished with emery papers viz. No. 3, No. 2, No. l, No. 0, No. 0-0, No. 0-0-0 and No. 0-0-0-0. In addition to this, wheel polishing with y-Al0$_3$ powder was also carried out to have better micrograph. After Polishing, the sample were cleaned of with dry cotton to remove any traces of polishing materials, Analysis were performed in an optical microscope (SWIFTMASTER II, Swift Instruments, Inc, Japan) coupled with a very high precision canon camera. All the analysis was carried out at room temperature.

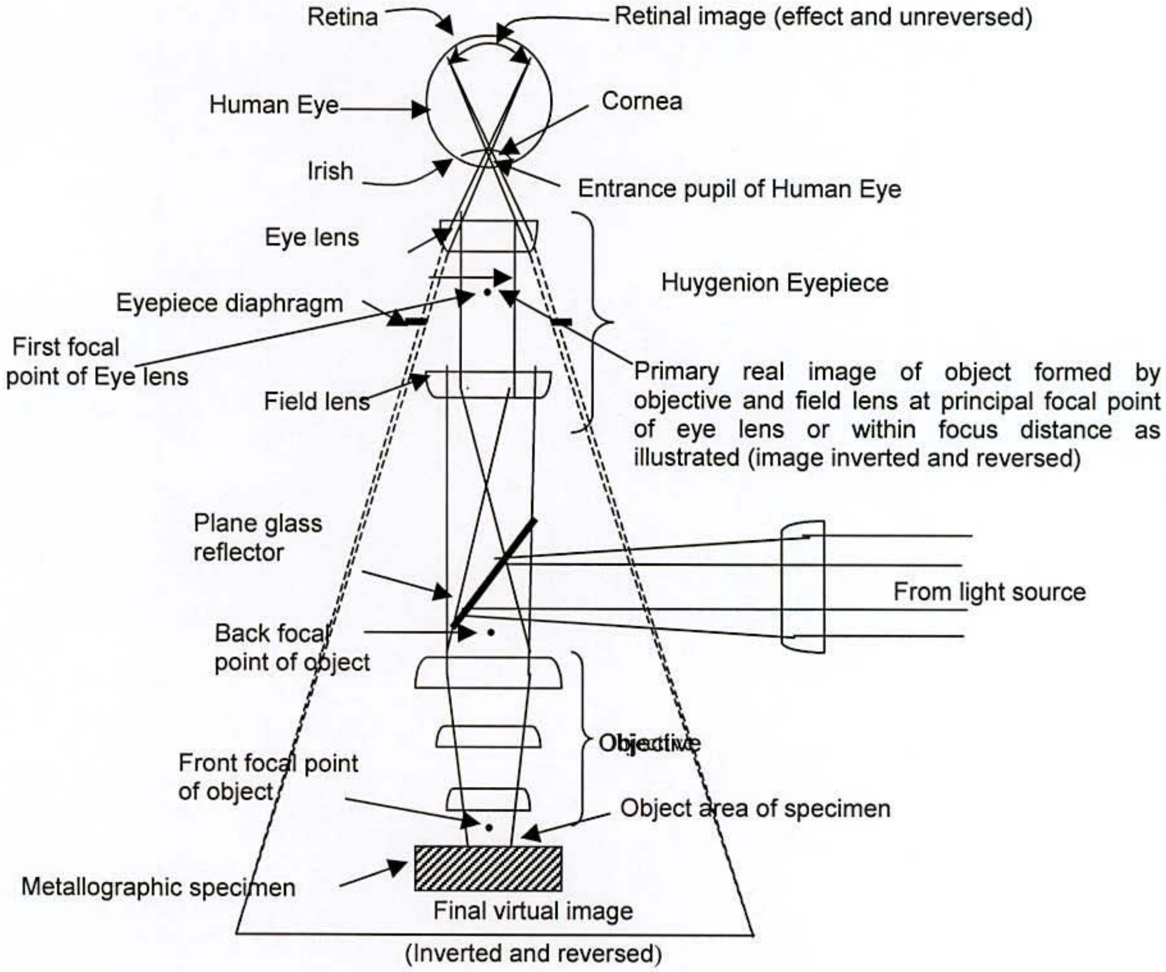

Fig. 2.4 Illustrating the principle of the optical compound microscope and the trace of rays though the optical system from the object field to the final virtual image.

2.7 Surface area

The volume of a gas taken up by a solid varies from one solid to another and from one gas to another, and in suggesting that the adsorptive power of a solid depends on the area of exposed surface [6]. Two factors (a) surface area (b) porosity, are now recognized to play complimentary parts in adsorption phenomena in a vast range of solids. It thus comes about that measurements of adsorption of gases or vapors can be made to yield information as to the surface area and the pore structure of a solid.

It is obvious that a solid will possess a large surface area if it exists in form of fine particles. There is an inverse relationship between the specific surface (the surface area of one gram of solid) and its particle size. For an idealized case where the particles are cubes of equal size with an edge length l, the specific surface area S, is given by the expression,

$$S = \sigma / \rho$$

where ρ = density of the solid.

large specific surface may arise by (a) aggregation, i.e., the fine particles of powder tends to stick together to a greater or lesser extent or by mere adhesion of particles to one another (b) removal of parts of a parent solid such a manner as to leave pores. The walls of pores will comprise the "surface area" of resultant solid.

Purpose of the adsorption study

The following information can be obtained in an adsorption experiment:

i) Nature of adsorption, that is whether it is adsorbed physically or chemically and the conditions (temperature, pressure, state of adsorbent etc.) under which the adsorption takes place.

ii) Thermodynamic data regarding the adsorption process. These include the amount of gas adsorbed under various equilibrium pressures at definite temperature.

iii) Specific surface area-surface area of one gram of the substance- by the adsorption process can be measured.

2.8 Determination of reduces Mn^{2+}-ion

15 mL $MnSO_4$ solution was taken in different adsorbent bottle and 1 % , 3 % , 6 % and 9 % composite materials were added. Then those were shaked (by shaker Model URN-480 Gemms Industrial Corporation, Made in Taiwan) for 3 hours, 6 hours, 9 hours and 12 hours batch wise. Then those were kept settled overnight. Finally the composites were separated by filtration and the water samples were investigated by an UV-Spectrophotometer.

To measure the concentration of present Mn^{2+} ion at first one Ascorbic acid pillow (each contain 0.5 g ascorbic acid) to the UV-cell. Then it is gently swirled to mix it homogenously. After those 15 drops of Alkaline Cyanide reagent solution was added to the cell and was mixed. The Alkaline Cyanide reagent solution is the mixture of NaOH and NaCN solution. After then 21 drops of 0.1% PAN indicator solution was added to the prior solution The PAN indicator solution is the mixture of Ammonium acetate, N,N-dimethylformamide and Octylphenexypolyethoxyethanol solution. The whole system was kept rest for two minutes. The concentration of Mn^{2+} ion was investigated by UV-Spectrophotometer DR/2500 HACH, USA.

2.9 Determination of reduces As^{3+}-ion

15 mL As_2O_3 solution was taken in different adsorbent bottle and 1 %, 3 % , 6 % and 9 % composite materials were added successively. Then those were shaked by a shaker machine (Model URN-480 Gemms Industrial Corporation, Made in Taiwan) for 3 hours, 6 hours, 9 hours and 12 hours batch wise. Then those were kept settled overnight. Finally the composites were separated by filtration and the water samples for the quantity of As^{3+} were

investigated by an Atomic Absorption Spectrophotometer.

To measure the concentration of present As^{3+} ion, at first 15 ml 5 M HCl was taken into deionized water and the total volume was made up to 1 L And the resultant solution became 0.075 M. Then 1L 1% NaOH solution was prepared 3g sodium tetrahydroborate was added to the 1% NaOH solution and the total volume was made 1 L. For calibration 50 mL stock solution (supplied by Perkin, USA) into 250 mL 0.075 M HCl solution, it prepared 200 mg/L standard solution. Similarly 150 mg/L, 100 mg/L, 50 mg/L and 0 mg/L standard solution was prepared. Here 0.075 M HCl solution act as diluent. It should be mentioned that here 3% $NaBH_4$ in 1% NaOH solution used as reductant. Another solution was prepared by dissolving 3g KI and 5g L (+)-ascorbic acid in 100 mL water.

10 mL water sample was taken in a 100 mL conical flax and previously prepared 1 mL KI-solution and 1 mL 5M HCl solution. The whole system was kept rest for 30 minutes. Then this pre-tested sample was transfer to the cell of AAS. Sodium tetrahydroborate solutions were taken in the hydride generation chamber of AAS from which hydride is pumped into the cell and reduce the As (V) present in the water sample to As (III). It is done to prevent the interference of As (V) with As (III). Finally the total concentration of As^{3+} ion was investigated by Atomic Absorption Spectrophotometer, Perkin. Elmer (Precisely) Analyst-200, USA.

2.10 References

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Chapter 3: Result and Discussion

3.1 General discussion on modified conducting polymer based composites

The preparation of stable colloidal dispersions of conducting polymers using polymeric dispersants [1-5] attracted special attention of the material scientists. In the present work sterically and chemically stabilized conducting polymer particles were synthesized in aqueous medium. Large anionic groups were impregnated in the polymer matrix. We used aqueous solution of silicate, EDTA, SDS and Stearate. pH of the solution were maintained 3.1 in all cases by using HCl. The polymerization process were carried out in presence of oxidant, $(NH_4)_2SO_4$. Following the same procedure similar composites has been reported in [6-8] and anion grafted conducting polymer in [9] anionic groups composite materials were synthesized. A wide variety of oxidant in the chemical polymerization of conducting polymers: H_2O_2 [10], $FeC1_3$ [11] and $(NH_4)_2S_2O_8$ [12] are well established reagents. When aniline was oxidized in presence of silicate, EDTA, SDS or stearate polymer composite were produced grafted with silica, EDTA, SDS and stearate. The ultrafine silica sol acts as a high surface-area colloidal substrate for precipitating PANI yielding stable colloidal dispersion of "raspberry" shaped [Fig. 2.1] particles in the range 100-300 nm [6-8]. These colloidal "raspberries" consist of micro aggregates of silica glued together by the conducting polymer component. First, PANI absorbs as an insoluble thin layer onto high surface area of silica substrate particles. This outer layer of PANI is non- solvated and also acts as a binder. Most of the colloidal silica has negative surface charge. Since PANI is poly cations [13, 14] the attractive electrostatic interaction may play a vital role in the formation of PANI-silica composite. Similarly, large anionic group like dodacyl sulfonate, stearate and EDTA can be incorporated into PANI polymer matrix as depicated for other counteranions [15-24].

Normally one would expect a macroscopic precipitate to be formed in these circumstances. However, under certain synthesis condition a stable dispersion of PANI-silica, PANI-SDS, PANI-EDTA and PANI-stearate composite were obtained. The chemical analyses of these composite were performed for their silica and EDTA content but those were not possible for SDS and stearate. The results have been shown in Table 3.1.1. This analysis indicates that approximately 11% silica and ~ 4% EDTA were incorporated in the prepared composite materials. Each value was an average of at least three analyses. The almost the same results for silica contain into the polymer matrix were found earlier [25-26]. They also found that different reaction condition e.g., pH, temperature, polymerization rate, cannot change the amount of silica content in the polymer matrix. The results also showed that the functional group like, $-CH_3$, Cl^-, OH^- present in the polymeric backbone have no effect on the silica content. Although the amount of SDS and stearate were not determined chemically but presence of them were proved by optical microscope view, adsorption data have been discussed later in this section. The density values of the synthesized materials determined by pyknometry have also been shown in Table-3.1.1. Each value was an average of at least three runs.

Table- 3.1.1. Summarized results of chemical analysis and density of the prepared samples.

Name of the sample	Preparation condition		Density (g cm^{-3})	Amount of (%)
	pH	Temp.(°C)		
PANI	3.1	25	1.39	
PANI-silica			1.76	silica -11.02
PANI-streate			1.21	
PANI-SDS			1.32	
PANI-EDTA			1.19	EDTA -3.99

The density of the bulk polymer has been found to be smaller than that of polymer-silica composite materials. This result seems to reasonable since heavier particles e.g., silica were incorporated in to the synthesized materials. Density data observed for the synthesized samples seems to be consistent with the previous reports [25-28] suggesting that bulk polymer may exhibit lesser density than that of the PANI-silica. On the other hand PANI-stearate, PANI-SDS and PANI-EDTA exhibit smaller densities than that of the bulk polymer.

These composite materials have also been characterized by optical microscope. The micrographs of the bulk PANI and the composite materials are shown in Fig. 3.1.1. Microscopic photo 3.1.1(a) shows the microstructure of PANI and Fig. 3.1.1(b-e) represent the same for PANI-silica, PANI-stearate, PANI-SDS and PANI-EDTA respectively.

A wide distribution of white images is found in the microstructures 3.1.1(b-e). These images may correspond the presence of silica particles in the polymer matrices. It may be considered for PANI-silica composite that its surface composition is silica rich relative to its bulk composition, i.e., the conducting polymer component is probably somewhat depleted from the surfaces of the particles. This hypothesis has been confirmed for the analogous to Polypyrrole-silica (PP-Silica) nanocomposites using x-ray photoelectron spectroscopy [28-29] and zeta potential [30]. Because of the limited magnification of the optical microscope, the free silica could not be identified separately. However, Scanning Electron Microscopy (SEM) studies of PP-silica and PANI-silica have been reported to identify clearly the free silica particles. [27-29]. Similar results were obtained for PANI-stearate, PANI-SDS and PANI-EDTA. The white images in the micrograph may correspond to stearate, SDS and EDTA. These results also correspond to [10] where polystyrene-sulfonate (PPS) anionic group was impregnated into PP-polymer matrix. The SEM pictures of electrochemically prepared PP-PSS film exhibited the typical cauliflower structure, whereas chemical polymerization leads to the formation of a nanoscale powder with a high specific surface area. This result leads to conclude that our chemically synthesized composite materials containing counteranions, such as, stearate, SDS and EDTA may be incorporated into the PANI-matrix and have high surface area.

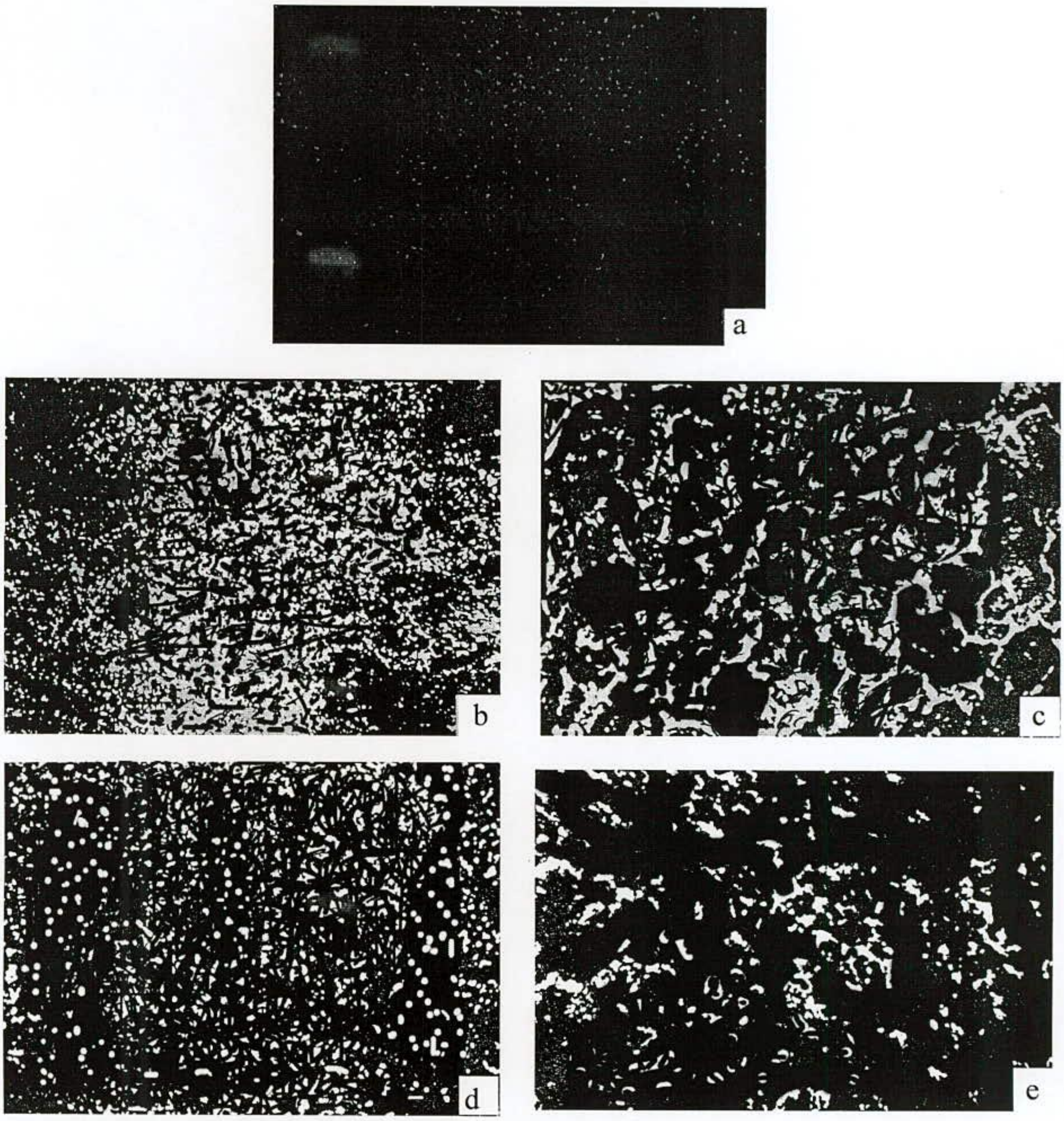

Fig.3.1: Optical micrographs of chemically synthesized
(a) PANI (b) PANI-Silica (c) PANI-Streate
(d) PANI-SDS (e) PANI-EDTA

3.2 IR spectral analysis of chemically synthesized samples

IR spectroscopic studies were performed in order to get some useful, albeit qualitative information on chemically synthesized PANI, PANI-silica, PANI-stearate, PANI-SDS and PANI-EDTA. IR spectra of the samples are presented in Figs. 3.2.1 - 3.2.5 while the observed and standard bands assigned for different functional groups are summarized in Table - 3.2. The assignment of the bands has been made on the basis of some standard literature [31-34].

Bands observed in the IR spectrum (Figs. 3.2.1 - 3.2.5) in the range 3590 - 3710 cm^{-1} may indicate water molecules that may absorbed by the samples. In fact, De Survill *et al.* [35] have observed that PANI has a strong affinity for water; its absorption capacity can be as large as 40% of the polymers weight. The peaks in between 3300 - 3500 cm^{-1} may correspond the N-H stretching of the aromatic secondary amines. The bands in the range 1640 - 1690 cm^{-1} may be considered for C = N - stretching. It therefore, seems that the present PANI consists of -N = sites, which might occurred by the high degree of oxidation of the polymer films [36]. The bands in the range 1450 - 1600 cm^{-1} and 1350 - 1250 cm^{-1} may represent C = C and C-N stretching of the aromatic amine, respectively. The bands in the region 690 - 900 cm^{-1} may provide an evidence for the mono-substitute benzene ring.

The absorption bands observed in Fig.3.2.2 observed around at 801 and 111 cm^{-1} for the samples PANI-silica may provide the evidence for the presence of silica. Therefore, the IR spectra of the above studies samples clearly exhibited absorption bands attributable to both the polymers and silica components. Fig.2.3.3 and peak at 1280-1300 cm^{-1} attribute the evidence of C-O groups on the other hand peak at 1710 and 1725 cm^{-1} in Fig, 2.3.3 and 2.3.5 respectively attribute the evidence of >C=O groups in the composite materials. Then the bands in Fig, 2.3.3 and 2.3.4 in 1450 cm^{-1} may provide an evidence for the C-H deformation. Finally peak at 1650 cm^{-1} in Fig. 2.3.4 attribute the evidence of >S=O groups in the PANI-SDS composites materials.

Table 3.2: Observed and standard IR absorption bands assigned for different functional groups for the samples prepared chemically.

Functional Groups	Standard absorption Band range (cm^{-1})	Observed absorption bands (cm^{-1}) for the samples					Probable assignment
		PANI	**PANI-silica**	**PANI-stearate**	**PANI-SDS**	**PANI-EDTA**	
Free O-H	3590-3710	3600	3665	3795	3635	3650	O-H stretching vibration,water may be present
N-H	3300-3500	3435	3420	3480	3435	3485	Aromatic secondary amine may be present
C = C	1600-1450	1554	1564	1591	1590	1604	C=C stretching in aromatic nuclei
C - N	1350-1250	1295	1320	1370	1376	1345	C-N stretching in aromatic amine
C - H	690-900	813	846	846	852, 829	863	C-H deformation. Mono substituted benzene
C = N	1690-1640	1660	1676	1667	1642	1710	>C=N- stretching in imine
Si-O	801, 1111		1109, 799				Presence of SiO_2
C-H	2850-2960	2900	2950	2985		2950	C-H stretching in CH;
Ar-H	-3030			3015		3100	Ar-H stretching
C = O; str	1700			1710		1745	Presence of >C=O
C –O; str	1410-1200			1280	1270	1290	Presence of >C-O-
S = O	1600-1800				1650		Presence of >S=O
C–H; def	1430-1470			1450	1435		Presence of C–H; def

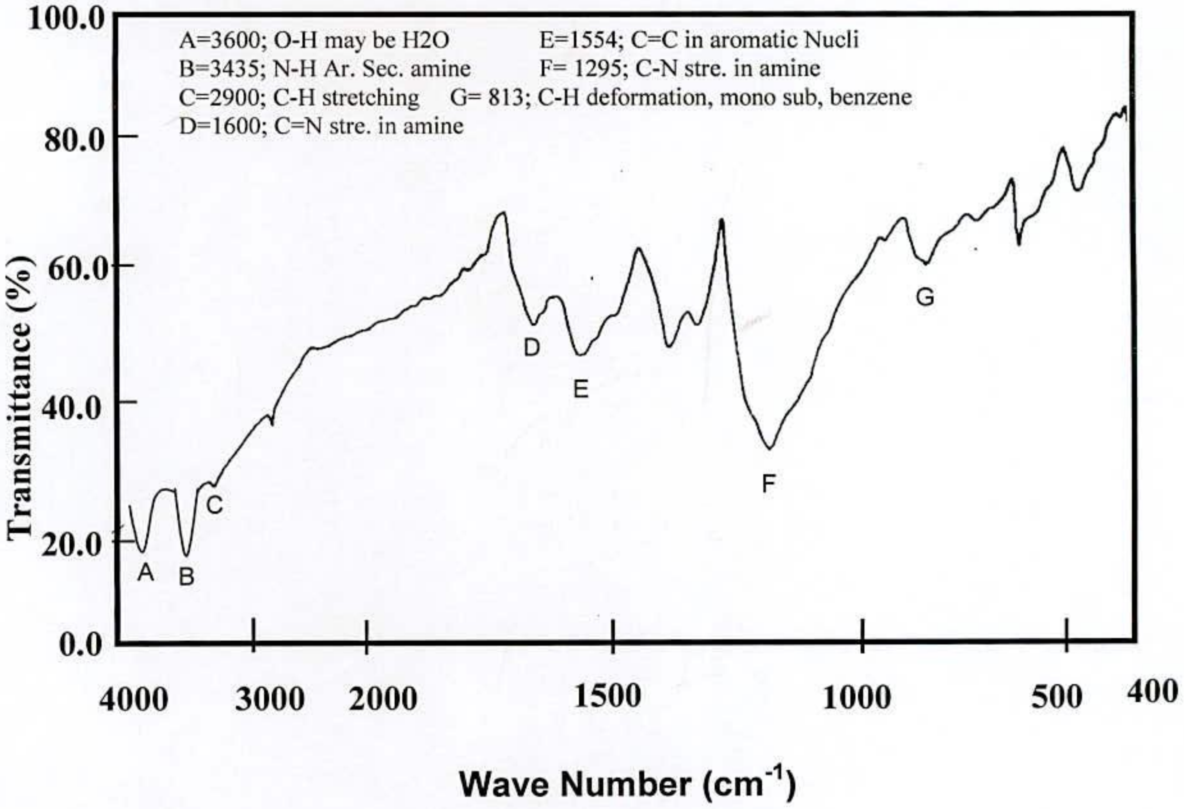

Fig. 3.2.1: IR spectrum of the PANI

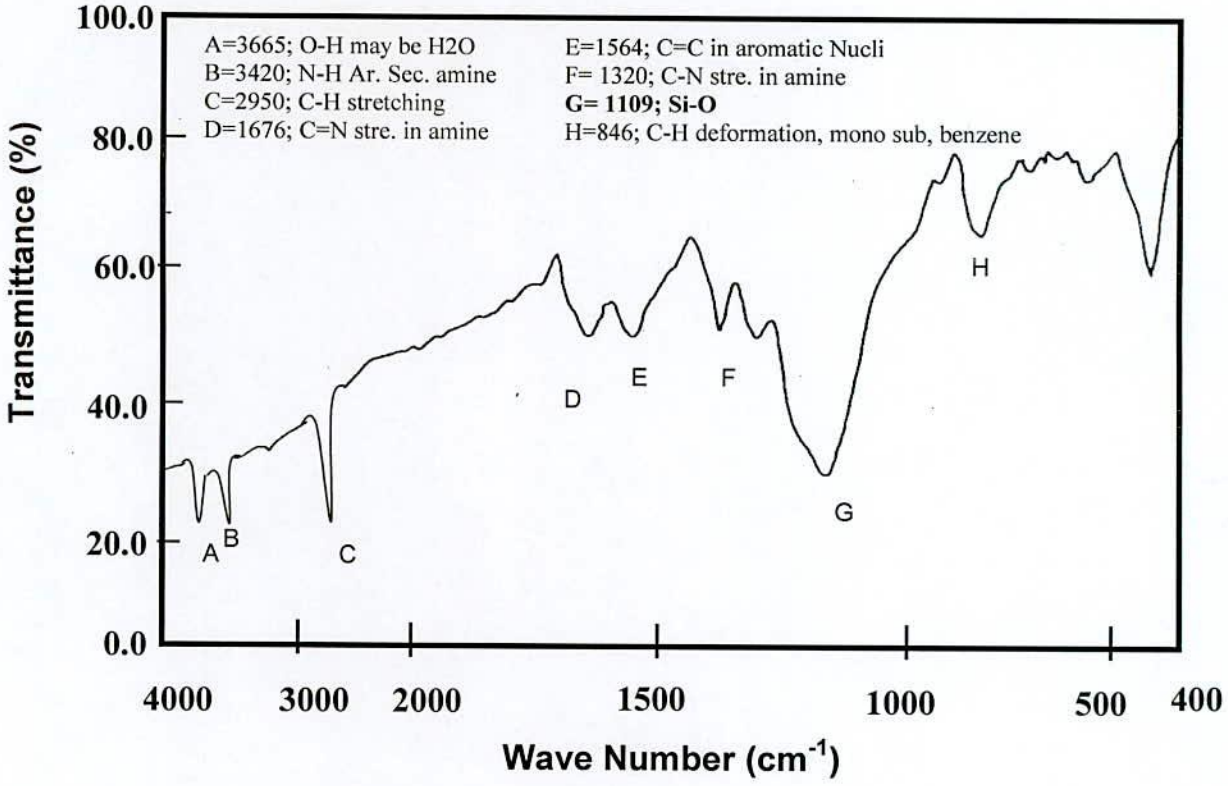

Fig. 3.2.2: IR spectrum of the PANI-silica

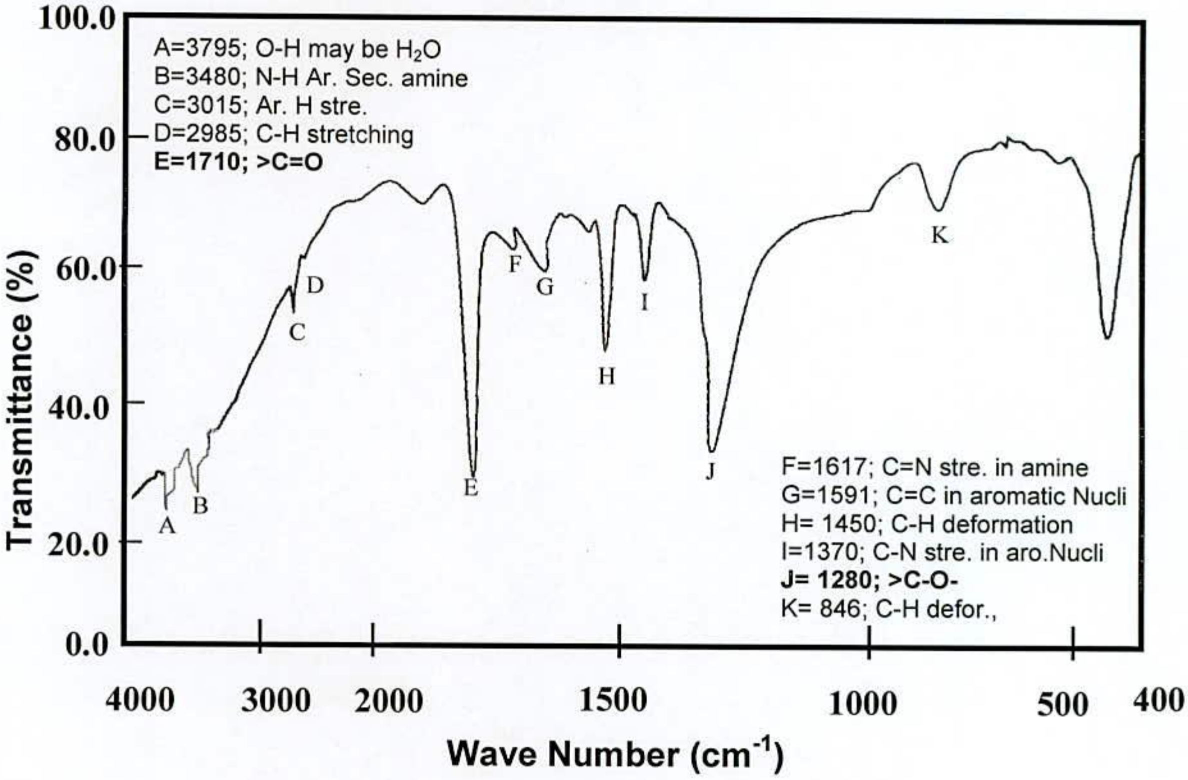

Fig. 3.2.3: IR spectrum of the PANI-stearate

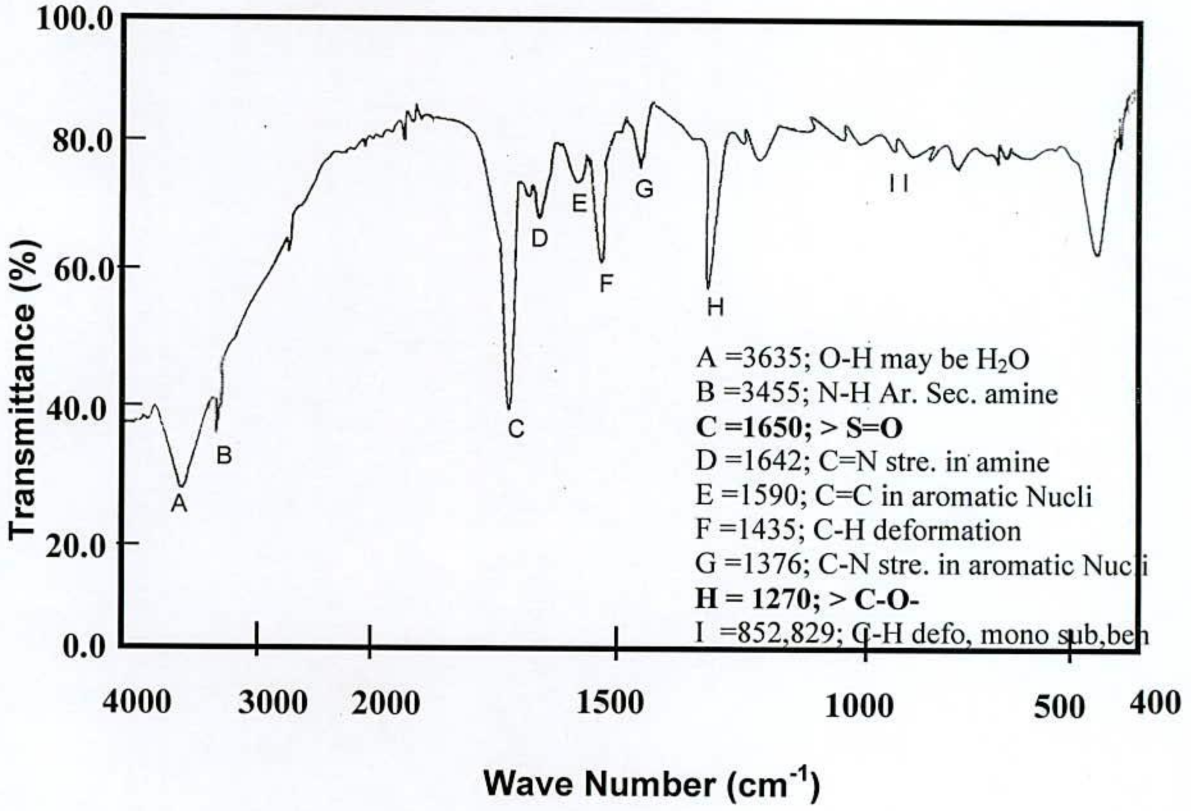

Fig. 3.2.4: IR spectrum of the PANI-SDS

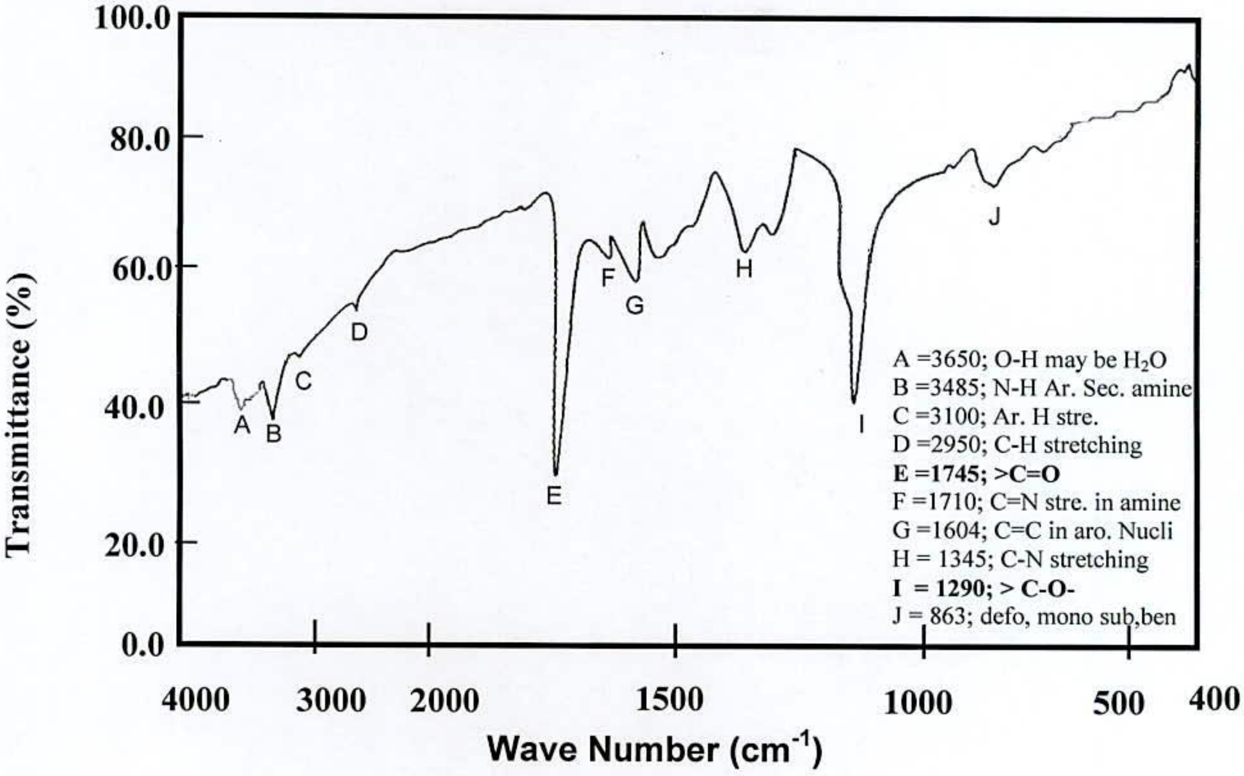

Fig. 3.2.5: IR spectrum of the PANI-EDTA

3.3 Thermal analyses of polymer based composites

Typical DTA and TGA curves for the bulk PANI and PANI-silica, PANI-stearate, PANI-SDS and PANI-EDTA composites materials are observed in Fig. 3.3.1-3.3.5. The TGA curves exactly correspond to DTA ones in each case. In case of PANI (Fig. 3.3.1) weight loss 40 °C to 110 °C corresponds to the loss of absorbed water molecules. From the TGA it is shown that the weight loss of moisture or water molecules is about 40% of the total mass. It indicates that the bulk PANI has strong affinity to adsorbed water molecules [35] and this result correlate with IR result discussed in section 3.2. The result of TGA of this part is supported by DTA curve. It is shown by the DTA curve i.e., from 40 °C to 110 °C is endothermic one which indicate that evaporation of adsorbed water molecules take heat from composite system. Weight loss <110°C to 390 °C may be attributable to the oxidation of carbon and hydrogen exist in PANI backbone, The loss of carbon and hydrogen by the oxidation as $CO_{2(g)}$and $H_2O_{(g)}$ is exothermic process [36]is also supported by DTA curve for the same temperature range. At higher temperature <390 °C the DTA curve shows that there is a endothermic process this may be correspond to the loss of nitrogen as NO_x [37]. The respective reactions are given below,

$$\text{PANI.} (H_2O)_n \xrightarrow{40 - 110^\circ C} \text{PANI} + n\,(H_2O)$$

$$\text{PANI} \xrightarrow{<110 - 390\ ^\circ C} CO_{2\,(g)} + H_2O_{(g)}$$

$$\text{PANI} \xrightarrow{<390\ ^\circ C} NO_x$$

Fig 3.3.2 - 3.3.5 show the DTA and TGA curves for PANI-silica, PANI-stearate, PANI-SDS and PANI-EDTA composites respectively. Both DTA and TGA curves support the loss of adsorbed water molecules in these composites in a similar manner like PANI bulk.

Loss of carbon, hydrogen and nitrogen show the similar trend as bulk PANI but the exothermic solder for the oxidation of carbon and hydrogen is stripper than that of the bulk PANI. Loss of silica composite takes relatively the higher temperature than the bulk polymer. Only when the PANI-silica composites is heated above 650°C the deep green colour of the composites change to brilliant white grains or powder with high density. This result shows that silica particles form the composite with PANI.

The thermogram (Fig.3.3.4) of PANI-stearate shows the similar trends for loss of carbon and hydrogen. In addition it also shows three endothermic process at near about 340°C, 370°C and 470°C which indicate the formation of Na_2O, NO_x and Na_2O_2 respectively. Here it should be noted that we used sodium stearate for the preparation of PANI- stearate composite.

The Fig.3.3.4 shows almost same DTA and TGA curve as above described composite polymers. In addition to those show the almost show the endothermic solder in between 400°C -450°C that may be attributable the formation of SO_2. Thermograms of PANI-EDTA exhibits a sharp endothermic process at 250°C that correspond to the loss of crystalline water present in the system.

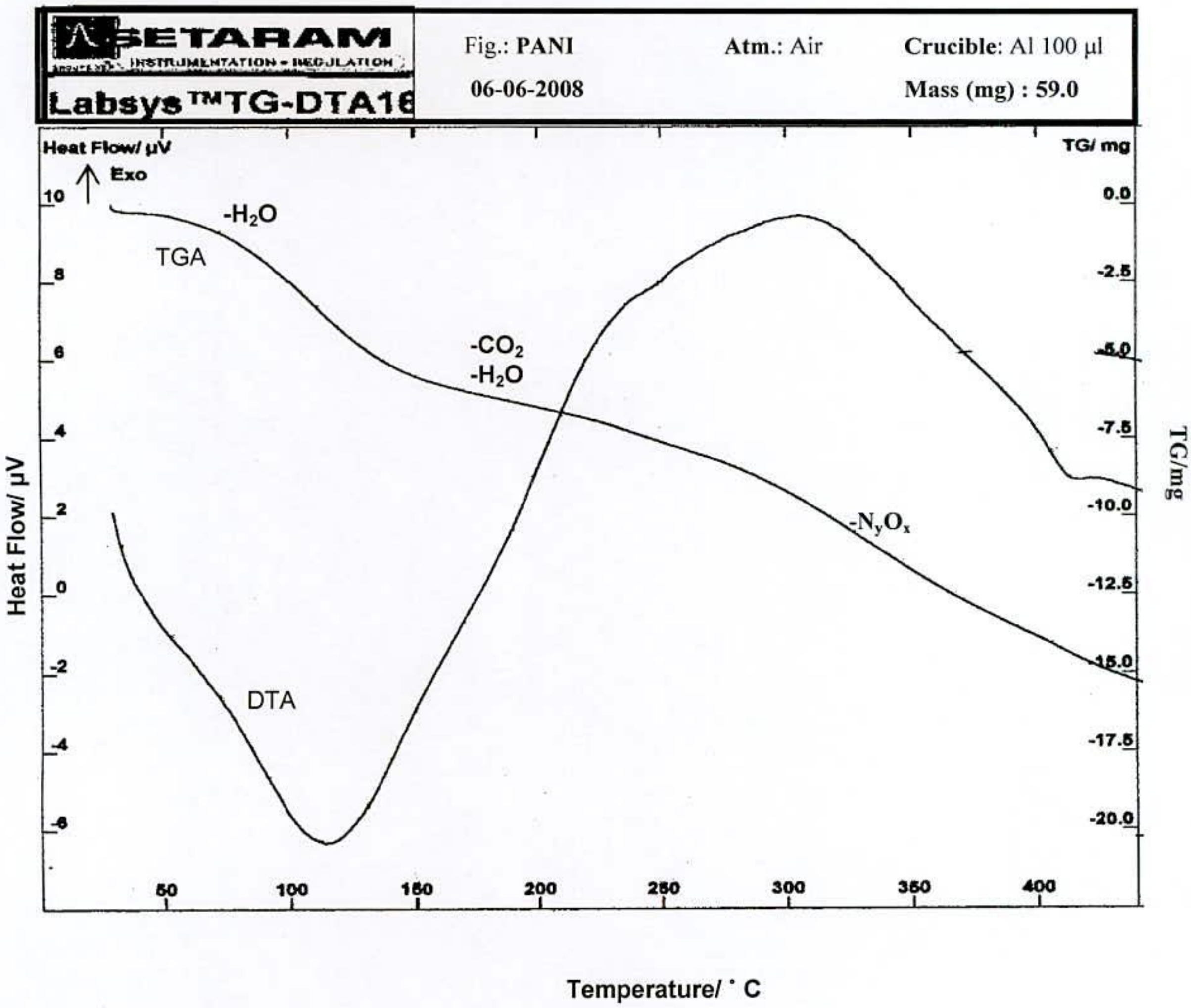

Fig. 3.3.1: Thermograms of PANI

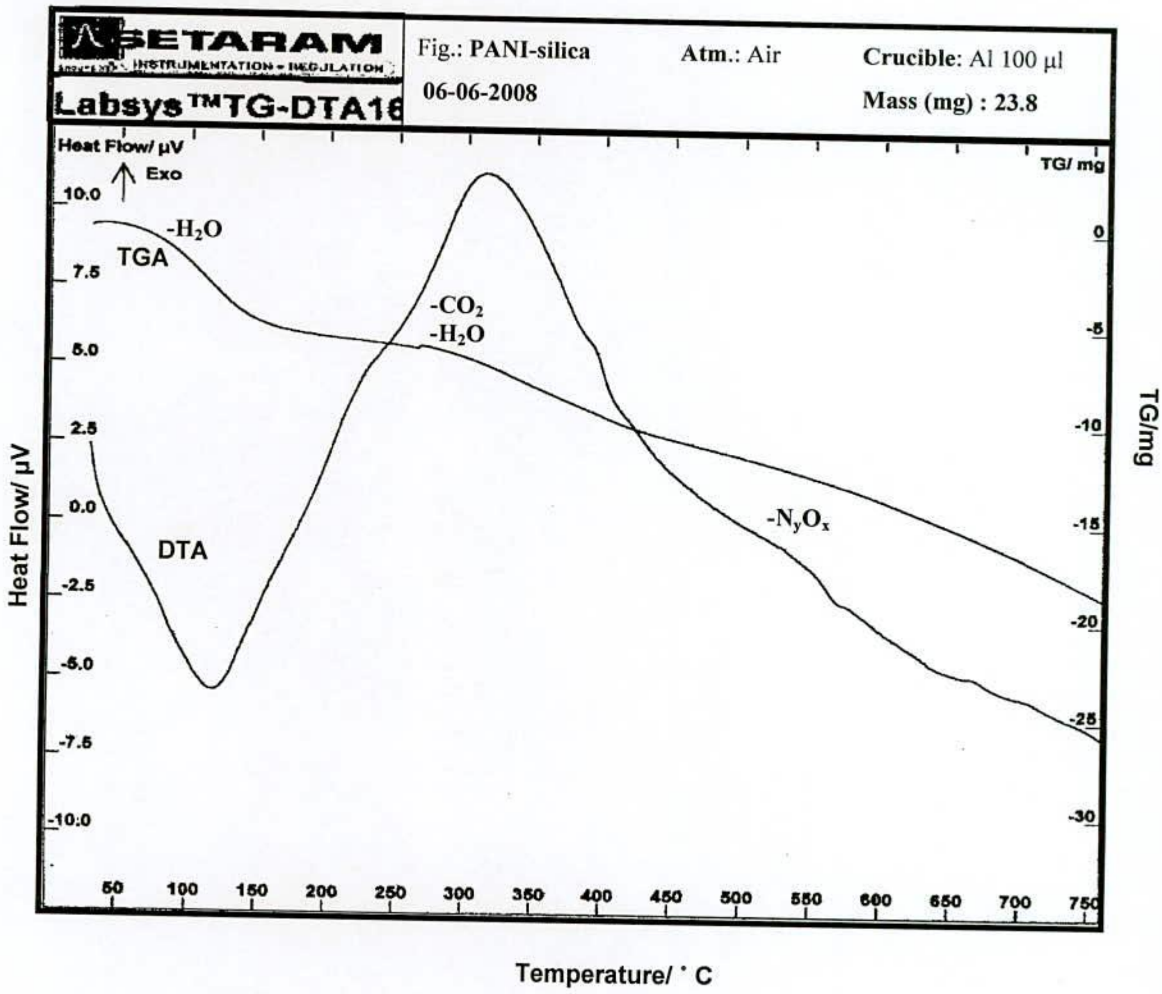

Fig. 3.3.2: Thermograms of PANI-silica

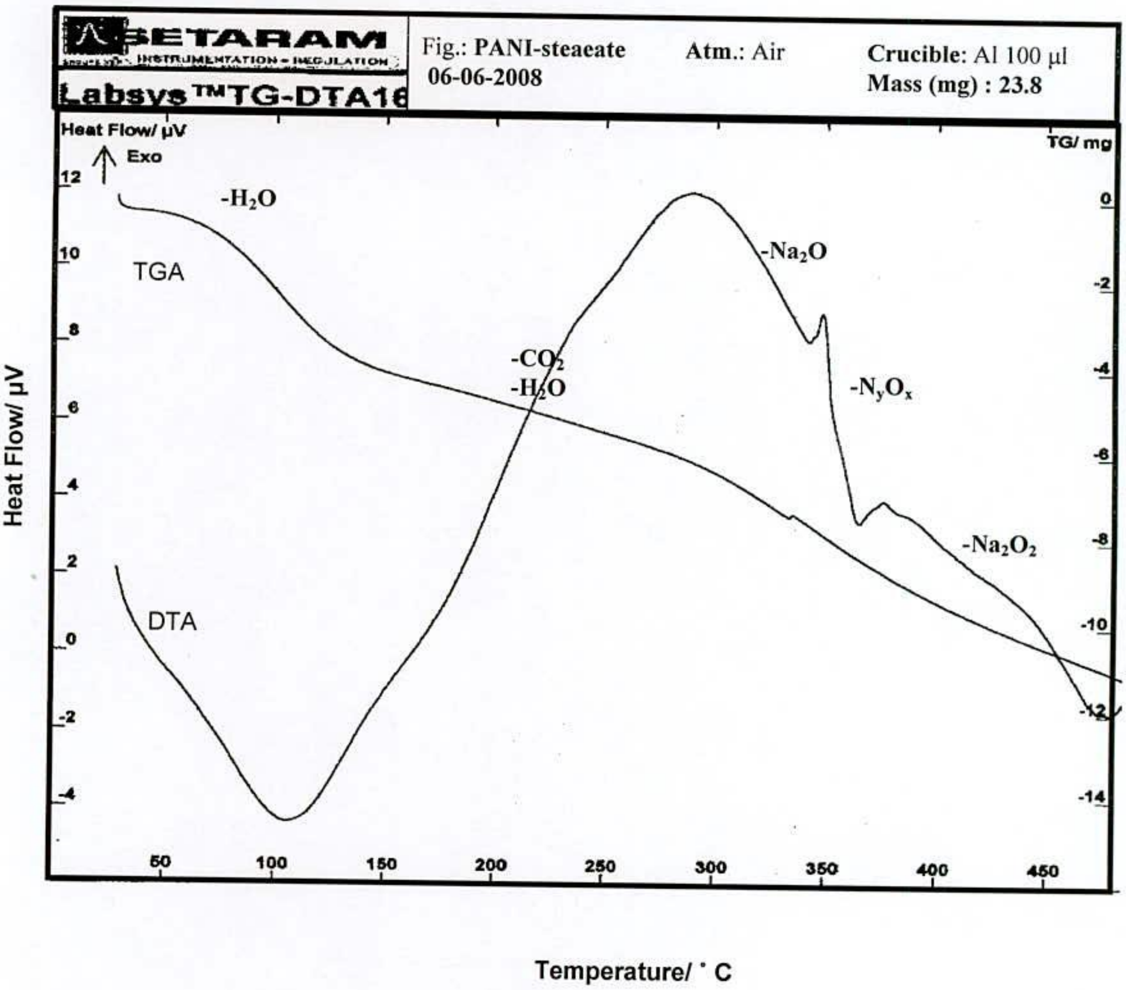

Fig. 3.3.3: Thermograms of PANI- steaeate

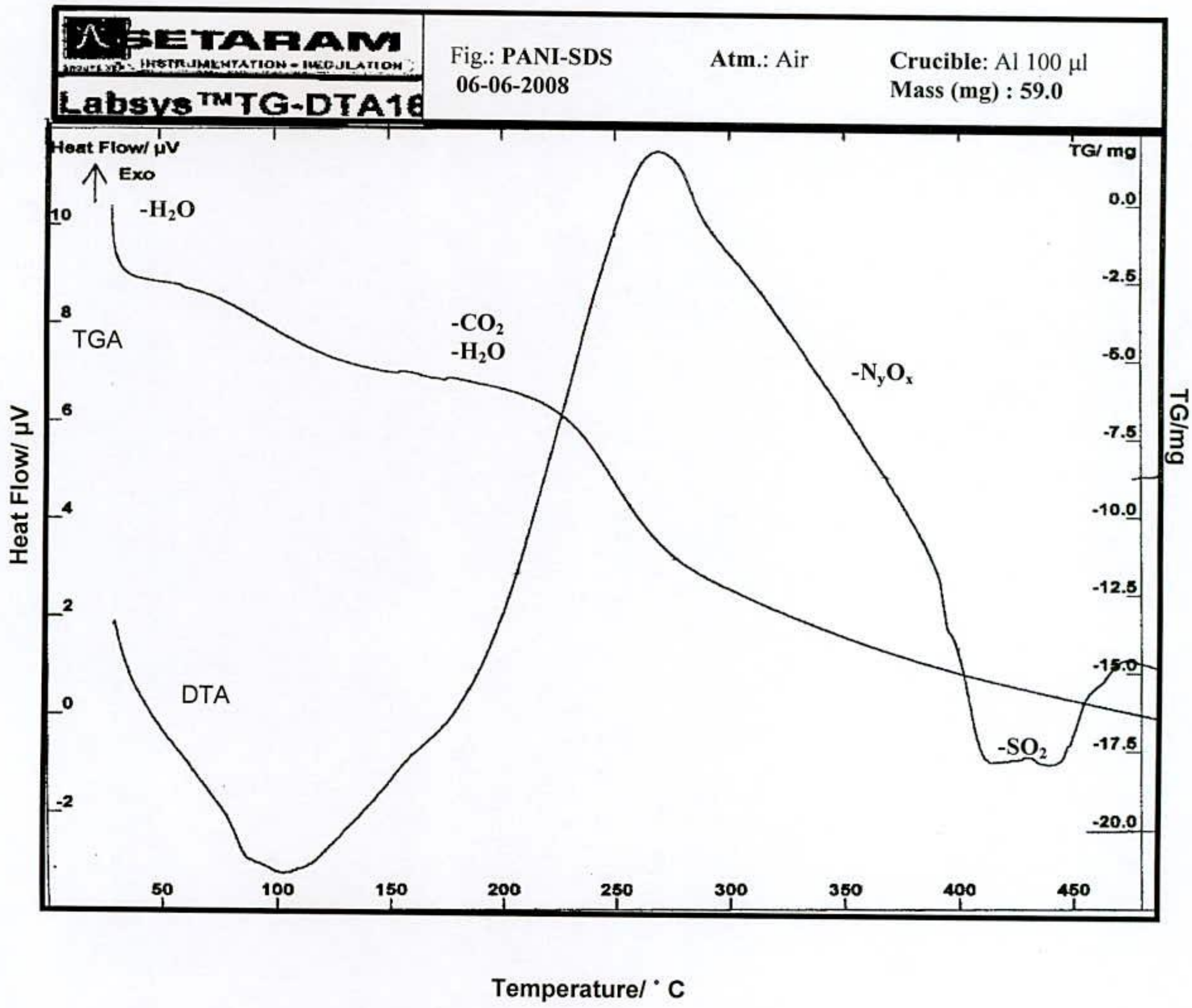

Fig. 3.3.4. Thermograms of PANI-SDS

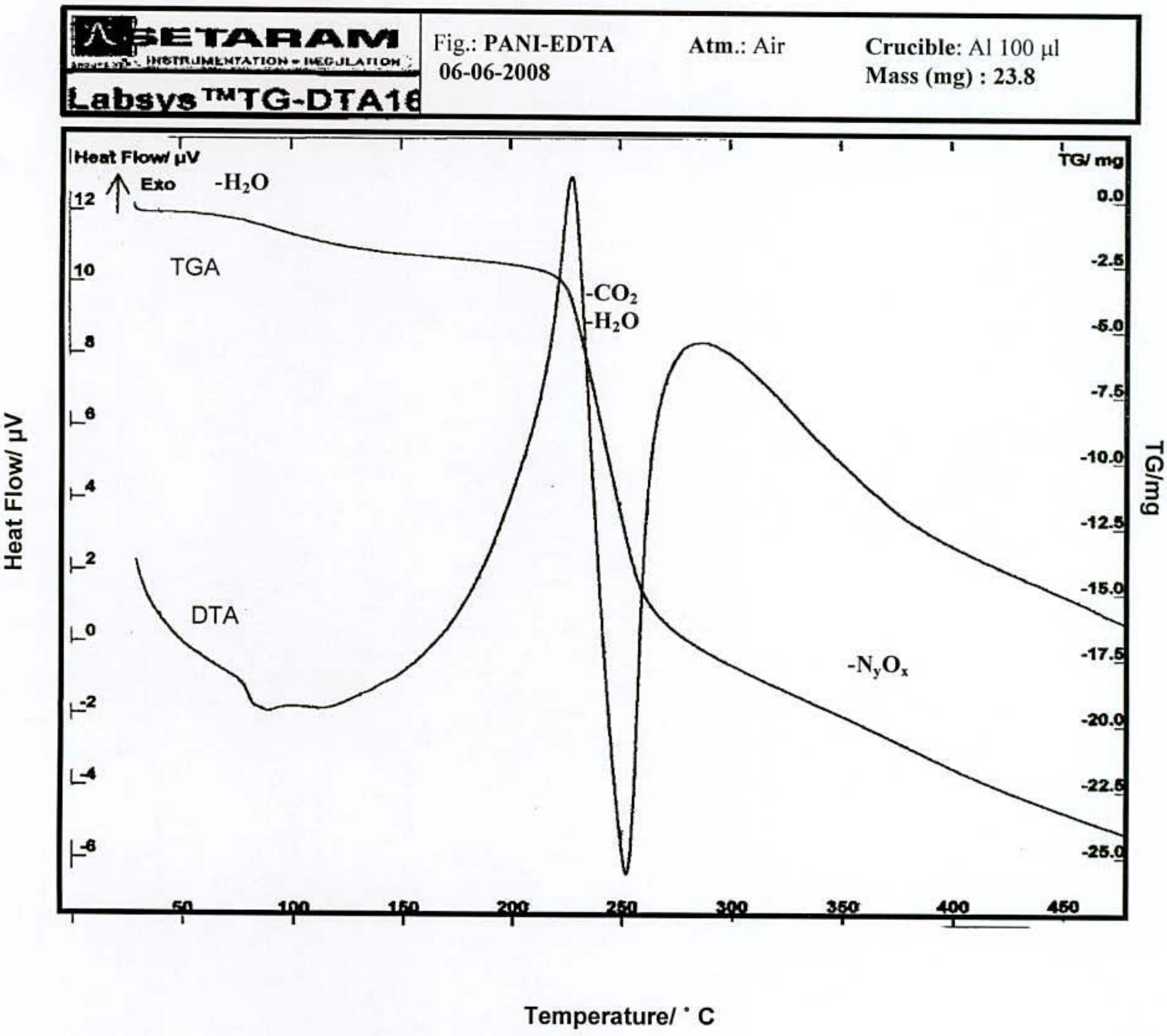

Fig. 3.3.5. Thermograms of PANI-EDTA

3.4 Adsorption study

Micromeritics Sedigraph examined PANI-silica sample prepared chemically for its surface area. The observed surface area vs. particle diameter exhibited by this sample is shown in Fig. 3.4.1. The result predicts that PANI-silica composite offer a surface area as high as 3.2 m^2/g. The surface area for the bulk PANI was not possible to study in this work. However, Maeda *et al.* [48] reported five times higher BET surface area for PP-silica composites than that of its bulk PP. As with the previous observation, we also expect that incorporation of the silica particles into the polymer matrix would lead an increase of surface area than the bulk polymer. Similar study by Micromeritics Sedigraph for PANI, PANI-stearate, PANI-SDS and PANI-EDTA were not possible to perform due to the lower densities of the materials and also for the limitations of the instrument.

Higher surface area for the studied PANI-silica matrix and incorporated anionic part in PANI-stearate, PANI-SDS and PANI-EDTA made us interested to study adsorption process on the sample. For the conduction of adsorption experiments 250mL conical flasks were used. A certain amount of each sample was taken in a conical flask and Mn^{2+} of a definite concentration in aqueous medium was mixed together. All the conical flasks were sealed with Para film and tightly bound with the rubber band. Then these samples were mounted on an orbital shaker (URN-480, made in Taiwan) and were shaken continuously at 300 rpm for 150 minutes. After that the suspensions were filtered using doubly attached whatmann filter paper No. 41. The filtrates were immediately measured using a UV-visible spectrophotometer (DR/2500 HACH, USA). The difference between initial and the equilibrium Mn^{2+} concentrations determine the amount of Mn^{2+} being adsorbed by the composites. All the experiments were triplicate and only mean values were reported. The maximum deviation is less than 5%. Similar experiments were performed As^{3+} ions present in the aqueous system. Change in concentration of Mn^{2+} and As^{3+} due to adsorption by the composite materials at different time intervals are shown in Fig. 3.4.2. and Fig. 3.4.3 respectively. It is seen that all the composites act as better adsorbent than that of bulk PANI in case of Mn^{2+}. The concentration, decay is very sharp for the Mn^{2+} in case of PANI-silica system Fig. 3.4.2. (Curve -b) compared to that of bulk PANI and other composite materials. The decrease of Mn^{2+} concentration appears to be rather faster in the initial few minutes and gradually become nearly unchanged with the lapse of time. This point of saturation may be termed as equilibrium time of adsorption. For PANI-silica system, this point observed nearly at about 120 minutes. The decrease in the concentration of Mn^{2+} on charging it to the absorbent, PANI and other composites may be attributed to the adsorption of the ions on those matrices. Silica particles have a net negative surface charge under the experimental conditions employed here [39]. Since Mn^{2+} is in the cationic form so adsorption of it on the PANI-silica is quite likely. However, the adsorption of Mn^{2+} on the bulk PANI is not understandable at present. Similar observation was also reported [40] for the adsorption of nitrogen on bulk PP and PP-silica matrices. The extent of adsorption of Mn^{2+} onto PANI-silica seems to be four times higher than that for bulk PANI. This finding may suggest that PANI-silica matrix possesses relatively high surface area. This surface area is nearly four times higher than that of the corresponding bulk PANI. This result seems to be consistent with a previous study involving nitrogen adsorption onto PP and PANI-silica matrix [41]. PANI-silica also adsorbs As^{3+} from the aqueous solution but in lesser extent. Cationic charge present on the As^{3+} may play an important role on the amount of adsorbed particles. PANI-EDTA, PANI-stearate and PANI-SDS decrease the concentration of Mn^{2+} ions from the aqueous solutions but in lesser extent than that of PANI-silica composite. Anionic part in stearate, SDS and ligand like properties of EDTA may act as trap for the Mn^{2+} ions. On the word it can be considered that PANI-EDTA, PANI-stearate and PANI-SDS may act as ion exchangers for the Mn^{2+} ions. C. Weidlicl et al have reported similar results [9]. That conducting polymers impregnated with anion may act as cation exchangers. PP synthesized in solutions with small counter ions, e.g. Cl^-, ClO_4^-, NO_3^-, mainly exhibits anion-exchanger behavior due to the high mobility of these ions in the polymer matrix, but under certain conditions cation exchange was also found to take place in such systems.

Cation exchange was primarily found to take place on PP modified with large counterions, e.g. polyvinylsulfonate, polystyrenesulfonate, due to the immobility of these ions in the polymer matrix [42-43]. May be in similar way PANI-stearate and PANI-SDS could adsorb As^{3+} from the aqueous solution. But on the other hand both bulk PANI and PANI-EDTA could not remove As^{3+} from the aqueous solution at al. May there was no any interaction between the adsorbate and adsorbent in this case. Most of the modified conducting polymer composites reported to be exhibited considerable porosity. This observation suggests that such composite particles might be interesting new stationary phase substrates for chromatography applications.

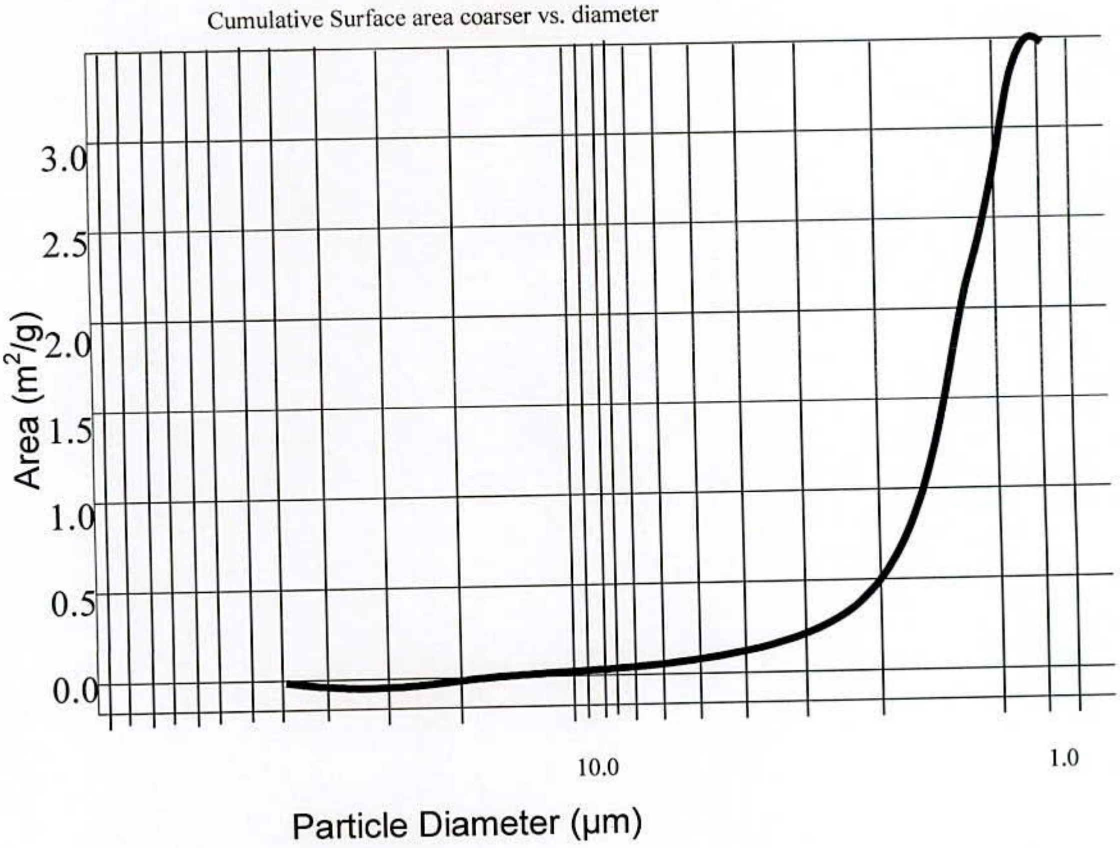

Fig. 3.4.1 Surface area vs. particle diameter plot for the chemically synthesized PANI-silica composite.

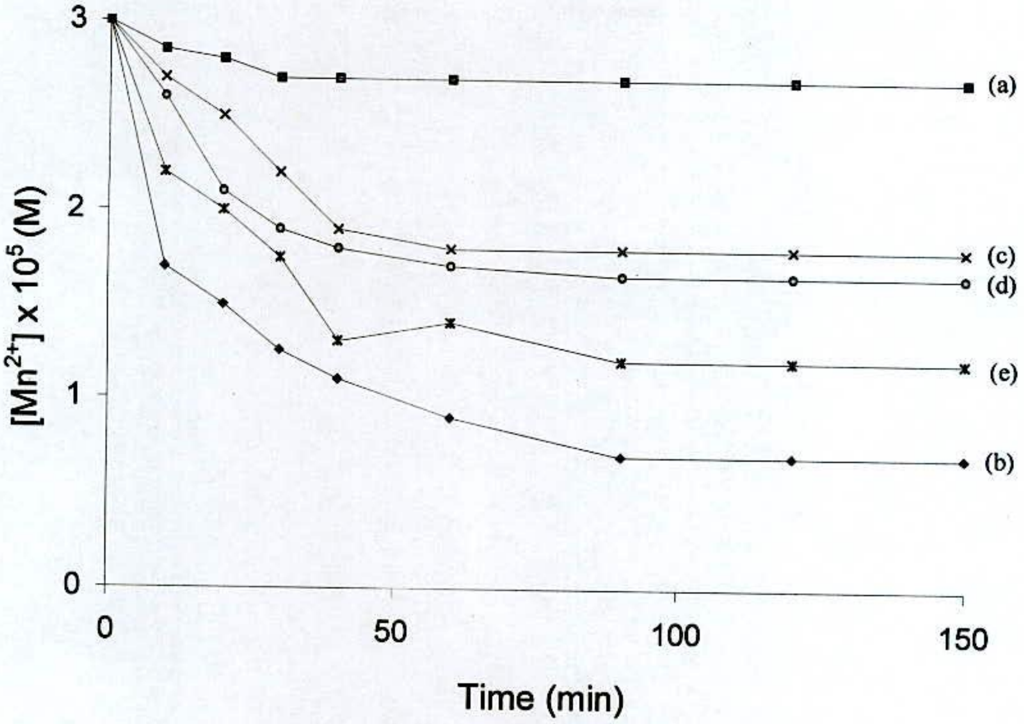

Fig.3.4.2: Change in Mn^{2+} with time on changing on to (a) PANI (b) PANI-silica (c) PANI-stearate (d) PANI-SDS and (e) PANI-EDTA

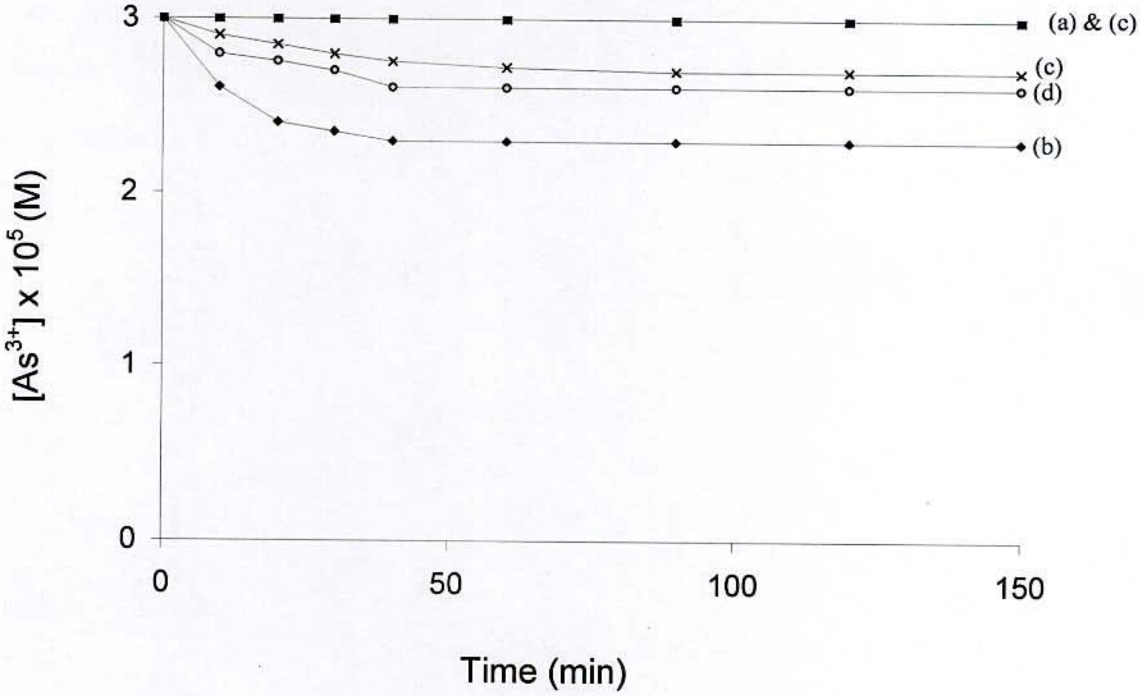

Fig.3.4.3: Change in As^{3+} with time on changing on to (a) PANI (b) PANI-silica (c) PANI-stearate (d) PANI-SDS and (e) PANI-EDTA

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Chapter 4: Conclusion

Conclusion

The polymerization of aniline in the presence of colloidal silica, sodium stearate, sodium dodecyl sulfate and ethylene diamine tetraacetic acid represents a novel and facile route for the synthesis of modified conducting polymer based composite dispersions where utilized commercially available fine silica particles, Na-stearate, SDS and EDTA as dispersant. The composites represent a potentially useful processable from PANI and its derivatives normally interactable conducting polymer. Optical microscopic studies confirm that the PANI-silica, PANI-stearate, PANI-SDS and PANI-EDTA composites are made up of micro aggregates of the original fine silica, sodium stearate, sodium dodecyl sulfate and ethylene diamine tetraacetic acid. Under appropriate reaction condition the silica content in the composite has been found as high as 11 % and that of EDTA content 3.9 % by mass. Since the silica is incorporated in to the polymer thus the density of PANI-silica composites is significantly higher than that of the corresponding bulk polymer. On the other hand the densities of the PANI-stearate, PANI-SDS and PANI-EDTA are smaller than that of the bulk polymer. The Infra red spectroscopy and the thermal analysis provide the strong evidence in favour of the formation of modified conducting polymer based composite materials.

The adsorption studies indicate that the synthesized modified conducting polymer based composites cassess relatively high surface areas. The polymer composite materials showed the higher removal capacity of Mn^{2+} and As^{3+}ions from the water sample than bulk polymer examined by the UV-spectroscopic analysis.

These composite materials seem to be very interesting for further investigations since the process both adsorption and ion exchange properties which might play an important role in the removal of various heavy metals present in water.

List of the symbols and abbreviations

Symbols / Abbreviations	Explanation
PANI	**PANI**
PP	**Polypyrrole**
IR	**Infra-red**
UV	**Ultra violet**
NMR	**Nucleo Magmatic Resonce**
DTA	**Differential Thermal Analysis**
TGA	**Thermo Gravimetric Analysis**
T_g	**Glass Transition Temperature**
T_{cr}	**Crystallization Temperature**
T_m	**Crystalline Melting Point**
FTIR	**Fourier Transform Infra-red**
SDS	**Sodium Dodecyl Sulfate**
EDTA	**Ethylene Diamine Tetraacetic Acid**
DMF	**Dimethyl Formamide**

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