Chapter 1

General Introduction
Chapter 1

1.1. Composite Materials

Mankind has been aware of composite materials since several hundred years before Christ and has applied innovations to improve the quality of life. It is not clear as to how one understood the fact that mud bricks made sturdier houses if lined with straw, he used them to make buildings that lasted. Long Ancient Pharaohs made their slaves use bricks with straw to enhance the structural integrity of their buildings, which testifies to the wisdom of the dead civilization. Although, composites were known to mankind since prehistoric times, the concept and technology have undergone a sea change with better understanding of the basics like the bonding mechanism between the matrix and dispersoids, dispersoid size and distribution, morphological features etc. [1].

The term "composite materials" may, perhaps, be simply defined on the basis of the classical definition of a “composite material” as given in “Longman’s dictionary” “something combining the typical or essential characteristics of individuals making up a group”. This short statement grasps the very essence of this new material, which has recently emerged as a leading contender for numerous applications in the automotive, aerospace, electronic and wears industry [1].

1.1.1. Classification of composite materials

Many composite materials are composed of just two phases; one is termed the
matrix, which is continuous and surrounds the other phase, often called the dispersed phase. The properties of composites are a function of the properties of the constituent phases, their relative amounts, and the geometry of the dispersed phase (i.e., the shape of the particles and particle size, distribution, and orientation); these characteristics are represented in Fig. 1.1.

One simple scheme for the classification of composite materials [1,2,] is shown in Fig. 1.2, which consists of three main divisions—particle-reinforced (dispersed phase is equiaxed, i.e., particle dimensions are approximately the same in all directions), fiber-reinforced (dispersed phase has the geometry of a fiber) and structural composites (combinations of composites and homogeneous materials).

As noted in Fig. 1.2, large particle and dispersion-strengthened composites are the two sub-classifications of particle-reinforced composites. The distinction between these, is based upon reinforcement or strengthening mechanism. The term ‘large’ is used to indicate that particle–matrix interactions cannot be treated on the atomic or molecular level. Some polymeric materials to which fillers have been added are really large-particle composites. Again, the fillers modify or improve the properties of the material and/or replace some of the polymer volume with a less expensive material—the filler. In dispersion-strengthened composites, materials may be strengthened and hardened by the uniform dispersion of several volume percent of fine particles of a very hard and inert material. The dispersed phase may be metallic or nonmetallic; oxide materials are often used. Again, the strengthening mechanism involves interactions between the particles and dislocations within the matrix, as with
Fig. 1.1. Schematic representations of the various geometrical and spatial characteristics of particles of the dispersed phase (a. shape, b. size, c. concentration, d. orientation and e. distribution) that may influence the properties of composites.
precipitation hardening; and the strengthening is retained at elevated temperatures and for extended time periods because the dispersed particles are chosen to be unreactive with the matrix phase.

Technologically, the most important composites are those in which the dispersed phase is in the form of a fiber. Design goals of fiber-reinforced composites (for those the potential for reinforcement efficiency is greatest) often include high strength and/or stiffness on a weight basis. These composites with exceptionally high specific strengths and moduli have been produced that utilize low-density fiber and matrix materials. As noted in Fig. 1.2, fiber-reinforced composites are sub-classified by fiber length. For short fiber composites, the fibers are too short to produce a significant improvement in strength. On the basis of diameter, fiber reinforcements are classified as whiskers, fibers, or wires. These types of composites are sometimes classified according to matrix type, viz. polymer-, metal-, and ceramic-matrix. Polymer-matrix are the most common, which may be reinforced with glass, carbon, and aramid fibers. Service temperatures are higher for metal-matrix composites, which also utilize a variety of fiber and whisker types. The objective of many polymer- and metal-matrix composites is a high strength and/or specific modulus, which require matrix materials having low densities. With ceramic-matrix composites, the design goal is increased fracture toughness. Other more advanced composites and promising engineering materials are carbon-carbon (carbon fibers embedded in a pyrolyzed carbon matrix) and the hybrids (containing at least two different fiber types).
A structural composite is normally composed of both homogeneous and heterogeneous composite materials, the properties of which depend not only on the properties of the constituent materials but also on the geometrical design of the various structural elements. Laminar composites (composed of two-dimensional sheets or panels that have a preferred high strength direction) and sandwich panels (consist of two strong and stiff sheets, or faces), separated by a layer of less dense material, or structure, or core, which has lower stiffness and lower strength.

In most cases composites consists of a bulk material (the matrix) and a reinforcement of some kind. So in another way, today’s most man-made composites can be divided in to four main groups depending on the matrix material as [1]- (i) polymer matrix composites (PMC), (ii) metal matrix composites (MMC), (iii) ceramic matrix composites (CMC) and (iv) carbon and graphite matrix composites.

Thus composite materials are those, which are formed by the combination of one or more other materials with a polymer matrix to produce a material with a combination of desirable properties from individual components [1]. Thus, in addition, the constituent phases must be chemically dissimilar and separated by a distinct interface. In designing composite materials, scientists and engineers have ingeniously combined various metals, ceramics, and polymers to produce a new generation of extraordinary materials. Most composites have been created to improve combinations of mechanical characteristics such as stiffness, toughness, and ambient and high temperature strength. But in this study we have to choose only polymer matrix composites.
1.2. Organic-organic Conducting Composites

During the last decades, extensive international research efforts has followed the initial discovery of intrinsically conducting polymers (ICP's) containing repeating units of oxidized or reduced monomers, first reported by MacDiarmid and co-workers [3]. After that, the interest in ICP's has developed through three stages: (i) an initial interest motivated by their unique properties and practical possibilities; (ii) a decline in interest owing to difficulties in processing and poor mechanical properties; (iii) renewed interest following the discovery of solution and melt processibility of polyaniline (PANI) in the early 1990s [4-9]. In recent years, there has been some optimism that striking advances in understanding the chemistry and physics of ICP's [10] will support the development of large scale applications, witnessed by the award of the Nobel Prize in Chemistry to Heeger, MacDiarmid and Shirakawa in 2000. Manufacturers and researchers, who are actively involved in research and development in this field, have also recognized this trend. For example, some leading companies have discussed their strategy and advances in applications of ICP’s at two European events: ‘Commercializing Conductive Polymers’ in February 2002 and 2003 in Brussels and Barcelona, respectively owing to their interesting electrical properties and their potential applications in various fields like electronics, microelectronics and medicine, corrosion protection [11], light emitting diodes (LEDs) [12], electro magnetic interference (EMI) shielding [13] and drug delivery [14], rechargeable batteries, gas separation membranes, antistatic agents and electroluminescent diodes (ELDs) [15-18], modified electrodes, chemical and
bio-sensors etc. Because of their important advantages most of the works with electrically conducting polymers have been focused on three main classes of polymeric materials viz. polyacetylene (PA) and its derivatives, polyphenylenes (PPh) and its derivatives, polyheterocyclics such as polypyrrole (PPy) and polythiophene (PTh) and polyaniline (PANI) etc. These polymers are relatively stable under ambient conditions and can be conveniently synthesized via oxidative or electro-chemical polymerization [19-22]. Oxidizing agents, such as iodine and FeCl₃, are convenient for oxidatively polymerizing monomers and to produce conductive polymers [21].

However, their poor mechanical properties and processibility constitute major obstacles to their extensive applications [23]. To improve the mechanical properties and processibility many kinds of method have been used, including the introduction of long alkyl groups into the main chain [24,25], the synthesis of soluble precursors [26,27], the preparation of conducting polymer composites [28] and so on [24,29]. Among these methods, the preparation of composites is the easier and more effective. In this consequent many kinds of conducting polymer composites, which combine the electrical conductivity of PPy, PANI, PTh and their derivatives with good mechanical properties of insulating polymers viz. polyethylene (PE) [29,30], PVC [31-34], poly(ethylene oxide) (PEO) [35,36], poly(vinyl alcohol) (PVAL) [37-41], poly(etherketone) (PEK) [42] poly(tetrahydrofuran) [43], polystyrene [44,45], polyurethane [46,47], ethylene vinyl acetate copolymer [48,49], polyamides and polyimide [50-53], rubber [54,55], polycarbonate [56] and poly(acrylonitrile) [57] have been reported.
This trend has been driven by the need to replace traditional inorganic conducting fillers and to improve the processibility of conducting polymers, along with their mechanical properties and stability. These composite materials have introduced conducting polymers to practical applications in different fields, including electromagnetic shielding and microwave absorption [58-61], static electricity dissipation [62-64], heating elements (clothing, wall papers, etc.) [65,66], conducting glues [67], conducting membrane materials [68,69], paint coatings for anticorrosion protection [70] and sensor materials [71,72].

As a consequence, conducting composites are very close to applications on a large scale for the industrial applications mentioned above [58-72]. Nevertheless, the choice of the best method to produce composites with specified characteristics remains an unresolved problem. The problem arises because the processing method may significantly determine the properties of the manufactured composite materials. Thus, our present discussion will be confined to the preparation and electrical properties of the composites of polyheterocyclics because of their attractive properties like relative ease of synthesis, good environmental stability and electrical conductivity.

1.3. Organic-inorganic Composite Materials

It is well-accepted fact that the progress of mankind today is directly or indirectly dependent on advanced technological materials (high performance materials) that perform better and open new dimensions in research and development. Among the major developments in materials in recent years are composite materials.
In fact, composites are now one of the most important classes of engineering materials, as they offer several outstanding properties as compared to conventional materials. These materials have found increasingly wider utilities in the general areas of chemical sensors, chromatography, fabrication of selective materials and electrical and optical applications.

Composite materials formed by the combination of inorganic materials and organic polymers are attractive for the purpose of creating high-performance or high functional polymeric materials. Of particular interest is the molecular level combination of two different components that may lead to new composite materials that are expected to provide different possibilities, termed "organic-inorganic hybrid" materials. These hybrid materials usually show properties intermediate between those of plastics and glasses (ceramics). Accordingly, hybrids can be used to modify organic polymer materials or to modify inorganic glassy materials. In addition to these characteristics, the hybrid materials can be considered as new composite materials that exhibit very different properties from their original components (organic polymers and inorganic materials), especially in the case of molecular level hybrids. Therefore, organic-inorganic composite materials are of intensive interest in the field of contemporary materials chemistry as these materials can exhibit synergetic extraordinary properties such as electrical, magnetic and optical properties [73], which arise from the synergism between the properties of the organic and inorganic components. There are several routes for the preparation of these materials, but probably the most prominent one is the incorporation of inorganic
building blocks in organic polymers by sol-gel process. These materials have gained much interest due to their remarkable change in properties such as mechanical [74], thermal [75-78], electrical [79] and magnetic [80] compared to pure organic polymers. Additionally, the properties of the composite materials depend on the morphology of the phases viz. organic and/or inorganic network, which has to be controlled over several length scales. Therefore, the development of such materials is a ‘land of multidisciplinary’ [81], where chemists, physicists, material scientists and engineers have to work closely together to fully exploit this technical opportunity for creating materials and device with benefits of the best of the two worlds namely inorganic and organic. Commencing a chemical point of view, one can distinguish between several ways to incorporate inorganic systems in organic polymers depending on the interactions between the moieties: materials with strong (covalent, coordination, ionic): weak (Van-der Waals, hydrogen-bonds, hydrophilic–hydrophobic balance) or without chemical interactions between the two components (Fig. 1.3) [81,82]. Based on the structural distinction, Sanchez and Ribot classified the organic-inorganic hybrid materials into two classes [83].

**Class I** (network modifiers) in which the organic polymer or organic molecules are simply embedded into the inorganic matrix. No covalent bonds exist between both phases only weak interaction such as Van-der Waals forces, electrostatic or H-bonds. As an example of this class I are the organic dyes or biomolecules incorporated in the porous inorganic gel via the H bond between organic and inorganic parts the transparency and no phase separation could be achieved.
Fig. 1.3. Different kinds of inorganic–organic composite materials. (a) embedding of the inorganic moiety into the organic polymer, (b) interpenetrating networks (IPNs) with chemical bonds, (c) incorporation of inorganic groups by bonding to the polymer backbone and (d) dual inorganic-organic hybrid polymer.
Class II (network formers) in which the organic and inorganic parts establish covalent or iono-covalent bonds. To this class correspond the hybrid materials that incorporate fictionalized alkoxy silanes such as poly(dimethylsiloxane). This sol-gel method is extensively used to obtain amorphous materials where the homogeneity is directly designed on a molecular scale, ranging from single-phase to multi-phase systems. The combination of several precursors for the synthesis of nanostructured materials hybrid polymers are an open door in the chemical route and can be used to form nanoparticles, coating, fibers or bulk solids with the corresponding technological applications.

Hybrid materials made in this way are termed creamers (ceramic polymers), ormosils (organically modified silicates) or ormocers (organically modified ceramics) [84]. Through the combinations of different inorganic and organic components in conjunction with appropriate processing methods, various types of primary and secondary bonding can be developed leading to materials with unique combination of properties which cannot be achieved by other materials. The concept of ‘molecular level mixing’ between two different materials can also be considered. Since the late 1980s, molecular level combination between organic polymers and inorganic materials has been of interest. Review articles concerning hybrid materials have been reported by Saegusa and Chujo [85], Sanchez and co-workers [81,83], Schubert et al. [86], Novak [87], Loy and Shea [88], Mark [89], Johan N Hay and Steve J Shaw [90] and others [91]. During this period, the study of organic-inorganic hybrid materials focused on the following points: firstly, exploration of new preparative
methodology for hybrid materials; secondly, new combinations between different materials; thirdly, functionalization of hybrid materials; and fourthly, modifications of hybrids for industrial applications. It is necessary to point out some important composite materials that are believed to have evolved and will result in interesting molecular hybrid materials in the near future. But due to numerous papers published on polymer organic–inorganic composite materials, it is impossible to completely review this field. Therefore, this review will focus on the most common principal concepts used to incorporate organic systems into an inorganic polymeric matrix and the resulting properties of such materials. The reader is referred to the literature cited for a more detailed description.

1.3.1. Organic-inorganic composite synthesis strategies

Although chemists from the sol-gel scientific community initially have worked out organic-organic and/or organic-inorganic composites and have attracted a great deal of attention in material science, but at the time of advancement in materials composites are elaborated by researchers coming from a variety of disciplines, polymers chemists, solid-state chemists, catalysis and material researchers etc. Each of these communities elaborate composites using their own tools, specific disciplinary methods and more important their own raw materials. It is not seldom to see that a polymer chemist will work out a composite system having an emphasis on the polymer side of the composite, using even pre-formed polymers, capped oligomers etc. Sol-gel and inorganic chemists will preferably use as precursors, silicon or metal alkoxides or even inorganic building units such as clusters or
nanoparticles. They can also use lamellar inorganic compounds as host for organic components. Many names have been given to these materials: ceramers, polycerams, ormosils or ormocers. These names were labeled by materials science researchers coming from different sides (polymers scientists, glass or ceramic scientists, organometallic scientists). However it is now commonly accepted that a molecular approach for the synthesis of hybrids reflects better the wide opportunities offered by this compounded chemistry. Thus, a critical challenge in the design of these hybrid organic-inorganic and/or inorganic-organic systems is a control of mixing between the two dissimilar phases.

1.4. Chromatography

It was the Russian botanist Mikhail Tsvet (Mikhail Semyonovich Tsvet), who invented the first chromatography technique in 1901 during his research on chlorophyll. He used a liquid-adsorption column containing calcium carbonate to separate plant pigments. The method was described on December 30, 1901 at the XI Congress of Naturalists and Doctors in St. Petersburg. The first printed description was in 1903, in the Proceedings of the Warsaw Society of Naturalists, section of biology. He first used the term chromatography in print in 1906 in his two papers about chlorophyll in the German botanical journal, *Berichte der Deutschen Botanischen Gesellschaft*. In 1907 he demonstrated his chromatograph for the German Botanical Society. The phenomenon of precipitational separation was observed before Tsvet as well. His contribution was turning the phenomenon into the method of scientific analysis. The Greek word *chroma* in *chromatography* means
color in English and refers both to Tsvet’s name that is literally translated from Russian as color and to the color of the plant pigments he was separating at that time. In 1952 Archer John Porter Martin and Richard Laurence Millington Synge were awarded the Chemistry Nobel Prize “for their invention of partition chromatography” [92]. The technology of chromatography advanced rapidly throughout the 20th century and Chromatography became a family of analytical chemistry techniques for the separation of mixtures. It involves passing the sample, a mixture which contains the analyte, in the “mobile phase”, often in a stream of solvent, through the “stationary phase”. The stationary phase retards the passage of the components of the sample. When components pass through the system at different rates they become separated in time, like runners in a mass-start foot race. Each component has a characteristic time of passage through the system, called a "retention time". Chromatographic separation is achieved when the retention time of the analyte differs from that of other components in the sample. In accordance, researchers found that the principles underlying Tsvet’s chromatography could be applied in many different ways, giving rise to the different varieties of chromatography described below. Simultaneously, advances continually improved the technical performance of chromatography, allowing increasingly similar molecules to be resolved.

1.4.1. Types of chromatography

As far as the knowledge of Human civilization concerned to the science and technology, a wide variety of instrumental and non-instrumental chromatographic techniques have been developed since the prehistoric time. As the field is very
diverse it is very difficult to summarize all the chromatographic techniques. Therefore, we have chosen to only some non-instrumental techniques in short and particularly ion-exchange chromatography in details. A brief principles and methods of non-instrumental chromatographic techniques are given below.

1.4.1.1. Liquid chromatography

Simple liquid chromatography consists of a column with a fitted bottom that holds a stationary phase in equilibrium with a solvent. Typical stationary phases (and their interactions with the solutes) are: solids (adsorption), liquids on an inert solid support (partitioning), porous inert particles (size-exclusion) and ionic groups on a resin (ion-exchange). The mixture to be separated is loaded onto the top of the column followed by more solvent. The different components in the sample mixture pass through the column at different rates due to differences in their partitioning behavior between the mobile liquid phase and the stationary phase. The compounds are separated by collecting aliquots of the column effluent as a function of time. Schematic diagram of a simple liquid chromatographic separation is given in Fig. 1.4.

1.4.1.2. Adsorption chromatography

Adsorption chromatography is probably one of the oldest types of chromatography around. It utilizes a mobile liquid or gaseous phase that is adsorbed onto the surface of a stationary solid phase. The equilibration between the mobile and stationary phase accounts for the separation of different solutes. Typical chromatogram is given in Fig. 1.5.
Fig. 1.4. Schematic diagram of a simple liquid chromatographic separation.

Fig. 1.5. Typical chromatogram of adsorption chromatography.
1.4.1.3. Paper chromatography

In paper chromatography, chemical interactions with the paper make compounds travel at different rates. Therefore, a small spot of solution containing the sample is applied to a strip of chromatography paper about one centimeter from the base. This sample is adsorbed onto the paper. This means that the sample will contact the paper and may form interactions with it. Any substance that will react with (and thus bond to) the paper cannot be measured using this technique. The paper is then dipped in to a suitable solvent (such as ethanol or water) and placed in a sealed container. As the solvent rises through the paper it meets the sample mixture, which starts to travel up the paper with the solvent. Different compounds in the sample mixture travel different distances according to how strongly they interact with the paper. A chemical interaction with the paper to demonstrate compounds travel is shown in Fig. 1.6. Paper chromatography takes some time and the experiment is usually left to complete for some hours.

1.4.1.4. Thin layer chromatography (TLC)

Thin layer chromatography (TLC) is a standard laboratory method in organic chemistry. Because of its simplicity and speed TLC is often used for monitoring chemical reactions and for the qualitative analysis of reaction products. This process is similar to paper chromatography with the advantage of faster runs, better separations, and the choice between different adsorbents. In this chromatography the stationary phase consists of a thin layer of adsorbent like silica gel, alumina or cellulose on a flat carrier like a glass plate, a thick aluminum foil, or a plastic sheet.
Fig. 1.6. A chemical interaction with the paper to demonstrate compounds travel.
TLC plates are made by mixing the adsorbent with a small amount of inert binder, like calcium sulphate (gypsum) and water, spreading the thick slurry on the carrier, drying the plate, and activation of the adsorbent by heating in an oven. The thickness of the adsorbent layer is typically around 0.1–0.25 mm for analytical purposes and around 1–2 mm for preparative TLC.

Several methods exist to make colorless spots visible:

- Often a small amount of a fluorescent dye is added to the adsorbent that allows the visualization of UV absorbing spots under a black light ‘UV<sub>254</sub>’.
- Iodine vapors are a general unspecific color reagent.
- Specific color reagents exist into which the TLC plate is dipped or which are sprayed onto the plate.

Once visible, the spots can be quantified by way of calculating their $R_f$ values. These values should be the same regardless of the extent of travel of the solvent, and in theory are independent of a single experimental run. They do depend on the solvent used, and the type of TLC plate. A chromatogram showing separation of black ink on a TLC plate is given in Fig. 1.7.

1.4.1.5. Partition chromatography

This form of chromatography is based on a thin film formed on the surface of a solid support by a liquid stationary phase. Solute equilibrates between the mobile phase and the stationary liquid as given in Fig. 1.8.
Fig. 1.7. A chromatogram showing separation of black ink on a TLC plate.

Fig. 1.8. Typical chromatograms of partition chromatography indicating solute equilibration between the mobile phase and the stationary liquid.
1.4.1.6. Molecular exclusion chromatography

Molecular exclusion or size exclusion chromatography, also called gel-permeation chromatography (GPC), uses porous particles to separate molecules of different sizes. It is generally used to separate biological molecules and to determine molecular weights and molecular weight distributions of polymers. Molecules that are smaller than the pore size can enter the particles and therefore have a longer path and longer transit time than larger molecules that cannot enter the particles. All molecules larger than the pore size are unretained and elute together. Molecules that can enter the pores will have an average retention time in the particles that depends on the molecules size and shape. Different molecules therefore have different total transit times through the column. Typical chromatographs are shown in Fig. 1.9.

1.4.1.7. Affinity chromatography

This is the most selective type of chromatography employed. It utilizes the specific interaction between one kind of solute molecule and a second molecule that is immobilized on a stationary phase. For example, the immobilized molecule may be an antibody to some specific protein. When solute containing a mixture of proteins are passed by this molecule, only the specific protein is reacted to this antibody, binding it to the stationary phase as shown in Fig. 1.10. This protein is later extracted by changing the ionic strength or pH.

1.4.1.8. Column chromatography

Column chromatography utilizes a vertical glass column filled with some form
Fig. 1.9. Two different schematic of molecular exclusion chromatographic columns.

Fig. 1.10. Typical chromatogram of affinity chromatography.
of solid support with the sample to be separated placed on top of this support. The rest of the column is filled with a solvent which, under the influence of gravity, moves the sample through the column. Similarly to other forms of chromatography, differences in rates of movement through the solid medium are translated to different exit times from the bottom of the column for the various elements of the original sample.

In 1978, W.C. Stills introduced a modified version of column chromatography called **flash column chromatography** "flash". The technique is very similar to the traditional column chromatography, except for that the solvent is driven through the column by applying positive pressure. When applying positive pressure on top of the column, most separations could be performed in less than 20 minutes with improved separations compared to the old method. This makes flash column chromatography the method of choice for most synthetic organic chemists when purifying organic compounds. In the modern flash chromatography systems which can be purchased, the glass columns are replaced with pre-packed plastic cartridges. Solvent is pumped through the cartridge, which is much quicker. Systems may also be linked with detectors and fraction collectors providing automation. The introduction of gradient pumps means quicker separations and less solvent usage. A picture of a standard column chromatography and a flash column chromatography setup is shown in Fig. 1.11.

1.4.1.9. **Ion-exchange chromatography**

Ion-exchange chromatography is a column chromatography that uses an oppositely charged stationary phase to the sample ion and is used almost exclusively
Fig. 1.11. A picture of a standard column chromatography and a flash column chromatography setup.
with ionic or ionizable samples. The stronger the charge on the sample, the stronger it will be attracted to the ionic surface and thus, the longer it will take to elute because solute ions of the opposite charge in the mobile liquid phase are attracted to the resin by electrostatic forces and the mobile ions held near cations that are covalently attached to the stationary phase as shown in Fig. 1.12. In particular, the stationary phase is usually anion- or cation-exchange resin that carries charged functional groups, which interact with oppositely charged groups of the compound to be retained:

- Positively charged ion-exchanger (anion-exchanger) interacts with anions.
- Negatively charged ion-exchanger (cation-exchanger) interacts with cations.

However, ion-exchange chromatography is a type of liquid chromatography in which ion-exchange process takes place. It has found numerous applications in science and industry, and is, at present, the most important analytical tool in environmental analysis, such as, in the recovery of the precious metals from industrial effluents, removal of arsenic and heavy toxic metal ions, recovery of important organics from paper, wine, cigarette and food processing industries, recovery of radioactive isotopes, separation and analysis of inorganics in the environment. Many classical methods have been greatly speeded up by the use of an ion-exchange process. In view of above-mentioned fact we have also planed to study in the field of ion-exchange chromatography.
Mobile anions held near cations that are covalently attached to stationary phase.

Anion-exchange resin; only anions can be attracted to it.

Fig. 1.12. Ion-exchange chromatography.
1.5. Ion-Exchange Properties of Materials

1.5.1. Ion-exchange phenomenon & its historical background

The phenomenon of ion-exchange is not of a recent origin. Many million years ago it had occurred in various sections of the globe. For example, some ions like potassium and lithium of ptalite of pegmatite veins had been replaced with rubidium and cesium ions of step wisely fluid from the maga. This is nothing but ion-exchange phenomenon between minerals like ptalite (solid phase) and fused salt fluid (liquid phase) [93]. It is well known that ion-exchange has been playing very important roles during the course of weathering; aqueous rocks, clay rocks and soils being very effective ion-exchangers. Since life had been created in the sea, ion-exchange through bio-membranes between living organs and outside matters has been giving the essential motive forces to life and its evolution. The earliest of the references were found in the Holy Bible establishing Moses’s priority that succeeded in preparing drinking water from brackish water [94], by an ion-exchange method. Later on, Aristotle found the seawater loses part of its salt contents when percolated through certain sand [95]. In Egypt and Greece as well as in China, ancient people were clever enough to use some soils, sands, natural zeolites and plants as the tools for improving the quality of drinking water by way of desalting or softening. However, they were not aware of the actual phenomenon occurring in the process. Basically, ion-exchange is a process of nature occurring throughout the ages before the dawn of civilization, has been embraced by analytical chemists to make use of difficult separation easier and possible.
Francis Bacon in 1623 brought the intentional use of ion-exchange, without knowledge of its theoretical nature, based purely on empirical experiences and he described a method for removing salts from seawater. The first half of the 19th century was characterized by the appearance of the first information leading to the discovery of the ion-exchange principle, based primarily on the work of soil chemists. Thompson and Way in 1850 described independently that calcium and magnesium ions of certain types of soils could be exchanged for potassium and ammonium ions [96,97]. They defined the special properties of soil as ‘base exchange’. In the second half of the 19th century, agro chemists published a great number of papers dealing with ion-exchange in soils. Eichorn (in 1858) demonstrated exchange processes are reversible in soils [98]. In 1859, Boedecker proposed an empirical equation describing the establishment of equilibrium on inorganic ion-exchange sorbents. In the 20th century, the majority chemists believed that the ‘base exchange’ in soils is nothing but a sort of absorption. Strong supports to ion-exchange come out with the synthesis of materials from clay, sand and sodium carbonate by Gans [99].

The discovery and development of the theory of ion exchange was reflected in practical applications. Gans [99] developed the basis for the synthesis and technical application of inorganic cation-exchangers at the beginning of the 20th century. He termed the amorphous cation-exchangers based on aluminosilicate gels “permutites”, having broad application, were actually the first commercially available ion-exchangers. In 1917, Folin and Bell developed an analytical method based on these
materials for the separation and collection of ammonia in urine [100]. However, the usefulness of these synthetic zeolites was limited because of their low chemical and mechanical stability, ion-exchange capacity that led the chemists to seek alternatives. During the period between the 1930s and 1940s, inorganic ion-exchange sorbents were replaced in almost all fields by the new organic ion-exchangers. The observation of Adam and Holms [101] that the crushed phonograph records exhibit ion-exchange properties, eventually resulted in the more significant development of synthetic ion-exchange resins (high molecular weight organic polymers containing a large number of ionic functional groups) in 1935. No scientist could then neglect ion-exchange phenomenon. However, it took nearly 85 years for the ion-exchange phenomenon to be fully recognized in chemistry since its scientific finding and understanding by Thompson and Way.

Just as applications of the organic resins are limited by breakdown in aqueous systems at high temperatures and in presence of high ionizing radiation doses; for these reasons there had been a resurgence of interest in inorganic exchangers in the 1950s. One of the possible ways of solving these problems involved replacing the organic skeleton of the ion-exchanger by an inorganic skeleton. Pioneering work was carried out in this field by the research team at the Oak Ridge National University led by Kraus, and by the English team led by Amphlett.

Further extensive research and study of inorganic ion-exchange sorbents were carried out in the 1960s and 1980s from the original amorphous type of ion-exchange sorbents to the study of crystalline ion-exchange materials. Clearfield and co-workers
made great contributions in this area. Since last two decades, intense research has continued on the synthesis of a number of new ‘organic-inorganic’ composite materials having excellent properties that not only met the requirements of modern laboratories but also led to solution of previously insolvable problems. An interest of inorganic as well as composite ion-exchange materials in ion-exchange operations in industries is increasing day by day as their field of applications is expanding.

1.5.2. Ion-exchange process and its mechanism

The ion-exchange process became established as an analytical tool in laboratories and in industries, as it was studied chiefly by practical chemists interested in effects and performance etc. The primary condition of an ion-exchange process is the stoichiometry. In organic resins, it is an established fact [102]. The exchange of ion takes place stoichiometrically, really by the effective exchange of ions between two immiscible phases, stationary and mobile. A typical ion-exchange reaction may be represented as follows:

\[
\overline{AX} + B(aq) \rightleftharpoons \overline{BX} + A(aq) \]

where A and B (taking part in ion-exchange) are the replaceable ions, and X is the structural unit (matrix) of the ion-exchanger. Bar indicates the exchanger phase and (aq) represents the aqueous phase.

In order to describe equilibria and to understand the mechanism of an ion-exchange process occurring on the surface of exchanger and to evaluate its theoretical behavior, it is important to have a study of its kinetics and thermodynamics. Since inorganic ion-exchangers possess a rigid matrix they do not
swell appreciably and hence such studies are simpler to perform on them as compared to the organic resins that swell appreciably. Ion-exchange equilibrium may be described by two theoretical approaches viz. (i) Based on law of mass action, and (ii) Based on Donnan theory.

From the theoretical point of view the Donnan theory has an advantage of permitting a more elegant interpretation of thermodynamic behavior in an ion-exchanger. Probably, the first time, quantitative formation of ion-exchange equilibria was made by Gane [103] using the mass action law in its simplest form without involving the concept of activity coefficients. This concept was further accounted by Kielland [104] and finally, a suitable choice of general treatment was given by Gaines and Thomas [105]. Many workers have studied the thermodynamics of cation-exchange on zirconium(IV) phosphate [106-109]. In a series of papers, the effect of crystallinity on the thermodynamics of ion-exchange of alkali metal ions/H+ ions on the samples of α-zirconium phosphate was examined. Ion-exchange isotherms and calorimetric heats of exchange were determined on samples varying from amorphous to highly crystalline [110-114].

However, from the practical point of view, the mass action approach is simpler. Nancollas and coworkers [115,116] have interpreted the thermodynamical functions in term of the binding nature between alkali metals and the ion exchange matrix. The ion-exchange equilibria of Li(I), Na(I) and K(I) on zirconium(IV) phosphate have also been studied by Larsen and Vissers [117], who calculated the equilibrium constants and other thermodynamical parameters viz. ΔG°, ΔH° and ΔS°.
Similar studies have been made on anion-exchangers also [118]. Ion-exchange equilibria of alkaline earth metal ions on different inorganic ion-exchangers such as tantalum arsenate [119], iron(III) antimonate [120], antimony(V) silicate [121,122], zirconium(IV) phosphosilicate [123,124] and alkali metal ions on iron(III) antimonate [125] and α-cerium phosphate [126] were studied. Other interesting thermodynamic studies relate to the adsorption of pesticides on inorganic and composite ion-exchangers have also been studied in these laboratories [127,128]. The study has revealed that the adsorption is higher at lower temperature and the presence of an ion-exchange material in soil greatly enhances its adsorption capability for the pesticides. Nachod and Wood [129] have made the first and detailed attempt on kinetic studies of ion-exchange. They have studied the reaction rate with which ions from solutions are removed by a solid ion-exchanger or conversely the rate with which the exchangeable ions are released from the exchanger. Later on Boyd et al. [130] have studied the kinetics of metal ions upon the resin beads and have given a clear understanding about the particle and film diffusion phenomenon that govern the ion-exchange processes. The former is valid at higher concentrations while the later at lower concentrations. The kinetic of metal ions on sulphonated polystyrene has been studied by Reichenberg who again confirmed that at high concentrations the rate is independent of the ingoing ion (particle diffusion); while at low concentrations the reverse is true (film diffusion).
1.5.3. Ion-exchange materials: An introduction and literature review

1.5.3.1. Inorganic ion-exchange materials

1.5.3.1.1. Natural inorganic ion-exchangers

Many natural mineral compounds, such as clays (e.g. bentonite, kaolinite and illite), vermiculite and zeolites (e.g. analcite, chabazite, sodalite and clinoptilolite), exhibit ion-exchange properties. Natural zeolites were the first materials to be used in ion-exchange processes. Clay minerals are often employed as backfill or buffer materials for the radioactive waste disposal sites because of their ion-exchange properties, low permeability and easy workability. Clay can also be used in batch ion-exchange processes but are not generally suited to column operation because their physical properties restricts the flow through the bed. In 1985 British Nuclear Fuels Plant (BNFP), successfully commissioned the Site Ion Exchange Effluent Plant (SIXEP), which use naturally occurring clinoptilolite to remove cesium and strontium from fuel cooling pond water [131]. Other natural aluminosilicate materials, such as green sand, are also used in some waste treatment applications, generally in column or large deep bed designs. In this capacity they can be used as a combination of an ion-exchanger and particulate filler. Clay minerals and natural zeolites, although replaced by synthetics to a large extent, continue to be used in some applications, owing to their low cost and wide availability.

The main disadvantages of natural inorganic ion-exchangers are:

- Their relatively low exchange capacities;
- Their relatively low abrasion resistance and mechanical durability;
• Their non-controllable pore size;
• That clay minerals tend to peptize (i.e. convert to a colloidal form);
• That zeolites are difficult to size mechanically;
• That they can be partially decomposed in acids or alkalis;
• That, owing to their limited chemical stability in many solutions, especially those with a very low salt content, they sometimes need a chemical or thermal pretreatment;

1.5.3.1.2. Synthetic inorganic ion-exchangers

Synthetic ion-exchangers are produced by creating chemical compounds with the desired physical and chemical properties. On the basis of chemical characteristics synthetic inorganic ion-exchangers are classified as follows:

➢ Synthetic zeolites (aluminosilicates)
➢ Hydrous oxides of metals
➢ Acidic salts of polyvalent metals
➢ Insoluble salts of heteropolyacids
➢ Insoluble hydrated metal hexacyanoferrate (II) and (III) (ferrocyanides)
➢ Other substances with weak exchange properties

Zeolites were the first inorganic materials to be used for the large-scale removal of waste effluents. Zeolites are crystalline alumino-silicate based materials and can be prepared as microcrystalline powders, pellets or beads. The main advantages of synthetic zeolites when compared with naturally occurring zeolites are
that they can be engineered with a wide variety of chemical properties and pore sizes, and that they are stable at higher temperatures.

The main limitations of synthetic zeolites are that:

- They have a relatively high cost compared with natural zeolites;
- They have a limited chemical stability at extreme pH ranges (either high or low);
- Their ion specificity is susceptible to interference from similar sized ions;
- The materials tend to be brittle, which limits their mechanical stability;

The selectivity and capacity of zeolites can provide a satisfactory processing of low strength salt solutions. The actual processing capacities obtained with zeolites are lower than their maximum capacities since the bed is changed at the early stages of breakthrough and because the waste streams usually contain other ions that will occupy some of the exchange sites and therefore reduce the processing capacity. Synthetic silica based ion-exchangers were produced for technical purpose by fusing soda, potassium carbonate, feldspar and kaolinite (Schmaltz permutite) and later from aluminum sulfate solution containing sodium silicate by precipitation with sodium hydroxide solution (Gel permutite). Since then artificial crystalline zeolites have also been successfully synthesized. The advantageous properties of the crystalline silicate based ion-exchanger with the modern synthetic resin based ion-exchangers are as follows: they are less sensitive to higher temperatures, their structure are stiff and uniform and they are therefore more selective and suitable for separation of ions on the basis of their different sizes. Because of this, some of them are now also used as
ionic or molecular sieves. In India a systematic investigation has been carried out to evaluate the performance of locally available synthetic zeolites for the removal of cesium, strontium and thorium from solution [132-134]. The zeolites, after exchange with cesium, strontium or thorium, were thermally treated to fix the ions successfully in the same matrix [135]. A locally available synthetic mordenite was used recently in a campaign to reduce activity in spent fuel storage pool water [136].

**Hydrous oxides** are of particular interest because most of them can function both cation and anion-exchangers, and at certain conditions, as amphoteric exchangers. Their dissociation may be schematically represented as follows:

![Chemical equations]

\[
\begin{align*}
M - OH & \rightarrow M^+ + OH^- \\
M - OH & \rightarrow M - O^- + H^+
\end{align*}
\]

(M represents the central atom)

Scheme '1.2' is favored by acid conditions when the substance can function as anion-exchanger, and scheme '1.3' by alkaline conditions, when the substance can function as cation-exchanger. Near the isoelectric point [137], dissociation according to both schemes can take place and both type of exchange may occur simultaneously. The hydrous oxides may be divided into two main types termed particle hydrates and framework hydrates [138]. Particle hydrates are both cation and anion-exchangers. Most of the group 3,4,13, and 14 metals form hydrous oxides that belong to this group. Metals in groups 5 and 15 in their higher oxidation states generally form framework hydrates. The pyrochlore nature (Fig. 1.13) of crystalline hydrous antimony(V) oxide exchanger was revealed by powder X-ray diffraction, which was
Fig. 1.13. Schematic diagram of the pyrochlore framework formed by antimonic acid, \((\text{H}_3\text{O}^+)\text{Sb}_2\text{O}_6\) showing the formation of a hexagonal shaped tunnel. Exchangeable \(\text{H}_3\text{O}^+\) ions reside within the tunnels.
established the composition as \((\text{H}_3\text{O})_2\text{Sb}_2\text{O}_6 \cdot x\text{H}_2\text{O}\) [138]. While the mixed metal oxide of the pyrochlore structure are also being obtained [139] as shown in Fig. 1.14. As a consequence cation-exchange selectivities are affected and metal ion uptake can be increased [140-142]. Layered double hydroxides (LDHs) (Fig. 1.15) constitute an interesting and extensive class of layered compounds [143]. An excellent review on LDHs has been published by deRoy et al. [144].

**Acidic salts of multivalent metals** form by mixing the solutions of the salts of III and IV group elements of the periodic table with the more acidic salts. These salts, acting generally as cation-exchangers, are gel like or microcrystalline materials and possess mostly a high chemical, thermal and radiation stability.

**Salts of heteropolyacids** have a general formula \(\text{H}_m\text{X.Y}_1\text{O}_{40}. n\text{H}_2\text{O}\), where \(m = 3, 4 \text{ or } 5\), \(\text{X can be phosphorous, arsenic, silicon, germanium or boron and Y, one of the elements such as molybdenum, tungsten or vanadium. The salts of heteropolyacids with small cations are more soluble in comparison to the salts with large cations. Their hydrolytic degradation occurs in strongly alkaline solutions.**

**Insoluble ferrocyanides** can be precipitated by mixing the metal salt solutions with \(\text{H}_4[\text{Fe(CN)}_6]\), \(\text{Na}_4[\text{Fe(CN)}_6]\), or \(\text{K}_4[\text{Fe(CN)}_6]\) solutions. The composition of such precipitates may depend on the acidity, order of mixing and the initial ratio of the reacting components. They are chemically stable in acid solutions up to a concentration of 2 M. Cu and Co ferrocyanides have been found to be radiation resistant. They have found various applications in analytical chemistry and in technological practice because of their highly selective ion-exchange behavior and
Fig. 1.14. Structure of Ti-antimonate (pyrochlore) viewed along the edge of the cubic unit cell. Structure refinement carried out using powder XRD and Rietveld method with GSAS program suite. Large red spheres: O. Small green spheres: Ti or Sb.

LDHs

Fig. 1.15. Schematic representation of a layered double hydroxide (LDH). (A) Top view of brucite layer. (B) Side view showing anions between the brucite like layers.

General Formula: \((M^{x+})_x(M^{y+})(OH)_{2(x-y)}(A^{z-})_{1+1.7}yH_2O\)
chemical and mechanical stability. In India potassium cobalt(II)–hexacyanoferrate(II) has emerged as a promising inorganic sorbent that can be prepared in a column-useable granular form that needs no resin support. A 5 L column of sorbent was recently used to reduce the $^{137}\text{Cs}$ activity in 12,000 L of ion-exchange regeneration waste from $3.7 \times 10^4$ Bq/mL to 3.7 Bq/mL. The sorbent was also found suitable for removing $^{137}\text{Cs}$ from alkaline reprocessing waste containing a high concentration of sodium salts [145].

There is now enormous literature available to the ion-exchanger practitioner on the use of inorganic ion-exchangers. The literature review shows the materials used as inorganic ion-exchangers have become an established class of materials of great analytical importance. The first monograph that is also of historical importance was written by C.B. Amphlett in 1964 [146], one of the first research workers in the development of modern inorganic sorbents who described the beginning of the rapid development of this subject. Barrer wrote an excellent monograph on contemporary zeolite and clay minerals. In the 1980s, the monograph of the Clearfield et al. made a great contribution to the understanding of the structure and mechanism of sorption processes on the acidic salts of multivalent metals and hydrous oxides [147].

Insoluble polybasic acid salts of polyvalent metals have shown a great promise in preparative reproducibility, ion-exchange behavior, and both chemical and thermal behavior. Many metals such as aluminium, antimony, bismuth, cerium, cobalt, iron, lead, niobium, tin, tantalum, titanium, thorium, tungsten, uranium and zirconium have been used for the preparation of ion-exchange materials. Also a large
number of anionic species such as phosphates, tungstate, molybdate, arsenate, antimonate, silicate, telluride, ferrocyanide, vanadate, arsenophosphate, arsenotungstate, arsenomolybdate, arsenosilicate, arsenovanadate, phosphotungstate, phosphomolybdate, phosphosilicate, phosphovanadate, molybdosilicate and vanadosilicate etc. have been used to prepare inorganic ion-exchangers. The majority of works carried out on zirconium, titanium, tin, niobium and tantalum. The literature survey reveals that a good volume of work has been carried out on single as well as three components (salts of heteropolyacids) inorganic ion-exchangers of both amorphous and crystalline nature. Inorganic ion-exchangers of double salts, based on tetravalent metal acid (TMA) salts often exhibit much better ion-exchange behavior as compared with single salts [147]. A comprehensive literature survey of various inorganic ion-exchange materials based on Tin(IV) and Th(V) prepared so far and their salient features [148-216] with their selectivities are summarized in Table 1.1. Varshney and Khan have published their findings on arsenophosphate [172], arsenosilicate [188], hexacyanoferrate(II) [197] of tin(IV), amine and silica based tin(IV) hexacyanoferrate(II) [197,198] and arsenophosphate [217], silicate and phosphate [218] of antimony(V) cation-exchangers. Different phases of these ion-exchangers have been found selective for $K^+$, $Cd^{2+}$, $Zr^{4+}$ and $Th^{4+}$ and some kinetic and thermodynamic parameters for $M^{2+}$-$H^+$exchanges have also been investigated on these cation-exchangers [219-225].
Table 1.1
List of various inorganic ion-exchange materials based on Tin(IV) and Th(V) prepared so far and their salient features

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Material</th>
<th>Nature</th>
<th>Composition</th>
<th>Empirical formula</th>
<th>Selectivity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Stannic phosphate</td>
<td>Amorphous</td>
<td>P:Sn = 1.25 - 1.50</td>
<td>SnO₂, 0.62P₂O₅, nH₂O</td>
<td>Na(I), Li(I), K(I), Rb(I), Cs(I), Cu(II), Zn(II), Ni(II), Co(II)</td>
<td>[148]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Crystalline</td>
<td></td>
<td>Zr(IV)</td>
<td>[150, 151]</td>
</tr>
<tr>
<td>2</td>
<td>Stannic tungstophosphate</td>
<td>---</td>
<td>Sn:W:P = 2:1:3.2</td>
<td></td>
<td>---</td>
<td>[152]</td>
</tr>
<tr>
<td>3</td>
<td>Stannic EDTA</td>
<td>Amorphous</td>
<td></td>
<td></td>
<td>---</td>
<td>[153]</td>
</tr>
<tr>
<td>4</td>
<td>Stannic molybdophosphate</td>
<td>---</td>
<td>Sn:Mo:P = 1:0.33:2.0</td>
<td></td>
<td>---</td>
<td>[154]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Semi-crystalline</td>
<td>Sn:Mo:P = 40:26.5:0.7</td>
<td></td>
<td>Cs⁺, Sr²⁺</td>
<td>[155]</td>
</tr>
<tr>
<td>5</td>
<td>Tin oxide (hydrated)</td>
<td>Amorphous</td>
<td>Sn/As = 1.84</td>
<td>---</td>
<td>[Fe(CN)₆]³⁻, [Fe(CN)₆]⁴⁻ - SCN⁻</td>
<td>[156]</td>
</tr>
<tr>
<td>6</td>
<td>Stannic arsenate</td>
<td>Amorphous</td>
<td></td>
<td></td>
<td>Pb(II), Fe(III), Al(III), In(III)</td>
<td>[157]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Crystalline</td>
<td>SnO₂, As₂O₅, 2H₂O</td>
<td>Li(I), Na(I), K(I)</td>
<td></td>
<td>[159]</td>
</tr>
<tr>
<td>7</td>
<td>Stannic antimonate</td>
<td>Amorphous</td>
<td>Sb/Sn = 1.0</td>
<td>SnO₂, Sb₂O₅, nH₂O</td>
<td>Cu(II), Ni(II), Co(II)</td>
<td>[160, 161]</td>
</tr>
<tr>
<td>8</td>
<td>Stannic molybdate</td>
<td>Amorphous</td>
<td>Sn/Mo = 1.0</td>
<td></td>
<td>Pb(II)</td>
<td>[162]</td>
</tr>
<tr>
<td>9</td>
<td>Stannic selenite</td>
<td>Amorphous</td>
<td>Sn/Se = 1.33, Sn/Sc = 1.0</td>
<td>[(SnO₄)(OH)₂] (ScO₃)₃, 6H₂O</td>
<td>Li(I), Na(I), K(I), Cu(II), Fe(III), Sc(III), La(III)</td>
<td>[163]</td>
</tr>
<tr>
<td>No.</td>
<td>Compound</td>
<td>Structure</td>
<td>Composition</td>
<td>References</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
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<td>----------------------------</td>
<td>------------------------------------------</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Stannic tungstate</td>
<td>Amorphous</td>
<td>Sn/W = 1.33</td>
<td>[1164]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Stannic vanadate</td>
<td>Amorphous</td>
<td>Sn/V = 1.0</td>
<td>[165]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Stannic vanado pyrophosphate</td>
<td>Micro-crystalline</td>
<td>---</td>
<td>[166]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Stannic ferrocyanide</td>
<td>Amorphous</td>
<td>Sn/Fe = 3.0</td>
<td>[167]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Stannic silicate</td>
<td>---</td>
<td>---</td>
<td>[168]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Stannic hexametaphosphate</td>
<td>---</td>
<td>---</td>
<td>[169]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Stannous ferrocyanide</td>
<td>Amorphous</td>
<td>Sn/Fe = 1.0</td>
<td>[170,171]</td>
<td></td>
<td></td>
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<td>17</td>
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<td>Sn:As:P 1:1:1</td>
<td>[172,173]</td>
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<td>Sn:Mo:As 2:1:1</td>
<td>[174]</td>
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<td>Stannic pyrophosphate</td>
<td>Amorphous</td>
<td>Sn:PO₄³⁻ 1:2</td>
<td>[175]</td>
<td></td>
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<td>20</td>
<td>Stannic sulfide</td>
<td>Amorphous</td>
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<td>[176]</td>
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<td>Stannic phosphosilicate</td>
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<td>Sn:Si:P 2:2:3</td>
<td>[177]</td>
<td></td>
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<td>Stannic pyroantimonate</td>
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<td>---</td>
<td>[178]</td>
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<td></td>
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<tr>
<td>23</td>
<td>Stannic selenophosphate</td>
<td>Amorphous</td>
<td>Sn:Se:P 1:1:1</td>
<td>[179]</td>
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<td></td>
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</table>

References:

[1164], [165], [166], [167], [168], [169], [170,171], [172,173], [174], [175], [176], [177], [178], [179], [180]
<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>State</th>
<th>Composition</th>
<th>Formula</th>
<th>Complexes</th>
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<td>Stannic selenopyrophosphate</td>
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<td>Sn:Se:PO$_4$$^{3-}$ 1:1:1</td>
<td>O$<em>4$)$</em>{6n}$. 4H$_2$O (15SnO.8OH) (10H$_2$P$_2$O$_7$.O$_2$ HSeO$_3$). 5n H$_2$O</td>
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<td>Amorphous</td>
<td>Sn:W:As 12:5:2</td>
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<td>Ba(II), Cu(II)</td>
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<td>Amorphous</td>
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<td>---</td>
<td>Pb(II), Ce(III), Sm(III)</td>
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<td></td>
<td></td>
<td>Crystalline</td>
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<td>Pb(II), Sm(III), La(III) Ba(II)</td>
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<td>[(SnO$_2$)$_7$.HSeO$_3$ (HWO$<em>4$)$</em>{18}$.45H$_2$O]</td>
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<td>---</td>
<td>---</td>
<td>Ba(II), Cu(II)</td>
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<td>Stannic vanadotungstate</td>
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<td>Sn:V:W 2:1:1</td>
<td>---</td>
<td>Al(III)</td>
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<td>32</td>
<td>Stannic arsenosilicate</td>
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<tr>
<td>33</td>
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<td>Sn:Sb = 2 :11</td>
<td>Sn$_2$[Sb (OH)$<em>6$]$</em>{11}$.8H$_2$O</td>
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<td>Tin(IV) sulphosilicate</td>
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<td>Stannic hexacyanoferrate(III)</td>
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<td>38</td>
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<td>Crystalline</td>
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<tr>
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<td>---</td>
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<td>Hg (II)</td>
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<td>[199]</td>
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<tr>
<td>42</td>
<td>Amorphous based stannic hexacyanoferrate(II)</td>
<td>Crystalline</td>
<td>Sn:Fe:Si 5:4:2</td>
<td>---</td>
<td>[199]</td>
</tr>
<tr>
<td>43</td>
<td>Stannic silicoborate</td>
<td>Sn:Si= 1:1</td>
<td>Na₂(SnO₂)ₓ (SnO₂)ᵧ · zH₂O</td>
<td>Ag(I)</td>
<td>[201]</td>
</tr>
<tr>
<td>44</td>
<td>Sodium stannosilicate</td>
<td>Sn:V:P= 3:3:10</td>
<td>---</td>
<td>---</td>
<td>[202]</td>
</tr>
</tbody>
</table>

**(II) Thorium based exchangers**

<p>| | | | | | |
|  | | | | | |
|---|---|---|---|---|
| 1 | Thorium phosphate | Amorphous | P'/Th = 1.9-2.1 | Pb(II), Fe(III), Bi(III) | [203] |
| 2 | Thorium arsenate | Crystalline | Th/PO₄ = 0.50 | Th (HPO₄)₂ · 2H₂O | Ca(II), Sr(II), Ba(II) | [204] |
| 3 | Thorium antimonate | Amorphous | Sb:Th = 3.67-4.27 | ThO₂.P₂O₅ · 2H₂O | Li (I) | [205,206] |
| 4 | Thorium | Crystalline | Pb(II), Fe(III), Bi(III) | Fe(III) | [208] |</p>
<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystallographic Form</th>
<th>Composition</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>molybdate</td>
<td>Amorphous</td>
<td>Th / Mo = 0.50</td>
<td>[209]</td>
</tr>
<tr>
<td>Thorium Tungstate</td>
<td>Crystalline</td>
<td>Th/W = 2.0</td>
<td>[210]</td>
</tr>
<tr>
<td></td>
<td>Granular</td>
<td>Th(OH)₂ (HO₄₂₇nH₂O)</td>
<td>[211]</td>
</tr>
<tr>
<td></td>
<td>Amorphous</td>
<td></td>
<td>Bi(III), Hg(II) [212]</td>
</tr>
<tr>
<td>Thorium oxide</td>
<td>Amorphous</td>
<td>Th(OH)n nH₂O</td>
<td>Na(I), Rb(I), Ca(II), Sr(II) [213]</td>
</tr>
<tr>
<td>Thorium tellurite</td>
<td></td>
<td>Th:Te = 1:2</td>
<td>Pb(II), Co(II), Cu(II) [214]</td>
</tr>
<tr>
<td>Thorium phosphosilicate</td>
<td>Amorphous</td>
<td>Th:P:Si = 1:1.2 8:1.12 (ThO₂₂H₃PO₄ H₄SiO₄) 6H₂O</td>
<td>Hg²⁺ [215]</td>
</tr>
<tr>
<td>Thorium iodate</td>
<td></td>
<td>Th:I = 1:1</td>
<td>ThO₂₂I₂O₅nH₂O [216]</td>
</tr>
</tbody>
</table>
1.5.3.2. Organic Ion-exchange Materials

1.5.3.2.1. Natural organic ion-exchangers

A large number of organic materials exhibit ion-exchange properties; these include polysaccharides (such as cellulose, algic acid, straw and peat), proteins (such as casein, keratin and collagen) and carbonaceous materials (such as charcoals, lignites and coals). Of these, only charcoals, coal, lignite and peat are used commercially. Although they exhibit a very low ion-exchange capacity compared with synthetics, they are widely available at a very low cost. They are normally used as general sorbents, with their ion-exchange properties being a secondary consideration. Commercially available materials are often treated or stabilized with other additives to improve their uniformity or stability. Some materials, such as charcoals, can be doped with chemicals to improve their capacity or selectivity.

The main limitations of natural organic ion-exchangers are:

- Their low exchange capacity compared with other materials,
- Their excessive swelling and tendency to peptize,
- There is very limited radiation stability of cellulosic and protein materials,
- Their weak physical structures,
- Their non-uniform physical properties,
- That they are non-selective,
- That they are unstable outside a moderately neutral pH range,

1.5.3.2.2. Modified natural organic ion-exchangers

To improve exchange capacity and selectivity, some naturally occurring organic ion-exchangers are modified; for example, cellulose based cation-exchangers
may be modified by the introduction of phosphate, carbonic or other acidic functional
groups. The sorption parameters of natural materials can be modified by a chemical
and/or thermal treatment; for example, by treating clinoptilolite with a dilute solution
of acids or some salts, a more selective form of sorbent can be developed for a
particular radionuclide [226].

1.5.3.2.3. Synthetic organic ion-exchangers

The largest groups of ion-exchangers available today are synthetic organic resins
in a powdered (5–150 μm) or bead (0.5–2 mm diameter) form. The framework, or
matrix, of the resins is a flexible random network of hydrocarbon chains. This matrix
carries the ionic groups such as: -SO₃⁻, -COO⁻, -PO₃²⁻, -AsO₃²⁻ etc. in cation-
exchangers, and -NH₃⁺, -NH₂⁺, -N⁺, -S⁺ etc. in anion-exchangers. Ion-exchange
resins thus are cross-linked polyelectrolytes. The resins are made insoluble by cross-
linking the various hydrocarbon chains. The degree of cross-linking determines the
mesh width of the matrix, swelling ability, movement of mobile ions, hardness and
mechanical durability. Highly cross-linked resins are harder, more resistant to
mechanical degradation, less porous and swell less in solvents. When an organic-ion
exchanger is placed in a solvent or solution it will expand or swell. The degree of
swelling depends both on the characteristics of the solution/solvent and the
exchanger itself and is influenced by a number of conditions, such as:

- The solvent’s polarity,
- The degree of cross-linking,
- The exchange capacity,
- A strong or weak solvation tendency of the fixed ionic groups,
- The size and extent of the solvation of counter ions,
- The concentration of the external solution,
- The extent of the ionic dissociation of functional groups,

The main advantages of synthetic organic ion-exchange resins are their high capacity, wide applicability, wide versatility and low cost relative to some synthetic inorganic media. The main limitations are their limited radiation and thermal stabilities. At a total absorbed radiation dose of $10^9$ to $10^{10}$ rads most organic resins will exhibit a severe reduction in their ion exchange capacity (a 10 to 100% capacity loss), owing to physical degradation at both the molecular and macroscopic level. Cation-exchange resins are generally limited to operational temperatures below about 150 °C, while anion-exchange resins are usually limited to less than 70 °C. This requires that some streams, such as reactor coolant water, be precooled substantially before their introduction to the ion-exchange media. A general comparison of organic and inorganic ion-exchanger is given in Table 1.2.

1.5.3.3. Chelating ion-exchange materials

The use of ligand or complexing agent in solution in order to enhance the efficiency of separation of cation mixtures (e.g. lanthanide) using conventional cation or anion-exchange resins is well established. An alternative mode of application of complex formation is, however, the use of chelating resins that are ion-exchangers in which various chelating groups (e.g. dimethylglyoxime, iminoacetic acid etc.) have been incorporated and are attached to the resin matrix. Thus, a chelating ion-exchange resin consists of essentially of two components, i.e., a chelating group and
### Table 1.2
General comparison of organic and inorganic ion-exchangers

<table>
<thead>
<tr>
<th>Properties</th>
<th>Organic exchangers</th>
<th>Inorganic exchangers</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal stability</td>
<td>Fair to poor</td>
<td>Good</td>
<td>Inorganics are especially good for long term stability</td>
</tr>
<tr>
<td>Chemical stability</td>
<td>Good</td>
<td>Fair to good</td>
<td>Specific organics and inorganics are available for any given pH range</td>
</tr>
<tr>
<td>Radiation stability</td>
<td>Fair to poor</td>
<td>Good</td>
<td>Organics are very poor in combination with high temperatures and oxygen</td>
</tr>
<tr>
<td>Exchange capacity</td>
<td>High</td>
<td>Low to high</td>
<td>The exchange capacity will be a function of the nature of the ion being removed, its chemical environment and the experimental conditions</td>
</tr>
</tbody>
</table>
| Selectivity         | Available          | Available            | For some applications, such as cesium removal, inorganics can be much better than organics, owing to their greater selectivity. 
Ion selective media are available in both organic and inorganic forms |
| Regeneration        | Good               | Uncertain            | Most inorganics are sorption based, which limits regeneration                                                                               |
| Mechanical strength | Good               | Variable             | Inorganics may be brittle or soft or may break down outside a limited pH range                                                              |
| Cost                | Medium to high     | Low to high          | The more common inorganics are less costly than organics                                                                                    |
| Availability        | Good               | Good                 | Both types are available from a number of commercial sources                                                                               |
| Immobilization      | Good               | Good                 | Inorganics can be converted to equivalent mineral structures, organics can be immobilized in a variety of matrices or can be incinerated   |
| Handling            | Good               | Fair                 | Organics are generally tough spheres, inorganics may be brittle; angular particles are more friable                                          |
| Ease of use         | Good               | Good                 | If available in a granulated form both types are easy to use in batch or column applications                                               |
a polymeric matrix. Therefore, the properties of both components have to be taken into account when designing and synthesizing a chelating ion-exchange resin. Several workers postulated criteria for a compound to act as a selective chelating ion exchanger. These are summarized as:

1. The chelating ligand attached to a solid matrix should possess strong binding properties and selectivity towards certain metal ions.
2. The chelating group should be capable of undergoing incorporation in a polymeric matrix and allow the process of polymerization or resinfication; in turn, the chelating polymer should be resistant to strong acids and alkalies at elevated temperature.
3. The chelating ligand should preferably be multidentate, permitting formation of a 1:1 or 1:2 chelate with a metal ion.
4. The chelating ion-exchanger should possess good swelling properties and compatibility between the polymer and the medium (generally aqueous) is essential; this can be regulated by the presence of hydrophilic groups on the polymer and by the extent of cross-linking.
5. Both arms of a chelate structure should be present on the monomer unit in proper special configuration.
6. The chelating agent must possess sufficient stability, so that the functional structure is not changed by polymerization during the synthesis of the resin.
7. It should be capable to substitution into a polymeric matrix and should be compact enough so that its chelating ability is not hindered by the dense polymeric matrix.
A chelating resin with desired selectivity can be prepared by applying these conditions. According to these conventional approaches chelating ion-exchangers have been extensively studied and modified synthetic materials such as cellulose [227,228], polystyrene [229], divinylbenzene [230], hydrazine-modified polyacrylonitrile [231], modified agricultural residues [232] and starch [233] have been also been demonstrated as efficient chelating adsorbents for heavy metal removal. Recently, Orlando et al. [234] have prepared modified chelating ion exchangers from bagasse (BC) by microwave radiation through reaction with reagents that contain chelating functional groups, such as thiourea, urea, melamine, polyethyleneimine, ethylenediamine, diethylenetriamine, iminodiacetic acid and glycine, and their resultant performance in removing mercury(II) from aqueous solution.

Chelating resins containing aminophosphonate [235], dithiocarbamate [236], hexylthioglycolate [237], iminodiacetate [238], isothiouronium [239], poly (ethylenemercaptoacetamide) [240], thioacetamide [241], thiol [242,243] and thiosemicarbazide [244] are also generally employed for heavy metal sorption. Examples of various chelating groups and their application for selective preconcentration of inorganic elements have been reviewed by Kantipuly et al. [245]. Diphonix resin containing both sulphonic and gem-diphosphonic acid groups exhibited a high affinity for extraction of actinide ions [246-248]. The removal of uranium, cadmium and chromium from phosphoric acid solutions using chelating resins has been reported by Kabay et al. [249,250]. Ion-exchange and chelating resins
were the subject of many reviews [251-253]. Among various types of ion-exchangers with acidic ligands those having phosphonate functionality are of particular interest since they are selective towards heavy metal cations [254-256]. Development of this type of ion-exchangers started in the late 1940s [257] with phosphorylation of poly(vinyl alcohol) using various phosphorylating agents. Next, were reports on introducing phosphonic [258] and phosphinic [259] functionality to styrene/divinylbenzene and to its chloromethyl derivative. This type of modification was also presented in ref. [260], where more attention was paid to the type of polymeric matrix and in ref. [261,262], where ion-exchange/complexing properties of phosphinic and phosphonic resins in the form of acid, monoester and diester were presented. Other types of phosphonic functionality immobilized on insoluble polymeric matrices include methylenediphosphonate [263] and ethylenediphosphonate carboxyethyl phosphonate [264] immobilized on vinylbenzyl chloride/divinylbenzene copolymers. The latter one contained also a carboxylate group as part of the ligand and the same situation pertained in the case of 1,1-dicarboxylate-2-ethanephosphonate and 1,1-diphosphonate-2-ethanecarboxylate immobilized on vinylbenzyl chloride/styrene/divinylbenzene copolymer [265]. In all cases resins displayed good selectivity towards multifunctional cations. The resin with phosphonate groups in the geminal position retained its ion-exchange/coordinating properties even at very low pH [263], whereas ethylenediphosphonate and carboxyl containing resins, being less acidic, more selective at pH 1–2. α-zirconium phosphonates chelating legand with
phosphonatomethyliminodiacetic acid was studied for the structure by Poojary et al. [266]. The arrangement of ZrO₆ as octahedra, PO₄ and PO₃ moieties as tetrahedra and the N(CH₂CO₂H)₂ group is given in Fig. 1.16. These types of chelating ion-exchangers have been developed recently and their analytical applications explored [267]. Complexions have been used for the preparation of new chelating resins for separating metal ions on the basis of complex formation [268]. A number of such ion-exchangers have been prepared by the incorporation of ligands on resins [269]. 8-hydroxy quinoline [270] sorbed on porasil is capable of separating metal ions at trace level. Eriochrome black–T modified graphite columns have been used for the separation of metal ions [271]. A PAN [1-(2-pyridylazo-2-napthol)] sorbed zinc silicate [272] has been used for the recovery of precious metal ions Pt⁴⁺ and Au³⁺, and ammonium-molybdophosphate [273], have been used for the quantitative separation of Cs⁺ ions. Separation and retention behavior of metal ions have been achieved on tetracycline hydrochloride coated alumina [274] and zirconium(IV) selenomolybdate [275], while tetracycline hydrochloride sorbed zirconium(IV) tungstophosphate chelating exchanger has been employed in the separation of La³⁺ ions [276]. D.K. Singh et al. [277] has been prepared zinc silicate bonded diethylthiocarbamate for the separation and preconcentration of some transition metal ions. A.C.S. Costa et al. [278] have developed a procedure for separation and preconcentration of cadmium, copper, lead and zinc by solid-liquid extraction of their cocrystalized naphthalene dithizone chelate in saline matrices. An important feature of chelating ion-exchangers is the greater selectivity, which they offer compared with
Fig. 1.16. Projection of the structure down the b axis showing the layer arrangement.

The sketch depicts ZrO$_6$ as octahedral PO$_4$ and PO$_3$ moieties as tetrahedral
and the N(CH$_2$CO$_2$H)$_2$ group and the hydrogen bonding (---).
the conventional type of ion-exchanger. The affinity of a particular metal ion for a certain chelating resin depends mainly on the nature of the chelating group. And the selectivity behavior of the resin is largely based on the different stabilities of the metal complexes formed on the resin under the various pH conditions.

1.5.3.4. Intercalation ion-exchangers

After the development of various types of inorganic ion-exchange materials, lately much interest has been developed in the study of pillared inorganic materials and intercalation compounds (new porous intercalates) that can be synthesized by introducing some organic molecules in the matrix of layered inorganic ion-exchangers (Fig. 1.17). However, the intercalating properties were first discovered in 1965 by Michel and Weiss [279,280]. Upto 1975 no paper was published on this subject, after that, the intercalation behavior of layered insoluble acid salts of tetravalent metals was written by Lagaly et al. [281]. The main advantage of a pillared structure is that it allows ready access of large ions and complexes to the interior due to the increase in the inter layer distances and pore sizes as shown in Fig. 1.18. This is very useful in radioactive waste cleanup. Amongst the new developments of ion exchangers, intercalation compounds have played an important role in the field of separation science and technology. These compounds can be synthesized by introducing some organic ions or molecules in the matrix of inorganic ion exchangers. Alumina, kaolin, clays, bentonite, pectin, alginic acid etc. have been used as adsorbent with stimulated considerable interest in medical science throughout world. Hence, intercalation is a process in which neutral polar molecules are inserted
Fig. 1.17. Intercalation compounds (A) Long chain amine intercalate of a metal disulfide (B) Cobaltocene intercalated in TaS₂.

Fig. 1.18. Schematic illustration of the intercalation of polar molecules.
between the sheets of a layered insoluble compound (Fig. 1.19). Layered inorganic ion-exchangers with a non rigid structure such as the acid phosphates of tetravalent metals $\text{Me(IV)(HPO}_4\text{)}_2\cdot n\text{H}_2\text{O}$; Me = Zr, Ti, Sn; $n=1,\ldots$ are able to exchange transition metal ions [282] and to intercalate organic molecules [283]. Each layer consists of tetravalent atoms sandwiched between tetrahedral phosphate or arsenate group [284-288]. The gamma phases of zirconium phosphate, $\gamma$-$\text{Zr(PO}_4\text{)(H}_2\text{PO}_4\text{)}\cdot 2\text{H}_2\text{O}$, ($\gamma$-$\text{ZrP}$) and titanium phosphate, $\gamma$-$\text{Ti(PO}_4\text{)(H}_2\text{PO}_4\text{)}\cdot 2\text{H}_2\text{O}$, ($\gamma$-$\text{TiP}$) may be considered among the most studied inorganic ion-exchange materials with a layered structure [289,290]. The organic diamine 2,9-dimethyl-1,10-phenanthroline (dmp) is able to be intercalated between the layers of $\gamma$-$\text{ZrP}$ and $\gamma$-$\text{TiP}$ to give the intercalated phases denoted as $\gamma$-$\text{ZrPdmp}$ and $\gamma$-$\text{TiPdmp}$ [291]. These materials subsequently exchange copper ions giving dmpCu complex formed in situ ($\gamma$-$\text{ZrPdmpCu}$ and $\gamma$-$\text{TiPdmpCu}$) (Fig. 1.20).

Alberti et al. [292] have reported the synthesis and characterization of a new type of zirconium phosphate such as zirconium phosphate hemihydrate [$\alpha$-$\text{Zr(HPO}_4\text{)}_{0.5}\cdot \text{H}_2\text{O}$]. A large number of other new materials have also been prepared on zirconium phosphate by pillaring methods. Alberti and coworkers [293] have intercalated $\alpha$-$\text{Zr(IV)(RPO}_3\text{)}_2\cdot \text{H}_2\text{O}$ by phenyl containing $-\text{SO}_3\text{H}$ groups and $\gamma$-$\text{Zr(IV)(PO}_4\text{)(H}_2\text{PO}_4\text{)}\cdot 2\text{H}_2\text{O}$ by crown ether. U. Costantino [294] has given a detailed description of intercalation of alkanols and glycols into $\alpha$-$\text{Zr(HPO}_4\text{)}\cdot \text{H}_2\text{O}$ and also developed zirconium phosphate-phosphite [295]. Clearfield and Tindwa [296] have studied in detail the uptake of $n$-phenylamine, $n$-butyl amine and ethylene diamine
Fig. 1.19. Schematic of (I) An intercalation reaction and (II) Pillaring in clays.

Fig. 1.20. Possible arrangements of dmp (a) and dmpCu complex (b) between the layers of the γ-ZrP exchanger.
on \( \alpha-Zr(HPO_4)_2\cdot H_2O \). Dines et al. [297] have prepared monophenyl, diphenyl and triphenyl bridging pillared zirconium phosphates by using phenyl disulphonic acids to bridge across the layers. They have also shown that it is possible to form three-dimensional or pillared analogous of the phosphonates by utilizing \( \alpha, \omega \)-diphasphonic acids. Varshney et al., Rawat et al., Singh et al. and Qureshi et al. have also studied on amine tin(II) hexacyanoferrate(II) [298], tin(IV) diethanol amine [299], iron(III) diethanol amine [300] and zirconium(IV) ethylene diamine [301], respectively.

Recently, some intercalation ion-exchangers have been developed and reported in the literature. Hudson et al. [302] have reported the intercalation of monoamine into \( \alpha-Sn(HPO_4)_2\cdot H_2O \) and investigated the ion-exchange behavior of amine in the presence of transition metal ions. Wang et al. have reported the selective separation of \( \text{Cs}^+ \) on zirconium phenyl diphosphonate phosphate [303]. Malik et al. [304] have reported pyridinium tungstoarsenate, selective for \( \text{Rb}^+ \) and \( \text{Cs}^+ \) and Singh et al. intercalated aniline into tin(IV) phosphate [305] and Zr(IV) phosphate, \( [(ZrO_2)_2.(C_6H_5NH_2)HPO_3. 3.7H_2O] \); selective for \( \text{Co}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Hg}^{2+} \) [306]. Nabi et al. have reported the synthesis, characterization and analytical applications of Zr(IV) sulfosalicylate [307] (selective for \( \text{Ag}^+ \) and \( \text{Hg}^{2+} \)) and pyridinium-tin(IV) tungstoselenate [308].

1.5.3.5. ‘Organic-inorganic’ composite ion-exchange materials

The conversion of inorganic ion-exchange materials has been taking place into composite ion-exchange materials is the latest development in this discipline. Sol-gel
derived composite materials have found numerous applications in the areas of chemistry, biochemistry, engineering, and material science [309,310]. The ‘organic-inorganic’ hybrid materials prepared via the sol-gel technique have attracted significant attention in the literature [311] and the materials as ion-exchangers prepared by this technique were also described. The combination of organic and inorganic precursors yields hybrid materials that have mechanical properties not present in the pure materials. Often, strain built up during drying and heat treatment (densification) results in cracking of the materials. To diminish this strain, the material can be made more compliant by the introduction of organic groups. The organic group can be reactive, which implies that it is able to form an organic network as well as an inorganic network. In this case, the organic group is classified as network builder. Another preparation of the composite ion-exchangers has been carried out with the binding of electrically conducting organic polymers, i.e. polyaniline, polythiophene and polypyrrole etc.

These polymers based composite ion-exchange materials show the improvement in a number of its properties. One of them is the improvement in its granulometric properties that makes more suitable for the application in column operations. In some of the cases, it is observed that increase in the number of cycles without affecting its ion-exchange capacity as well as ion-exchange equilibria. The binding of organic polymer also introduces the better mechanical properties in the end product, i.e. composite ion-exchange materials.

More recently, some organic-inorganic composite ion-exchange materials
have been developed in these laboratories. Khan et al. have reported polypyrrole Th(IV) phosphate [312], polyaniline Sn(IV) phosphate [313] (tentative structures are shown in Fig. 1.21 and 1.22), polypyrrole/polyantimonic acid composite system [314], polyaniline Sn(IV) tungstosarnenate [315], polyaniline Sn(IV) arsenophosphate [316], poly-o-toluidine Th(IV) phosphate [317], nylon-6,6, Zr(IV) phosphate [318], and polystyrene Zr(IV) tungstophosphate [319] and used for the selective separation of heavy metal ions. The ion-exchange kinetics of $M^{2+}$-$H^+$ exchange [320-324] and adsorption of pesticide [325,326] have also been carried out on these materials. Beena Pandit et al. have synthesized such type of ion-exchange materials, i.e. o-chlorophenol Zr(IV) tungstate and p-chlorophenol Zr(IV) tungstate [327]. Chudasama et al. [328] synthesized a new inorganic-organic ion exchanger by anchoring p-chlorophenol to Zn(WO$_4$)$_2$ and reported the material has a good ion-exchange capacity and stability.

Styrene supported Zr(IV) phosphate [329] and Zr(IV) tungstophosphate [319] hybrid material and fibrous ion-exchange materials such as polymethyl methacrylate, polyacrylonitrile, styrene, pectin and acrylamide based Ce(IV) phosphate, Th(IV) phosphate, Zr(IV) phosphate and tin(IV) phosphate [330-337] having a great analytical applications, have been investigated by Varshney et al. These materials can be used as ion-exchanger membranes and electrodes. Polyacrylonitrile fibers and zeolites composites have also been reported in literature. Polyaniline Zr(IV) tungstophosphate has been synthesized by Gupta et al. [338], which was used for the selective separation of La$^{3+}$ and UO$_2^{2+}$. Chanda et al. reported polyacrylic acid
Fig. 1.21. Tentative structure of polypyrrole Th(IV) phosphate organic-inorganic composite cation-exchanger.

Fig. 1.22. Tentative structure of polyaniline Sn(IV) phosphate organic-inorganic composite cation-exchanger.
coated SiO\textsubscript{2} as a new ion-exchange material. \textit{C.A Borgo et al.} [339] have studied ion-exchange properties and equilibrium constant of Li\textsuperscript{+}, Na\textsuperscript{+}, and K\textsuperscript{+}, on zirconium phosphate highly dispersed on a cellulose acetate fiber surface. \textit{S.K. Tiwari et al.} [340] reported the thermolytic degradation behavior of inorganic ion-exchanger incorporated perfluoro-sulphonate ionomer membrane (nafion-117).

1.5.4. Applications of Ion-exchange Materials

Ion-exchangers find applications in a wide variety of industrial, domestic, governmental and laboratory operations. The composite ion-exchangers show some better granulometric properties that facilitates its stability in column operations especially for separation, filtration and preconcentration of ionic species. The column operation suitability makes it more convenient in regeneration of exhausted beds also. These hybrid ion-exchangers having good ion-exchange capacity, higher stabilities, reproducibility and selectivity for specific heavy metal ions indicating its useful environmental applications. As in general these materials have their applications in following disciplines:

- Water softening [99,341]
- Separation and preconcentration of metal ions [342]
- Nuclear separations [343]
- Nuclear medicine [344]
- Synthesis of organic pharmaceutical compounds [345]
- Catalysis [346]
- Redox systems [347]
- Electrodialysis [348]
- Hydrometallurgy [349]
- Effluent treatment [350]
- Ion-exchange membranes
- Chemical and biosensors
- Ion memory effect [351]
- Ion-exchange fibers [352-354]
- Ion-selective electrodes [314,315,355-357]
- Proton conductors [358,359]
1.6. Electrical Properties of Materials

Consideration of the electrical properties of materials is often important when materials selection and processing decisions are being made during the design of a component or structure. The electrical behaviors of the various materials are diverse. Some need to be highly electrically conductive, whereas electrical insulativity is required of others. In order to explore the electrical properties of materials, that is, their responses to an applied electric field, it is necessary to discuss the phenomenon of electrical conduction: the parameters by which it is expressed, the mechanism of conduction by electrons, and how the electron energy band structure of a material influences its ability to conduct. These principles are extended to metals, semiconductors, and insulators. Nowadays, particular attention is given to the characteristics of semiconductors.

1.6.1. Electrical conduction in materials

Electrical conductivity $\sigma$ is used to specify the electrical character of a material. It is simply the reciprocal of the resistivity, or

$$\sigma = \frac{1}{\rho}$$  \hspace{1cm} (1.4)

and is indicative of the ease with which a material is capable of conducting an electric current. Materials show electrical conduction due to the movement of charge carriers on application of voltage as given by the basic equation -

$$\sigma = q n \mu$$  \hspace{1cm} (1.5)

where $\sigma$ is electrical conductivity of material, $n$ is the number of charge carriers, $q$ is
the charge and \( \mu \) is drift mobility of charge carriers. Drift mobility characterizes the ease with which the charge carriers can move under the influence of applied electrical field. There are several carriers that contribute to the conductivity of the materials. Electrons and holes in the electronic conductors and cations and anions in ionic conductors.

Mechanisms that have been employed to explain the electrical conduction in materials, include ionic conduction, band type conduction, hopping and excitonic conduction, quantum mechanical tunneling between metallic domains etc.

1.6.2. Electrically conducting materials

The ability of materials to conduct electricity varies widely allowing their classification into good conductors (metals), semiconductors and non-conductors (insulators). Another classification of solids may be based upon the number of current carriers (electrons). A conductor has a large number of current carriers and this number is independent of temperature. An insulator has relatively few numbers of current carriers at ordinary temperatures and a semiconductor has current carriers, the number of which in a particular material depends on the temperature.

We already know that electrical conductivity is one of the most important properties of metals. Silver has the highest electrical conductivity. Copper comes next and is similar to silver from the point of view of atomic structure. Aluminium, which is light and has a high conductivity, is rapidly becoming more important as a conductor material. Gold which has conductivity higher than that of aluminium but lower than that of silver or copper does not find use in electrical industry because it is expensive.
The resistivity of metallic conductors at room temperature lies between $1.6 \times 10^{-6}$ to $100 \times 10^{-6}$ ohm cm$^{-1}$ and that of insulators between $10^9$ to $10^{18}$ ohm cm$^{-1}$. The corresponding value for semiconductors is intermediate between those for conductors and insulators. It is the order of 0.01-50 ohm cm$^{-1}$ at room temperature. The resistivity of semiconductors is considerably more sensitive to changes in temperature than is the case for metals. As a result compact temperature measuring instruments using semiconducting thermal resistors (thermistors) may be constructed.

At high temperatures, the number of current carriers in a semiconductor is fairly large while at low temperatures this number is relatively small. The number of current carriers in a semiconductor however is many orders of magnitude smaller than in a conductor.

**K. Onnes** first observed superconductivity in 1911; on cooling a sample of mercury below 4.2 K the resistivity of the metal suddenly decreased to an immeasurably small value. Since then many metals and their alloys, many compounds have been found which have zero resistance below a certain critical temperature; $T_c$. Electrical conductivities of various elements, compounds and polymers are shown in Fig. 1.23.

### 1.6.3. Electrically conducting polymers

Polymers have traditionally been utilized in electrical and electronic applications in view of high resistivity (their electrical conductivity lies in the range of $10^{-11}$ to $10^{-18}$ Scm$^{-1}$) and excellent dielectric properties. Research and development have demonstrated the possibility of obtaining polymers with almost properties
Fig. 1.23. Conductivities of main electrically conducting polymers with other classical conductors, semiconductors, and insulators
typical of any structural material, semiconductor or metal. However, due to the electrical insulating properties, polymers remain unsuccessful in replacing metals and semiconductors in electrical and electronic applications. To improve gas sensors characteristics, novel sensitive organic layers, electronic conducting polymers were developed. Now the electrically conducting polymers are establishing their place as the central constituents of various electronic and photonic systems. The award of the Noble Prize has recognized the interest of these materials for the year 2000 in Chemistry to Heeger [360], MacDiarmid [361] and H. Shirakawa, who synthesized the first conducting polymers and proved their potentialities in a large number of applications. The first account of observation of the electrical conductivity was reported in 1800s when it was seen that by incorporation of carbon black, the conductivity of natural rubber could be enhanced. The combination of electronic and optical properties of the semiconductors with the mechanical properties and the processibility of the polymers makes conjugated polymers rather unique and potentially useful for a wide array of applications. Conjugated polymers such as polyacetylene, polyphenylene, polythiophene, polypyrrole, polyaniline etc. possess a backbone that can produce, sustain and assist the motion of charge carriers in the form of electrons or holes (Fig. 1.24).

1.6.3.1. Polyaniline

In recent years, polyaniline has attracted much attention [362-364] on account of its ability, under certain conditions, to exhibit a high level of electrical conductivity [365] having potential applications such as in the fabrication of novel
Fig. 1.24. Bond-alternate backbone of the most studied electroconductive conjugated polymers (ECPs).
batteries. Although polyaniline was first produced in the nineteenth century, interest in this polymer and its derivatives did not really begin to develop until the mid-1980s. Several chemical methods exist for the preparation of polyaniline although the preferred method utilizes electrochemical polymerization. It is known to exist in a variety of forms differing in color, some of which are not electrically conducting as shown in Fig. 1.25. Under appropriate conditions the so called emeraldine base form of the polymer reacts with dilute acids to give corresponding emeraldine salts, with protonation of the nitrogen atoms. This reaction is accompanied by a 9-10 order of magnitude increase in conductivity to $1 \times 10^2 - 5 \times 10^3 \text{ S m}^{-1}$. Hence it can be used in aqueous electrolyte rechargeable batteries [366]. Key attractions of polyaniline are the relatively low cost of the synthetic route from aniline and the fact that it has very important features that distinguish it from other conductive polymers.

### 1.6.3.2. Polypyrrole

Polypyrrole have encouraged considerable research because they are a group of polymers that can be easily produced in the doped state. It can be prepared by the electro-polymerization of pyrrole and it is then obtained as highly colored dense conducting films. It can also be prepared by chemical methods. It has been one of the first polymers used in gas sensors. Conductivities of this polymer have been reported up to $10^4 \text{ Sm}^{-1}$ [367]. One of the principal advantages of polypyrrole over other doped polymers is its excellent thermal stability in air. It is thermally stable upto 250 °C. Although chemical analysis of polypyrrole varies with preparative conditions, elemental analyses have indicated that the pyrrole rings remain intact with each unit being connected by its $\alpha$-carbons (Fig. 1.26).
Fig. 1.25. Different forms of polyaniline.

Fig. 1.26. Structure of polypyrrole.
1.6.4. Electrically conducting ‘organic-inorganic’ composites

The conjugated backbone of electrically conducting organic polymers is responsible for their electroactive character and, therefore, possesses good tunable electrical conductivity as well as electrochromic properties [368-371]. But they are chemically sensitive and have poor mechanical properties and pose processibility problems. The inherent instability is also due to highly unsaturated backbone of conjugated polymers. Stability problems have, therefore, caused many research groups to search for conjugated polymers of high stability. To meet the demand of materials of improved performance, explosive research is going on to synthesize the composites (combinations of desirable properties of each component) of ‘organic-organic’ and ‘organic-inorganic’ nature. In the view of the above-mentioned facts, researchers have shown much interest in the study of electrically conducting behavior of ‘organic-inorganic’ composite materials [86,372-376]. Special interest today is focused on composite system having high conductivity at ambient and sub-ambient temperatures, since they find unique applications, such as separators in high power and rechargeable lithium batteries. Moreover, composite materials composed of oxides or polyvalent metal acid salts and conducting polymers have brought out more fields of applications, such as smart windows, toners in photocopying, conducting paints etc. [377-379].

These organic-inorganic electrically conducting composites may be prepared by mixing a conducting material in an insulating or a conducting polymer matrix. The insulating polymer matrix acts as a solid adhesive, which keeps the conducting
components together and provides mechanical strength without any contribution in electrical conduction. Thus, one or more materials (for e.g. insulating polymers, organic molecules, metal powder, inorganic compounds etc.) can be combined with electrically conducting polymer matrix to produce a new conducting material with different physical, mechanical, thermal and electrical properties. Thus, the synthesis of polymeric-inorganic composites has received a great deal of attention because it provided new materials with special mechanical, chemical, electrochemical and optical as well as magnetic properties [380-414]. Various research groups have also successfully applied conventional dispersion polymerization techniques for the preparation of sterically stabilized particles of electrically conducting polymers such as polypyrrole (Ppy) and polyaniline (PANI). The preparation of dispersions solves some problem of their limited processibility. A wide range of steric stabilizers based on various water-soluble polymers, e.g. poly(2-vinylpyridine) [415,416], poly(vinylalcohol) [417,418], poly(vinylalcohol-co-vinylacetate) [419-426], poly(oxyethylene) [427-429], poly(N-vinylpyrrolidone) [421,422,430,431], poly(vinyl methyl ether) [432-434], proteins [435] and cellulose ethers [436] have been reported by various research groups. Armes et al. have recently shown that polyaniline and polypyrrole colloids can be prepared by using colloidal silica [437-441] and, in case of polypyrrole, also tin oxide sols [442] instead of polymeric stabilizer. The electrical conductivity measurements of polyaniline-silica composite [442] prepared by dispersion polymerizing are illustrated Fig. 1.27. Its conductivity at 25 °C is $6.1 \times 10^{-2}$ S cm$^{-1}$. As expected with semiconductors, the conductivity
Fig. 1.27. Temperature dependence of electrical conductivity, $\sigma_e$ for a PANI (37.8 wt. %)-silica composite (full line) and its comparison with polyaniline (48.3 wt. %):poly(vinyl alcohol) and, polyaniline (39.4 wt. %): poly(N-vinylpyrrolidone) composites (broken lines).
increases with increasing temperature (Fig. 1.27). The electrical conductivity of the polyaniline-silica composite is virtually the same as that of polyaniline:poly(vinyl alcohol) (PVA) or polyaniline:poly(N-vinylpyrrolidone) (PVP) composites \( [443,444] \) of comparable polyaniline content (Fig. 1.27). Consequently, the electrical properties are independent of the type of the stabilizer, particulate or polymeric, used for the preparation of polyaniline. Recently, several groups have also combined conductive polymers with transition metal oxides to generate hybrid organic-inorganic composites \( [445-448] \), which possess higher reversible capacity \( [445] \), redox cyclability \( [447] \) and structure stability \( [448] \). Among the transition metal oxides, several researchers studied \( [449-451] \) the \( \text{V}_2\text{O}_5:\text{PANI} \) and \( \text{V}_2\text{O}_5: \text{PPy} \) nanocomposites. E. Ruckenstein \textit{et al.} synthesized the \( \text{V}_2\text{O}_5:\text{PANI} \) nanocomposite, which showed a relatively high conductivity \( (10^2 \text{ S cm}^{-1}) \) \( [452] \). The steps of the intercalative polymerization in the mesostructured \( \text{V}_2\text{O}_5 \) are presented schematically in Fig. 1.28. Nevertheless, electronic devices based on inorganic materials still dominate the market due to their well-defined and the wide spectrum of electronic properties. But the approach of organic-inorganic composites materials could quickly lead to a new generation of inexpensive computer displays or solar cells that are either flexible or embedded within curved plastic, glass or other materials. Because, wholly inorganic semiconductors require processing at high temperatures, making it impossible to embed circuits in plastic or other heat-sensitive materials. On the other hand, the new hybrid materials "self-assemble," crystallizing from a liquid solution at low temperatures to form alternating organic and inorganic layers of material with the correct semiconducting properties.
Fig. 1.28. Synthesis of a mesostructured $V_2O_5$:Polyaniline nanocomposite.
1.6.5. Applications of electrically conducting polymers and composites

1.6.5.1. Optical Devices

Optics was certainly one of the first applications of hybrid materials [453]. Thus, organic:inorganic/organic:organic hybrid materials with high transparency are expected to be new optical materials such as optical fiber, wave-guide and optical lens. Materials with high refractive index, low density and good transparency in visible region are in demand as optical lenses especially for glasses. In order to implement optoelectronic or photonic properties into devices, the materials have to fulfill high optical quality demands and have to be stable over a long period. Furthermore, the control of the refractive index as well as the thickness and therefore, the processibility of the materials are important. Due to its low optical losses (high optical quality), silica glass and composites made from it seem to be very useful for these devices [454,455]. For example, photoconducting composites were prepared by the incorporation of cadmium sulfide particles in a polyvinylcarbazole matrix. The resulting materials allowed the tuning of the band gap of the sensitizing nanocrystals so that their spectral response was adjusted to suit a particular wavelength of operation [456,457].

Thus, the optical properties of organic-organic/organic-inorganic composites have attracted much interest, particularly their transparency and 'active' optical properties. Transparent products can be obtained from layered systems under certain conditions. Hybrids of clay and nematic liquid crystals prepared by Kawasumi et al. [458], exhibit interesting electro-optical properties. These materials can be
transparent (Fig. 1.29(a)) or opaque (Fig. 1.29(c)) depending on the frequency of the applied electric field. The effect is reversible and can be repeated many times. The transparent and opaque states exhibit a memory effect after switching off the field (Fig. 1.29(b) and Fig. 1.29(d)). Such materials have potential applications in optical storage devices, displays and light-controlling glass. Another interesting example of optoelectronic ‘organic-inorganic’ hybrid is TiO₂/polyacrylate, which shows good visible light transparency as compared to TiO₂ as shown in Fig. 1.30. The development of optically activated hybrid organic-inorganic mesostructured silica composites has led to a number of advanced optical applications, such as optical switches and sensors and low threshold wave-guide microlasers. However, the low refractive index of silica composites (n = 1.43) requires that the optically active layer be supported by an ultra low refractive index layer for wave guiding to occur. This obstacle could be overcome by using a higher refractive index inorganic component. Recently, D. Stucky et al. [459] demonstrated a new synthetic approach for high refractive index, dye-activated, hybrid mesostructured materials utilizing a fluorocarbon stabilized titania precursor. These titania composites can readily be processed into solid, optically transparent, crack free fibers and planar wave-guides.

Several research groups [460-466] have studied light emitting diodes using hybrid composites. Compared to classical organic or polymer based diodes, those fabricated with composites as an emitting layers exhibited low turn-on voltage [460,461,463,464], improved stability [465]. Depending on the nature of material as well as the adopted structure, the obtained emitted light could be that of the organic
Fig. 1.29. Electro-optical properties of clay:nematic liquid crystal hybrids. (a) low frequency, on, (b) low frequency, off, (c) high frequency, on and (d) high frequency, off.

Fig. 1.30. TiO₂:Polyacrylate shows good visible light transparency (left) and TiO₂ film of thickness about 20 nm (right).
or both of them as a function of the applied voltage [459,460]. Color conversion of light from short wavelength to longer one could also be achieved using particular arrangement of the layers [467].

Among conjugated polymers poly(p-phenylene vinylene)s have been studied extensively for their electro luminescence and potential applications in light emitting diodes (LEDs) because of its easy processibility and relatively good optical and electrical performance. On the other hand, porous silicon was found to have high conductivity and to exhibit interesting electroluminescence properties. Optical study of composites made of porous silicon and a non-conjugated polymer has been performed by Guha et al. [464,468] using mixed structures but no LEDs result was reported. The synthesis of intercalated hybrids of smectic clay and a substituted poly(p-phenylene vinylene) has also been reported. These hybrids exhibit electroluminescence and the luminescence appears to be color tunable depending on the degree of intercalation. Organically modified silicates (ormosil) and organically modified ceramics (ormocer) synthesized with sol-gel route have also been intensively studied in the last ten years due to their wide spectrum of integrated optics applications such as the fabrication of passive and active wave guides, sensors, electro-optical modulators and solid-state microlasers [469].

The desirable electrical and optical properties exhibited by the hybrid perovskites, along with the potential for simple, low-cost processing techniques, make it interesting to consider building devices with these materials. These useful optical characteristics make the perovskites attractive as potential emissive materials
in electroluminescent (EL) devices. The first attempts to induce EL in these materials involved attaching silver paint contacts to single crystals of \((\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_{2}(\text{CH}_3\text{NH}_3)\text{Pb}_2\text{I}_7\) \[470\]. More recently, EL devices were prepared, with a structure analogous to that of traditional organic light emitting diodes (OLEDs), but with hybrid \((\text{R-NH}_3)\text{PbI}_4\), perovskite light-emitting layers \[471,472\]. In addition to their potential applications in ‘organic-inorganic light emitting diodes (OLEDs)’ systems, semiconducting hybrid perovskites are also attractive as a new class of channel materials for thin-film field-effect transistors (TFTs) \[473\]. The ‘organic:inorganic’ hybrid materials are interesting for this application because they can combine the higher carrier mobilities of ionic and covalently bonded inorganic semiconductors with the simple, low-cost and low-temperature thin-film techniques that make organic semiconductors exciting as alternative channel materials. Recently, C.R. Kagan et al. \[473\] demonstrated the first ‘organic:inorganic’ hybrid material as the semiconducting channel in a TFT, using the hybrid perovskite \((\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)\text{SnI}_4\) Fig. 1.31 depicts a typical ‘organic-inorganic’ TFT device structure.

1.6.5.2. Conductors

Electrically conducting composite materials show various applications in electronic and photonic systems. Most of them show the electrical conduction behavior in the semiconductor region and hence they can be used as semiconducting materials. Nowadays, these materials have been used in the preparation of potentiometric sensors, i.e., gas sensors, chemical sensors, biosensors, ion-sensors as
Fig. 1.31. Schematic diagram of a TFT device structure employing a layer ‘organic:inorganic’ perovskite.
well as ion-selective electrodes, which are of vital analytical and environmental interest. The integration of chemically sensitive membranes with solid state electronics has led to the evolution of miniaturized, mass produced potentiometric probes known as ion-selective field effect transistors (ISFETs). Thus, the electrical and electronic properties exhibited by solid-state materials are crucial in a large number of inorganic as well as organo-inorganic materials applications [474-478]. These unique electronic properties result from their extended structures, where strong interactions between the atoms, ions or molecules occur throughout the lattice. In terms of conductivity, the behavior ranges from insulating through semiconducting to metallic and superconducting many types of electrically conducting composite materials classified as electrolytes or polymer ionics have been developed and characterized in recent years [479] for applications such as solid-state lithium batteries or supercapacitors produced using ‘organic:inorganic’ polymeric systems formed by the mixture of organic polymers and inorganic moieties prepared by the sol–gel techniques. In these systems at least one of the network forming species should contain components that allow an interaction to the conducting ions. This is often realized using organic polymers, which allow an interaction with the ions such as poly(ethylene oxide) (PEO) [480-482]. Solid electrolytes, having conductivities of $10^{-2}$ to $10^{-1}$ Scm$^{-1}$, are required in several systems operating either with high current densities (electrolyzers, batteries, etc.) [483], or at very low current levels (gauges, electrochemical memories, coulometers, etc.) [484], in order to avoid excessive Joule-heat losses or excessive cell impedance. Furthermore, high conductivities are
required for materials employed in the preparation of charged membranes or in thermoelectric generators [485]. Only a few solid electrolytes are presently known to exhibit such a favorable conductance and most of them only at high temperature. The combination of conducting polymers with inorganic species is another example for nanocomposites with a potentially important application. A variety of combinations have already been tested and especially polyaniline and polypyrrole show an interesting potential in combination with iron oxides, barium titanate, platinum and tungsten oxide for magnetical, energy storage, catalytic and electrochromic devices, respectively [486]. Metallo and metal free phthalocyanines and their polymers are also known for almost a centaury and have become one of the most intensively studied macrocycles due to their resemblance to biologically occurring porphyrins [487]. They possess useful optical, electronic, electrical, photoelectric and electrochemical properties and hence, have become ideal candidates for use in the fabrication of novel electronic devices [488-499], molecular electronic devices [500-504], gas sensors and detectors [505-508]. They can be reversibly doped to achieve metallic conductivity by exposure or co-crystallization with a variety of electron acceptors. Thus, the electrical conductivity can also be improved by effecting refinements in these polymers via thermal and reactive treatments. Proton conducting composites were also obtained by the formation of interpenetrating networks (IPNs) from silicon alkoxide end-capped PEO, phenyltriethoxysilane using monododecylphosphosphate or phosphotungstic acid to induce the proton conductivity [509]. High temperature protonic conducting polymers membranes provide new
technological applications in the electrochemical devices including electrochromic displays, chemical sensors, fuel cells and others. Organic/inorganic composite membranes, consisting of SiO₂:PEO hybrids, are remarkable family of isotropic, amorphous polymer material, which shows good protonic conductivities at high temperatures above 100°C. At the same time hybrid materials with ionic conductivity have also been described. These hybrids are being produced by dissolving lithium salt in a suitable phase, an organically modified silica (amines, sulphonic acid, sulfonamides [510] or silica polymer networks such as poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG) etc. [511]. Transport phenomena of cations in polymeric structures have been widely studied and demonstrate that reasonable values of Li⁺ mobility are reached if the surrounding solvating media also experiences a high degree of mobility [512]. In PEG:silica structures, the dependence of ionic conductivity (σ₁⁺) on temperature demonstrate polymer like behavior, in agreement with thermal analysis and the NMR experiments which present a value of Tg in the range -60°C to +20°C, depending upon the exact material composition.

Ionic conduction in organic-inorganic composite based on poly(propylene glycol) has been described by R.F. Bianchi et al. [513]. At last we can say that more and more compounds presenting electronic properties are also under study. Redox targets have been entrapped in hybrid matrices, leading to photo- or electro active materials [514]. These properties have also been used to study the change of structure during the sol-gel transition via the determination of self-diffusion coefficients [515]. These properties are also expected for redox sensors and biosensors. Because of the
flexibility of the chemistry, the redox properties of materials can be tuned. Very promising results arise from electronic conductors such as silica-polypyrrole, silica-aniline interpenetrated networks and V₂O₅-polypyrrole layered structures. The search of anisotropic conductivity properties is clear evidence by this last example. Recently, semiconductor research has also found interesting isolating materials that can be used in organic transistors and chips [516].

1.6.5.3. Sensors

Organic or inorganic semiconductors have been reported to change their conductivities when exposed to variety of organic and inorganic vapors. Thus, these materials can be expected to behave as sensors. Composite materials of tin oxide and derivatives of polypyrrole [507] gave reversible changes in electrical resistance at room temperature when exposed to a variety of organic vapors. Composite materials containing 2.5% polymer by mass were fabricated and exposed to low concentrations of ethanol, methanol, acetone, methyl acetate and ethyl acetate vapors [517-520], the composite materials were found to give more significant and reversible decrease in electrical resistance in comparison with sensors constructed solely of tin dioxide or polypyrrole. These materials could be used in the quality control of foodstuff, especially in the early detection of soft rot in potato tubers. Some researchers incorporated preformed polypyrrole and poythiophene in to clay (montmorillonite) by the interaction of colloidal nanoparticles of the polymers with the colloidal layered host [521]. This method using a colloid-colloid reaction [522] might provide a general route to incorporation of intractable polymers within layered host structures.
that can be exfoliated, such as smectite clays [523], metal disulfides and some metal oxides. These composite materials have potential to be used as hybrid sensors.

Chemical sensing properties of the electrochemically prepared polypyrrole-poly(vinyl alcohol) (Ppy-PVA) films were studied by exposing them to NH$_3$ gas [524]. The results shown in Fig. 1.32 reveal that the sample has a very good sensitivity towards NH$_3$. A remarkable increase in resistance of the sample is observed within 5 min from purging and this change is reversible within 5% of the initial resistance. Increasing the concentration of NH$_3$ more obvious changes are observed but NH$_3$ concentration above 10% results in almost reversible change of resistance.

Lastly, the possible applications of the composite materials are diverse and the future of these materials appears bright. Therefore, in general the application of composite materials can be exemplary introduced in the following field.

- Rechargeable batteries
- Electrochromic devices
- Optoelectronics
- Photovoltaics
- Field effect transistors
- Display devices
- Printed circuit board
- Chemical indicators
- Bio-sensors
- Gas sensors
- Solar cells
- Electroplating
- Conducting textiles
- Electrochemically switchable
- Ion-exchangers
- Transparent coatings

- Adhesives
- Radiation detectors
- Schottky diodes
- Fillers
- Solid lubricants
- Corrosion inhibitors
- Photocatalysis
Fig. 1.32. Resistance changes recorded for Ppy:poly(vinyl alcohol), interpenetrating networks on exposure to NH₃-argon mixtures of different NH₃(%).
1.6.5.4. Electrically conducting polymers and composites as ion-exchangers

The ion-exchange behavior during charging and discharging processes of conducting polymers, e.g. polyaniline and polypyrrole, has been widely studied in recent years [525-536]. It was found that the conducting polymers exchange both anions and cations depending on the polymerization conditions, the type and size of the counter ions incorporated during the polymerization process as well as on the ions present in the electrolyte solution, the polymer thickness and the aging of the polymer. By an appropriate choice of counter ion conducting polymers can be tailored to work as anion or cation exchangers. Polyaniline (PANI) and polypyrrole (PPy) can work as anion-exchangers, whereas PANI and PPy modified with polyanions in the polymeric complexes such as poly(vinyl sulfonic acid) (Fig. 1.33), poly(styrene sulfonic acid), (Fig. 1.34) poly(acrylic acid), poly(methacrylic acid), poly(2-acrylamido-2-methyl-1-propenesulfonic acid), poly(methylacrylate-co-acrylic acid) [527,528,533,534] as well as inorganic polyanions, work as cation-exchangers. Such a modified polymer can be applied as electrochemically switchable ion-exchanger based on electrically conducting polymers [526,527,531,534,535] for water treatment; especially water softening. Some electrically conducting organic-inorganic composites can be used as ion-exchangers have also been reported in literature [537-544].
Fig. 1.33. Side-by-side molecular complex of polyaniline and a functionalized polyanion working as cation-exchanger.

Fig. 1.34. Polypyrrole with incorporated polystyrene sulfonate counterions (PSS) working as cation-exchanger.
1.7. Membranes: An Introduction

A precise and complete definition of the word "Membrane" is difficult to make, and any complete definition given to cover all the facets of membrane behavior will be incomplete. According to Sollner [545], a membrane is a phase or structure interposed between two phases or compartments which obstructs or completely prevents gross mass movement between the later, but permits passage, with various degree of restriction of one or several species of particles from one to the other or between the two adjacent phases or compartments, which thereby acting as a physico-chemical machine transforms with various degree of efficiency according to its nature and composition of the two adjacent phases or compartment. In simple terms, it is described as a phase, usually heterogeneous, acting as barrier to the flow of molecular and ionic species present in the liquids and for vapors containing two surfaces [546]. The term heterogeneous has been used to indicate the internal physical structure and external physico-chemical performance [545,547,548]. From this point of view, most of the membranes in general are to be considered heterogeneous, despite the fact that, conventionally, membranes prepared from coherent gels have been called homogeneous [549].

The usefulness of a membrane in a mass separation process is determined by its selectivity, by its chemical, mechanical and thermal stability and its overall mass transport rate. The chemical nature of the membrane material is of prime importance when components with more or less identical molecular dimensions and similar chemical or electrical properties have to be separated. The chemical, mechanical and thermal stability of the membrane determines to a large extent its useful lifetime,
especially when the feed solution contains strong solvents, strong oxidants and
extremely low or high pH values, when the process has to be carried out at
elevated temperatures or when frequent cleaning procedures of the membrane are
required. The mechanical properties of a membrane are of special significance in
pressure driven process such as reverse osmosis, ultra filtration, etc. Ideally, a
membrane should not change its useful properties when it is derived out or when
the composition of feed solution is changed drastically. For economic reasons,
finally the flow rate of the permeable components through a given membrane area
under a given driving force should be as high as possible to minimize investment
costs which are generally proportional to the membrane area installed to give a
certain process capacity. To significantly expand the use of membranes in mass
separation processes beyond their present applications, membranes with more
specific transport properties, longer lifetimes and higher flux rates are required.

1.8. Electrochemical Sensors

Electrochemical sensors represent an important subclass of chemical
sensors in which an electrode is used as the transduction element. According to
such devices hold a leading position among sensors presently available, having
reached the commercial stage, and have found a vast range of important
applications in the field of clinical, industrial, environmental and agricultural
analyses. The field of sensor is interdisciplinary, and future advances are likely to
occur from progress in several disciplines.
Potentiometric sensors work through the measurement of an equilibrium potential i.e., the potential at zero current, of the sensor versus a suitable reference electrode. These potentials are a function of the activity of the species in solution, not of their concentration. The Debye-Huckel equation relates concentrations to activities and can often be employed; indeed potentiometric measurements can be used to test the Debye-Huckel theory. However, for dilute solutions it is reasonable to assume that activity and concentration are equal. There are few reviews [550,551], which compare potentiometric and amperometric sensors in terms of their performance and limitations. However, the rapid development of new selective electrodes and more sensitive and stable electronic components over the past 25 years has expanded tremendously the range of analytical applications of potentiometric measurements. The speed at which this field has developed is a measure of the degree to which potentiometric measurements meet the need of the analytical chemist for rapid low-cost and accurate analysis. Many general books have been devoted exclusively to direct potentiometry [552-554]. Several review articles have been appeared in literature time to time [555-561].

1.8.1. Ion-selective electrodes

Ion-selective electrodes are mainly membrane-based devices; consist of perm-selective ion-conducting materials, which separate the sample from the inside of the electrode. On the inside is a filling solution containing the ion of interest at a constant activity. The membrane is usually non-porous, water insoluble and mechanically stable. The composition of the membrane is designed to yield a potential that is
primarily due to the ion of interest (via selective binding processes, e.g. ion-exchange, which occur at the membrane-solution interface). The purpose is to find membranes that will selectively bind the analyte ions, leaving co-ions behind. Membrane materials, possessing different ion-recognition properties, have thus been developed to impart high selectivity.

The Ion-Selective Electrodes (ISEs) are commonly known as “Ion Sensors” or “Electrochemical Sensors”. The history of ion-selective electrodes in the past decade shows the typical behavior of expansion followed by consolidation. The rapid growth of new electrodes for ion activity measurement, new formats and new material of construction has given a way to more in prospective research on “How and Whys” of the functioning of various electrodes and extensive application studies, uses of ISEs as instrumental components and in diverse field, particularly in clinical and environmental chemistry.

1.8.2. Physico-chemical properties of ion-selective electrodes

In order to study the characteristics of the electrode, the following parameters were evaluated: electrode response or membrane potential, lower detection limit, slope response curve, response time, working pH range, etc.

1.8.2.1. Electrode response or membrane potential

The use of ion-selective electrodes depends on the determination of potentials \[562,563\]. The potentials cannot be determined directly but can be easily derived from the e.m.f. values for the complete electrochemical cells which comprise the membrane separating solutions 1 and 2 as well as the two reference electrodes when the ion
exchange membrane separates two solution 1 and 2 both containing the same counter ion or A, a membrane potential \( (E_m) \) is developed across the membrane due to the diffusion of counter ions from the higher to the lower concentration. The membrane potential is expressed in equation (1.6):

\[
E_m = \frac{RT}{Z_A F} \left[ \ln \left( \frac{[a_A]^2}{[a_A]^2} \right) - (Z_Y - Z_A) \sum \Gamma_i \alpha_i \ln a_\pm \right]
\]

where \( A = \) counter ion, \( Y = \) co-ion, \( Z = \) charge on ions, \( \tau_Y = \) transference number of co-ions in the membrane phase, \([a_A]^1\) and \([a_A]^2\) = activities of the counter ions in the solution 1 and 2, \( a_\pm = \) mean ionic activity of the electrolyte. It is quite evident from the equation that ‘\( E_m \)’ is the sum of diffusion and Donnan Potential. In equation (1.6) the right hand side consists of two terms, the first term represents the thermodynamic limiting value and the second term denotes the diffusion potential due to co-ion flux membrane.

If the membrane is considered to be ideally perm-selective membrane \( (\tau_Y = 0) \) then equation (1.6) takes the form of the well known Nernst Equation as follows:

\[
E_m = \pm \frac{RT}{Z_A F} \ln \left( \frac{[a_A]^2}{[a_A]^1} \right)
\]

The equation (1.7) simply represents Donnan potential for an ideally perm-selective membrane or it can be said that it gives the thermodynamic limiting value of concentration potential. Equation (1.7) takes positive sign for cations and negative sign for anions. The membrane potential measurement is carried out using a cell set up of the following type:
In general practice, the concentration of one of the solution (say 1) is kept constant (usually 0.1 M) and this solution is referred as internal or reference solution and a SCE is dipped in this internal solution as an internal reference electrode. The membrane together with internal solution and internal reference electrode is one compact unit, which as whole is called as membrane electrode. This membrane electrode is then immersed in solution 2, usually referred as external solution or test solution, having an external reference electrode. The e.m.f. of this potentiometric cell is given by the following expression:

$$E_{cell} = E_{SCE} + E_{L(2)} + E_m + E_{L(1)} - E_{SCE}$$  \[1.8\]

where $E_{SCE}$, $E_L$ and $E_m$ refer to Calomel Electrode, junction and membrane potentials, respectively. On combining equation (1.7) and (1.8), the following equation takes the form:

$$E_{cell} = E_{SCE} - E_{SCE} + E_{L(2)} + E_{L(1)} \pm \frac{RT}{ZAF} \ln \frac{[a_{A}]_2}{[a_{A}]_1}$$  \[1.9\]

For cation-exchange membrane,

$$E_{cell} = E_{L(2)} + E_{L(1)} - \frac{RT}{ZAF} \ln [a_{A}]_1 + \frac{RT}{ZAF} \ln [a_{A}]_2$$  \[1.10\]
$E_{L(2)}$ are also almost constant, the term in parenthesis may be taken equal to a constant, $E^\circ$. Furthermore, the values of $E_{L(1)}$ and $E_{L(2)}$ are negligible (due to salt bridge in use), the cell potential in above equation may approximately be taken as membrane potential. The equation (1.10) reduces to-

$$E_{cell} = E^\circ + \frac{RT}{Z_AF} \ln [a_A]^2$$  \hspace{1cm} \ldots \ldots 1.11

Now, it is quite clear from equation (1.11) that the cell potential would change with the change in concentration (or activity) of the cation in external or test solution 2. At 25 °C, value of $RT/Z_AF$ comes out to be $0.059/Z_A$ volts. The membrane is said to give Nernstian response if the slope of a plot between cell potential and log activity comes out to be $0.059/Z_A$ volts. These plots are called Nernst plots and the slope as Nernstian slope.

From the calibration graph, it can be observed that the response curve is linear down to a particular concentration after which the curve tends to become parallel to the x-axis. Suitable concentrations were chosen corresponding to the sloping portion of the linear curve for the measurement of potentials. The slope of this linear curve is important and tells whether the electrode response follows the Nernstian response or not. A potentiometric sensor is said to be behaving in a Nernstian or close to Nernstian fashion, if the slope is ±1-2 mV of the theoretical value. Below this range it is sub-Nernstian, above it, it is hyper-Nernstian. Sensors which are outside the Nernstian range can still be useful analytically.
1.8.2.2. Selectivity coefficients

A selectivity coefficient is one of the most important factors of ion-selective electrodes (ISEs), on the basis of which the potential application of an electrode in a given system can be predicted. Generally, ISEs are mainly membrane-based devices, consisting of perm-selective ion-conductive materials, which separate the sample from the inside of the electrode. Inside the electrode, a filling solution containing the ion of interest at a constant activity is taken into consideration. The membrane is usually non-porous, water-insoluble and mechanically stable. The composition of the membrane is designed to yield a potential that is primarily due to the ion of interest. The purpose is to find membranes that will selectively bind the analyte ions, leaving co-ions behind. Thus, membrane materials, possessing different ion-recognition properties, have been developed to impart high selectivity. Detailed theory of the processes at the interference of these membranes, which generate the potential, is available elsewhere [564-566]. Such a potential arises whenever the membrane separates two solutions of different ion activities. The resulting potential of the ion-selective electrode, which reflects the unequal distribution of the analyte ions across the boundary, is generally monitored relative to the potential of the reference electrode. Since the potential of the reference electrode is fixed, the measured cell potential reflects the potential of the ISE, and can thus be related to the activity of the target ion. Ideally, the response of the ISE should obey equation (1.12):

\[ E = E^0 + (2.303 \frac{RT}{Z_f}) \log a_i \]  \hspace{1cm}  \text{…….. 1.12}

However, equation (1.12), has been written on the assumption that the electrode
responds only to the ion of interest, ‘i’. In practice, no electrode responds exclusively to
the ion specified. The actual response of the electrode in a binary mixture of the primary
and interfering ions (‘i’ and ‘j’, respectively) is given by the *Nikoloskii-Eisenman*
equation [567]:

\[ E = E^o + (2.303 \frac{RT}{Z_i} \log a_i + K_{ij}^{\text{pot}} a_j^{Z_i/Z_j}) \] ....... 1.13

where \( E \) = potential of the electrode, \( E^o \) = standard potential of the electrode, \( a_i \) =
activity of ‘i’ ions, \( a_j \) = activity of ‘j’ ions, \( Z_i \) = charge on the ‘i’ ion, \( Z_j \) = Charge on
the ‘j’ ion, \( K_{ij}^{\text{pot}} \) = selectivity coefficient of the electrode in the presence of j ions, which
measure the relative affinity of ions ‘i’ and ‘j’ towards the ion-selective membranes.

No electrode is absolutely selective for a particular ion. Thus, the selectivity of
the electrode depends on selectivity coefficients. The lower the value of \( K_{ij}^{\text{pot}} \), the more
selective is the electrode. For ideally selective electrodes, the \( K_{ij}^{\text{pot}} \) would be zero. So, it
is important for the analytical chemist to realize the importance of selectivity coefficient
of a particular electrode. The inconsistent values of selectivity coefficient may cause
problems [568-570]. Various methods [571] have been suggested for determining the
selectivity coefficient, however, it falls in two main groups, namely- (1) Separate-
solution method and (2) Mixed-solution method.

**Separate-solution methods** [572-574]: In the separate-solution method, the
potential of the electrode \( E_i \) and \( E_j \) are measured separately in solutions containing ‘i’
only of activity \( a_i \) (no ‘j’ present) and ‘j’ only of activity \( a_j \) (no ‘i’ present), respectively
and are given by the following equations:

\[ E_i = E^o + (2.303 \frac{RT}{Z_i} \log a_i) \] ....... 1.14

\[ E_j = E^o + (2.303 \frac{RT}{Z_j} \log K_{ij}^{\text{pot}} a_j) \] ....... 1.15
$K_{ij}^{\text{pot}}$ can be calculated either with the so-called equal activity or with the equal potential method. In both cases, it is assumed that the electrode standard potentials are equal in the presence of ion ‘$i$’ as well in that of ion ‘$j$’ and also that the response is Nernstian for both ions. According to the method of equal activities the solution of ion ‘$i$’ and ‘$j$’ are prepared at the same concentration and the potentiometric measurements are carried out. From the equations (1.14) and (1.15), we get

$$\log K_{ij}^{\text{pot}} = \frac{E_j - E_i}{2.303RT/Z_iF} + \log \frac{a_i}{(a_j)^{Z_i/Z_j}} \quad \ldots \ldots \quad 1.16$$

The term $2.303RT/Z_iF$ is the slope of Nernst plot. As most of the solid membranes exhibit deviation from Nernstian behaviour, the experimental slope ($S$), usually differs from the theoretical slope i.e., $2.303RT/Z_iF$. Thus, it is a practice to use ‘$S$’ instead of Nernstian slope for the calculation of $K_{ij}^{\text{pot}}$. As such equation (1.16) takes the form.

$$\log K_{ij}^{\text{pot}} = \frac{E_j - E_i}{S} + \log \frac{a_i}{(a_j)^{Z_i/Z_j}} \quad \ldots \ldots \quad 1.17$$

Thus, using equation (1.17) selectivity coefficient $K_{ij}^{\text{pot}}$ can be calculated. The separate solution technique for determining selectivity coefficients is simple and allows a number of $K_{ij}^{\text{pot}}$ values to be measured on the basis of different activities and potentials.

**Mixed solution methods** [575-581]: In the mixed solution techniques, the electrode potentials are measured in solutions containing both the primary ion ‘$i$’ and the interfering ion ‘$j$’. There are two procedures for determining the selectivity coefficients using Mixed Solution Method.
**Procedure 1**  In this procedure, the potentials of the electrode $E_i$ and $E_j$ are measured in solutions of primary ion ‘$i$’ only and a mixture of primary and interfering ion ‘$j$’, respectively.

\[
K_{ij}^{pot} = \log \left[ 10^{(E_{i+j} - E_i/m)} - 1 \right] + \log a_i - \frac{Z_i}{Z_j} \log a_j \]

Or, in other form, it can be written as

\[
K_{ij}^{pot} = \frac{a_i}{a_j^{(Z_i/Z_j)}} \left\{ \frac{E_{i+j} - E_i}{2.203 \text{RT}/Z_j F} \right\} - 1
\]

**Procedure 2**  In this method, the selectivity coefficients were calculated by the following procedure:

When electrode potentials measured in a number of solutions of varying $a_i$ and constant $a_j$ are plotted against the activity $a_i$, a curve of the type shown in Fig. 1.35 is obtained. This plot generally has three distinct regions. In the first region PQ, the response of the electrode is linear that indicates the electrode is responding only to primary ion ‘$i$’ with no interference caused by ‘$j$’ in this concentration range. In the second region QR, derivation from linearity is caused because now the electrode also responds to the activity of ‘$j$’ as the concentration of ‘$i$’ decreases. So, in this region (QR), the response of the electrode is mixed and is due to both the ions ‘$i$’ and ‘$j$’. The third region (RS) indicates that the electrode is now only responding to interfering ion ‘$j$’ with no contribution arising due to primary ion ‘$i$’. This generally occurs at lower activity of ‘$i$’. As the activity of ‘$j$’ is constant and ‘$i$’ is not affecting the potential in this concentration range, the potential of the electrode remains constant. The linear portion PQ and RS are then extrapolated to point T. The potential corresponding to
Fig. 1.35. Calibration curve illustrating determination of selectivity coefficient by fixed interference method (FIM).

Point T can be generated by constant activity of 'j' or by the activity of 'i' corresponding to point T. Thus for point T, $E_i$ is equal to $E_j$ ($E_i$ is generated by 'i' of activity $a_i$ and $E_j$ by 'j' of activity $a_j$). Under this condition of $E_i = E_j$, the following equation is obtained from equation (1.19) –

$$K_{j/pot}^{pot} = \frac{a_i}{a_j^{(z_i/z_j)}}$$

(……. 1.20)

The value of $K_{j/pot}^{pot} = 1$ at $Z_i = Z_j$ indicates equal response to both 'i' and 'j'. Similarly the values of $K_{j/pot}^{pot} < 1$ indicates that the sensor responds more to 'i' in comparison to 'j' and vice-versa for $K_{j/pot}^{pot} > 1$. However, when $Z_i \neq Z_j$, the value of selectivity coefficients indicating equal response to primary (i) and interfering (j) ions.
This method is also known as Fixed Interference method (FIM) and is the most widely used procedure as per IUPAC recommendation for determining selectively coefficients. In conclusion, it must be pointed out that the selectivity coefficient data depends to a great extent on the method used for the determination and also on the concentration level of the primary as well as the interfering ion, and on the nature of the electrode membrane.

1.8.2.3. Response time

Another important factor besides linear response that commends the use of ISEs or membrane electrode is the promptness of the response of the electrode. The response time of an ion-selective electrode is the time needed to attain equilibrium value (i.e. to obtain a steady potential) within ±1 mV after a ten-fold increase or decrease in the concentration of the test-solution. However, the interpretation of response time varies from a group of workers to others. Punger et al. [582-585] have discussed this aspect in details.

1.8.2.4. Effect of pH

The membrane electrodes with polymer binders like PVC do response to change in the pH value of the solutions. So it is necessary to study the effect of pH and the favorable working range of pH has to be evaluated for accurate measurements. Since in membrane electrodes one or other polymeric binder was used for the construction of the membrane, it is necessary that one finds out the effect of pH on the electrode response. The electrode could be safely used for measurements of their ions provided the pH of
the solutions used falls in the range where the electrode response does not change with the pH, and this pH range is used as working pH range of the electrode.

1.8.2.5. Life span of membrane electrode

Ion-exchanger membrane electrodes can be used for one to three months in continuous service. This short lifetime may be related to the gradual loss of the ion-exchanger through the porous membrane. The membrane, internal filling solution and the ion-exchanger are replaced when the electrode response becomes noisy or drifts.

So, in order to find out the life time of the electrode, the electrode response were noted every week and response curve is drawn for the data usually at the initial period some changes in the response are noted vis-à-vis the slope of the response curve but after the week or so, the electrode response remains fairly constant over a period of time after this period the electrode starts behaving erratic, therefore cannot be used for any measurements. This period over which the electrode response is constant can be called a life of electrode. The life of studied membranes ranges from 45 to 120 days.

1.8.3. Literature review on membranes and ion-selective electrodes

At present the membrane technology has been a thrust area of research. The membrane research involves several scientific disciplines. Polymer chemists, physical chemists, chemical engineers, medical professionals, bio-technologists and environmentalists, all are keenly taking interest in the membrane science and technology. A number of separation processes like electrodialysis, ultrafiltration, hyper filtration (reverse osmosis), microfiltration, nanofiltration and gas separation
processes involve the membranes in one way or the other way. A particular category of membranes has also been used as potentiometric sensors. The present thesis deals with the ion-exchange membranes obtained by embedding composite ion-exchangers as electroactive materials in polymer binders, i.e. epoxy resin (Araldite) or poly(vinyl chloride) (PVC) and have been extensively studied as potentiometric sensors, i.e. ion-sensors, chemical sensors or more commonly ion-selective electrodes. Keeping these limitations in mind the review is confined mostly on the ion-exchange membranes mainly studied as potentiometric sensors.

A large number of ion-selective electrodes using ion-exchangers have been developed during the past 25 years. The literature survey reflects good volume on this topic and it is very difficult as well as unmanageable to compile all of them here. The research work on these ion-selective electrodes has begun in 1920’s but their systematic studies started after E. Pungor et al. [586,587] in 1961. They studied the behavior of silver iodide precipitates as a model substance. Undoubtedly, the findings of Pungor’s group given like an opening for the research in this field. These ion-selective electrodes (ISEs) become alternate of complicated instruments like visible spectrophotometer, atomic absorption spectrophotometer, inductively coupled plasma instrument and electron spectrophotometer for chemical analysis etc. for the determination of various cations and anions. Research in the field of ISEs was enormously stimulated by the publication by Frant and Ross [588,589] of their articles on the fluoride and calcium ion-selective electrode. A number of review articles [590-599] have come across from time to time towards the work done by various eminent persons. These review articles deals with the subject on theoretical
as well as on practical fronts. A lot of applications have also been their interest in
analytical, chemical, pharmaceutical and in environmental disciplines. Most of the
membranes have been prepared in the form of pellets by pressing the material in an
inert polymer like PVC, silicone rubber, polystyrene, polyethylene etc. Use of PVC
matrix membrane is not by any means restricted to ion-selective electrodes and the
simple fabrication can easily put their selectivity to wider service in selective
extraction and even for the transport of ions against their concentration gradients.

An epoxy resin (e.g. Araldite) first used by Coetzee et al. proved to be the
most suitable and widely used material. They have worked on thallium(I)
heteropolyacid salt-epoxy resin membranes in their studies and they also have
determined Cs⁺ potentiometrically [600,601]. Tungstoarsenate based ion-selective
membranes have been developed by Malik et al. [602] and found very much suitable
in the determination of Cs⁺ and Ti⁺ ions. However, there have been only a few
reports concerning thallium(I) ion-selective membrane electrodes [603-612]. They
need to be improved with regard to their low selectivities against alkali metal ions,
linearity and pH-dependence [612]. The thallium(I) selective electrodes based on
crown ether were described [607-610]. These crown ether-based ISEs exhibited good
slope of calibration plots and the electrode response was stable over a wide pH range.
However, the Ti⁺ selectivity against K⁺ for one of the bis(15-crown-5)s was fairly
poor [607]. Yamashoji et al. [613] found that Ti⁺-selective PVC membrane electrodes
based on dibenzo-20-crown-6 (DB20C6) and dibenzo-22-crown-6 (DB22C6) show
higher selectivities to Ti⁺ than that of symmetrical dibenzo-18-crown-6 (DB18C6).
The electrode based on DB18C6, DB20C6 or DB22C6 showed a linear response to

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the $\text{Tl}^+$ activity over a range of $3.2 \times 10^{-2} - 1.0 \times 10^{-1}$ M $\text{TiNO}_3$ with a slope of 59 mV per decade. Calix[4] pyrrole and quinoline-carbonitriles have been reported as $\text{Tl}^+$ PVC based ion-selective electrodes [614,615]. Park et al. [616] have reported different calix[4] for the preparation of $\text{Tl}^+$ ion selective membrane electrodes. Recently, thallium(1)-selective membrane potentiometric sensor based on dibenzyl diaza-18-Crown-6 was reported by Khayatian et al. [617].

There has been widespread interest in developing ion-selective electrodes (ISEs) for determining alkaline earth metals, as they exist in diverse samples. Amongst the alkaline earth metals, most investigated and developed ISEs are $\text{Ca}^{2+}$-selective electrodes. The first $\text{Ca}^{2+}$-selective electrode was a liquid membrane electrode developed by Ross [589]. It was prepared by using a liquid membrane of didecyl-phosphate in di-n-octyl phosphonate. The useful $\text{Ca}^{2+}$-selective electrodes were developed by Thomas, Moody and coworkers [618,619] by incorporating Ca-bis[2,6-dinitro-4-(1,1,3,3-tetramethylbutyl)] phenoxide and Ca-bis[di{4-(1,1,3,3-tetramethylbutyl) phenyl}] phosphate in PVC. These electrodes have fast response time, showed good selectivity for $\text{Ca}^{2+}$ over a large number of cations. McKervey and coworkers [620] have reported the $\text{Ca}^{2+}$-selective electrodes based on Calix[6] arene tetraphosphine oxide with excellent characteristics. The ligand, calix[6] arene bearing phosphine oxide ligand groups on the lower rim and this is the first report that such ligands can discriminate in favor of calcium ions against magnesium ions and other alkaline metal ions. This calcium selectivity is in complete contrast to the behavior of the known calix[6] arene tetraester derivatives, which are selective for sodium against other alkali metal ions and group II ions. Electrodes based on PVC
membrane incorporating ligand display almost Nernstian slopes and excellent selectivity against common interferents, including magnesium. The electrodes demonstrated effective lifetimes of at least 7 weeks and very fast response times.

Didina et al. [621] studied the influence of H\(^+\), Li\(^+\) and Cs\(^+\) on the potential of the Ca\(^{2+}\)-selective PVC electrode membrane comprising thenoyl trifluoroacetone, a complexing ion-exchanger and triheptylphosphate, as a plasticizer. The anomalous behavior of these cations was explained by the formation of association between cations and ion-exchanger. Chattopadhyaya and Misra [622] reported the Ca\(^{2+}\)-selective heterogeneous precipitate based membrane using Ca(II) rhodizonate as the electroactive material. The electrode was used as an indicator electrode in the precipitation titration of CaCl\(_2\) with Na\(_2\)C\(_2\)O\(_4\).

Little work has been done on the developments of ISEs for two alkaline earth metal ions, Mg\(^{2+}\) and Sr\(^{2+}\). Only few such electrodes are reported which show interference to other alkaline earth metal ions. Recently, an electrode prepared using a membrane of phenylene bis(ditolyolphosphinoxide) in PVC was reported as Mg\(^{2+}\)-sensor [623]. The electrode showed good selectivity towards Mg\(^{2+}\) over Ca\(^{2+}\) and worked well in the concentration range 6.0 \(\times\) 10\(^{-5}\) - 1.0 \(\times\) 10\(^{-1}\) M. Another electrode for Mg\(^{2+}\) has been developed by O'Donnell and coworkers [624] using various octamethylene bis(malonic acid diamides) and tris(malonic acid diamides) in PVC with 2-nitrophenyloctyl ether as solvent mediator. Maj-Zurawska [625] has reviewed the requirements for the magnesium ionophores used in ion-selective electrodes. The search for the best magnesium ionophores, in particular having good selectivity for magnesium over calcium led to study of different groups of compounds, \(\beta\)-diketones,
monoamides of carboxylic acids, bis- and tris-malondiamides, as well as some of their compounds. As the analytical applications of magnesium ion-selective electrodes are mainly connected with clinical analysis, so the possibility of simple determination of ionized magnesium in blood offers a number of diagnostically important information in medicine.

The characteristics of Mg$^{2+}$-selective electrode with a polymeric membrane and self-made electrode body are presented by Leoca and coworkers [626]. Membranes are based on PVC-HMW, with different plasticizers N,N'-diheptyl-N,N'-dimethyl-1,4 butanediamide (ETH 1117) as neutral ligands and a various amounts of lipophilic salt. The electrode exhibits a linear response in the concentration range $10^{-5}$-$10^{-1}$ M Mg$^{2+}$ ions with a slope of 23.1 mV/decade. The electrode showed good selectivity towards Na$^+$ and K$^+$ and presented considerable interference from Ca$^{2+}$. The pH of the test solution influences the response which was found to be over pH = 10 and under pH = 5. Meyerhoff et al. [627] described the effect of non-ionic surfactant containing poly(ethylene oxide) units (Brij 35 and Triton X-100) within these structure and alkyl-N-methyl glucamide (MEGA) based surfactants on the potentiometric response of neutral carrier based Mg$^{2+}$-selective electrodes. Results are presented for plasticized PVC membranes doped with Mg carrier ETII 7025 along with the lipophilic anionic additives. Experiments were carried out in model electrolyte solutions and the compositions were found to be similar to that of the blood serum. The ion selectivities of Mg$^{2+}$-selective membrane electrodes can be affected greatly by the presence of Brij 35 or Triton X-100 in the sample.
The first useful Sr\(^{2+}\)-selective electrode was developed by Baumann [628] using strontium complex of polyethylene glycol as electroactive material. The electrode was selective towards Sr\(^{2+}\) over Ca\(^{2+}\) and other bivalent cations with the exception of Ba\(^{2+}\) and Hg\(^{2+}\). Srivastava and Jain [629] have reported a heterogeneous membrane using hydrous thorium oxide embedded in polystyrene while Jain et al. [630] have used strontium tungstoarsenate in araldite for Sr\(^{2+}\)-selective electrodes. The membrane electrode has been used as an end point indicator in the potentiometric titration involving Sr\(^{2+}\) ions against diammonium hydrogen phosphate. Jain et al. [631] have also reported strontium(II)-selective potentiometric sensor based on ester derivative of 4-tert-butylcalix[8] arene in PVC matrix. The sensor exhibited a good potentiometric response to Sr\(^{2+}\) over a wide range 3.2 \times 10^{-5} - 1.0 \times 10^{1} \text{ M} with a Nernstian slope 30 mV per decade. The membrane electrode was utilized in the potentiometric titration of Sr\(^{2+}\) against EDTA. Cs\(^{+}\) ion-selective membrane electrode based on ethylene glycol-functionalized polystyrene microspheres into a palsticized PVC matrix containing sodium tetrakis-[3,5-bis(trifluromethyl)phenyl] borate as ion-exchanger was developed by Peper et al. [632]. The electrodes were evaluated with respect to Cs\(^{+}\) in terms of selectivity, sensitivity and dynamic response.

Ba\(^{2+}\)-selective polymeric membrane electrodes have been constructed from lipophilic electrically neutral carriers [633] and neutral carboxylic polyether antibiotic [634,635] and have been found suitable for the titration of Ba\(^{2+}\) in non-aqueous media as well as for the determination of SO\(_4^{2-}\) in the combustion products. The membranes of benzo-15-crown-5 and its Ba\(^{2+}\)-complex prepared by using an
epoxy resin binder were also found suitable as Ba\(^{2+}\)-sensor [636]. These electrodes showed good selectivity for Ba\(^{2+}\) and also used for the titration of Ba\(^{2+}\) against SO\(_4^{2-}\).

Thomas and coworkers [637] have prepared two ISEs for Ba\(^{2+}\) that make use of the membranes of non-ionic, Antarox CO-880 and its Ba-complex in PVC matrix. The electrodes were assessed for measuring SO\(_4^{2-}\) by analate subtraction. Bouklouze and coworkers [638] have used ethylene/vinylacetate-based membranes of binaphthyl polyether as Ba\(^{2+}\) sensors. The sensors worked in the concentration range 3.0 \(\times\) 10\(^{-6}\) - 1.0 \(\times\) 10\(^{-1}\) M Ba\(^{2+}\) and have been used as indicator electrodes for determining the end point in the potentiometric titration of SO\(_4^{2-}\) in mineral water.

Zhang [639] published a micro review on the determination of rare earth with ion selective electrodes. The review reports the construction of rare earth electrodes, the types of electroactive materials including metal oxides, salts and rare earths containing polymers and organic reagents used. W. Jinlan et al. [640] prepared a heavy rare earth ion-selective electrode containing Ag/AgCl as an internal electrode using ytterbium-containing polystyrene as the active material. The electrode is found to be feasible for the determination of heavy rare earths at pH 5.5-6.3 in flow injection system. Solid-state electrodes were prepared in PVC matrix showed the better sensitivity than other electrodes for the rare earth determination [641-643]. Chattopadhyaya et al. [644] prepared the coated wire ion selective electrode (CWISE) for La(III) using lanthanum(III)-p-nitrobenzeneazo-chromotrope-213 as an electroactive material. Agarwal et al. [645] have reported the rare earth hydroxamate complexes as sensor material for the ion-selective electrodes. The use of crown ethers in the determination of rare earth metal ions has also been explored. Shih [646]
has reported the Cs\(^+\) selective PVC membrane electrodes based on 15-crown-5-
phosphotungstic acid (PW), 12-crown-4-PW, 1,4-dithia-12-crown-4 and 1,4-dithia-
15-crown-5 as neutral carriers. These crown ether electrodes exhibited good linear
response of 60 mV/decade for cesium. Pan et al. [647] synthesized the saturated
urushiol crown ether rare-earth complexes (Ln = La-Nd) by the reaction of lanthanide
nitrate and DSU 30C10 in acetonitrile solution. The lanthanum ion-selective
electrode exhibited the linear responses in 1 \(\times\) 10\(^{-2}\) - 1 \(\times\) 10\(^{-6}\) M La(NO\(_3\))\(_3\). This
electrode showed better selectivity than other La(III) electrodes reported in the
literature.

Only few zinc selective electrodes [648-659] are reported in literature and
most of them have poor sensitivity, selectivity, long response time and short life time
[648-655]. An electrode was fabricated by incorporating zinc salts of bi(4-
octylphenyl) hydrogen phosphate in PVC matrix [648] but the electrode showed
serious interference from some metals. Linnersund and Bhatti [649] tried zinc
complex of bis(2-ethylhexyl) phosphate, an extractant, as electroactive material for
preparing Zn\(^{2+}\)-selective electrodes but it had a very narrow working pH of range 4.5-6.0.

Lebedeva and Jansons prepared Zn\(^{2+}\)-selective electrodes using saturated
solutions of Zn-quinoline-8-carbodithioatein chloroform [650]. Kojima and Kamata
[651] used tetrabutylthiuram disulfide as the carrier in PVC based membrane
electrode. Zinc orthophosphate and zinc mercuric thiocyanate [652] were used by
Rocheleaw and Purdy as electroactive material on a carbon support for the
fabrication of Zn\(^{2+}\)-selective sensors. The electrode worked well but suffered
interference from Cu\(^{2+}\), Cd\(^{2+}\) and Pb\(^{2+}\). Another electrode, based on salicylaldoxime-
formaldehyde resin, for zinc [653] exhibited a working concentration range of 3.0 \mu M - 0.1 M with a near Nernstian slope. A zinc-selective electrode was used by Obmetho et al. [654] for the determination of zinc in zinc alloys. Srivastava et al. [655] used a cryptand for the fabrication of zinc selective sensor but it exhibited a non-Nernstian response. Zn-bis(2,4,4-trimethylpentyl) thiophosphinic acid complex was also used for fabricating Zn^{2+}-selective sensor [656] but it suffers interference from copper. Crown ether based electrode has also been reported [657] in literature for zinc. It exhibited a working concentration range of 70 \mu M - 0.1 M with a Nernstian slope of 29.5 mV/decade of activity. Shamsipur et al. [658] reported a zinc-selective sensor based on benzo substituted macrocyclic diaramides. An electrode based on 5,6,14, 15-dibenzo-1,4-dioxo-8,12-diazacyclpentadecane-5,14-diene showed response for zinc [659]. It has a working concentration range of 5\mu M - 100 \mu M in the pH range of 1.5-7.0.

Chelating ion-exchanger resins are found to possess specific selectivity for some metal ions and play an important role in separation processes. Wardak et al. [660] studied the properties on the ion selective electrode with a chelating pseudo-liquid membrane phase for Zn^{2+} determination. A porphyrin based potentiometric sensor for Zn^{2+} determinations was prepared by Gupta et al. [661]

Literature survey reveals that the first Ni-ISE was developed by Pungor and coworkers [662] using nickel-dimethyl glyoxime complex. Later on, heterogeneous membranes of nickel phosphate [663] in paraffin and silicone rubber, bis-2-(ethylhexyl) phosphate [664] in PVC and nickel complex of 1,4,8,11-tetraazacyclotetradecane [665] in araldite were used for preparing Ni^{2+} selective
electrodes. Chelating ion-exchange resin (1-hydroxy-2-naphthaldoxime-formaldehyde polymer) containing nitrogen and oxygen donor atoms are prepared and characterized by Srivastava et al. [666]. The resin behaved as a selective cheating ion-exchanger for some metal ions. The PVC based membrane electrodes for the resin showed a Nernstian response for Ni$^{2+}$ over a wide concentration range ($2.94 \times 10^{-3} - 5.87 \times 10^{-3}$ M) between pH 3.0 and 7.5. The electrode is found to possess adequate stability and specific selectivity with a response time of 10 s. The sensor can also be used in partially non-aqueous medium having a 35% (v/v) non-aqueous content.

Polyvinyl chloride based membrane of 4,4',4",4"'-21H,23H-porphine-5,10,10,15,20-teray) tetrakis (benzoic acid) (TBAP) and 2,3,7,8,12,13,17,18-octamethyl-21H, 23H-porphine (OMP) were prepared using dibutylphthalate (DBP), dioctylphthalate (DOP), dibutyl(butyl)phosphonate (DBBP) and 1-chloronaphthalene (CN) as plasticizing solvent mediators and sodium tetraphenylborate as an ion-excluder for Ni$^{2+}$ selective sensor [667].

A PVC membrane nickel(II) ion-selective electrode was constructed by Mousavi et al. [668] using 1,10-dibenzyl-1,10-diaza-18-crown-6 (DBzDA18C6) as a neutral carrier. The sensor exhibited a Nernstian response for Ni(II) ions over a wide concentration range $5.5 \times 10^{-2} - 2.0 \times 10^{-5}$ M. It has a relatively fast response time and can be used for at least 6 weeks without any considerable divergence in potentials. The proposed sensor revealed relatively good selectivity for Ni(II) over a wide variety of other metal ions.
Pentacyclooctaaza have been explored as a neutral ionophore for preparing poly(vinyl chloride) (PVC)-based membrane sensors selective to Ni(II) [669]. The optimized membrane incorporating pentacyclooctaaza as the active material, dibutyl phthalate as plasticizer and sodium tetraphenyl borate as an anion excluder and membrane modifier in PVC in different ratio's was directly coated on the surface of a platinum-wire electrode. The electrode exhibited a near Nernstian response in the concentration range of $1 \times 10^{-6}$ to $1 \times 10^{-1}$ M Ni(II). The limit of detection, as determined from intersection of the extrapolated linear segments of the calibration graph, was $6 \times 10^{-7}$ M. It has a response time between 5 and 40 s for nickel concentrations ranging from $1 \times 10^{-1}$ to $1 \times 10^{-6}$ M. The electrode revealed moderate selectivities over a number of alkali, alkaline earth and several transition and heavy metal ions. The electrode is suitable for use in aqueous solutions in a wide pH range of 3-6. It was applied as an indicator electrode for the end point detection in the potentiometric titration of Ni(II) with ethylenediaminetetraacetic acid (EDTA) and determination of nickel content of chocolate and milk powder samples.

Due to the vital importance of copper in many biological systems [670,671] and industry [672], the urgent need for a copper-selective electrode for potentiometric monitoring of Cu$^{2+}$ in different industrial, medicinal and environmental samples, a variety of ion carriers have been used in the construction of copper(II) selective electrodes. These copper ion carriers include small size thiacrown ethers [673,674], non-cyclic neutral ionophores containing dithiocarbamate groups [675,676] and nitrogen atom [677], calix [673], arenes [678], Schiff's bases [677,678-681] and macrocycles di-amides [682] various species.
However, all of these copper sensors have one, two or in some cases, all of the following problems: (1) high detection limit, (2) narrow working concentration range and (3) serious interfering effect of cations such as Fe$^{3+}$, Na$^+$, Sr$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cs$^+$, K$^+$, Hg$^{2+}$, Ag$^+$. Potentiometric measurements with a Cu$^{2+}$ ion-selective electrode allow directly determining free ion concentration in water samples. For copper determination, solid membrane electrodes based on copper sulfide [683-686], tungsten oxide [687], ion-exchangers [688,689] and copper(III) complexes [690-695] as electroactive material have also been tried as copper potentiometric sensors. In order to obtain on macrocyclic polyethers [696,697] and polymethylidene [698] have been developed. Talantsev and Syroratskaya [699] determined Cu$^{2+}$ potentiometrically by using ISEs with a crystal membrane, which is found to be more sensitive than the photometric method using diethylthiocarbamate. Comparative analyses were made with river water and the method has better characteristics than the photometric method and can be used for the analysis of natural and wastewaters. Banes et al. [700] have synthesized a novel highly copper(II) selective chelating ion-exchanger electrode based on poly(glycidyl methacrylate-co-ethylene dimethacrylate) beads modified with aspartic acid derivatives.

A copper(II) ion-selective electrode based on copper(II) salicylaniline Schiff’s base complex in styrene-co-acrylonitrile copolymer (SAN) has been developed by Gupta et al. [701]. The SAN-based membrane electrode containing copper(II)-Schiff’s base complex, dioctylphthalate as plasticizer and sodium tetraphenylborate as an anion excluder exhibited a linear response with a Nernstian slope of 30 mV/decade within the concentration range of $1 \times 10^{-6} - 1 \times 10^{-2}$ M of Cu$^{2+}$ ions. The
selectivity of electrode for Cu^{2+} ion has been found to be better in comparison to other various interfering ions. The prepared electrode can be used successfully as an indicator electrode for the potentiometric titration of the Cu^{2+} ion using EDTA. Ganjali et al. [702] have also reported a novel copper selective electrode by using a new Schiff’s base bis-2-thiofenal propanediamine (TPDA) as an excellent neutral carrier for the potentiometric monitoring of ultra trace amount of Cu^{2+} ions. The membrane electrode was successfully used for the direct determination of copper in black tea and as an indicator electrode in potentiometric titration of copper ion.

Mashhadizadeh et al. [703] have prepared a new PVC membrane electrode that was highly selective for Cu(II) ions. The electrode was prepared by using 3,6,9,14-tetraithiabicyclo [9.2.1] tetradeca-11,13-diene as a neutral carrier. The electrode exhibited a Nemstian slope of 28 mV per decade change in concentration over a wide range i.e. 10^{-7} M Cu^{2+}.

Polypyrazolylmethanes, represented by the general formula II_{4n}C(pz)n (pz:1-pyrazolyl), form a six-membered MN_{4}C chelate ring of a shallow boat configuration, acting as tridentate or bidentate ligands. Yoshimoto et al. [704] developed novel ion-selective membrane electrodes based on polypyrazolylmethanes and report the first results of their use. HC(pz)_{3} (1), HC(3,5 Me_{2}pz)_{3} (2), HC(3-Phpz)_{3} (3), HC(3-iPrpz)_{3} (4), HOCH_{2}C(pz)_{3} (5), and C(pz)_{4} (6) were prepared as described in the literature and incorporated as an ionophore in PVC membrane. The selectivity of the electrodes changed with the substituents of polypyrazolylmethanes. The electrodes of 3,4 and 6 were selective for Cu^{2+} at pH 5.5. The electrode 4 showed rapid response time (~ 10 s) and reproducible results for more than 4 months, and successfully applied to
potentiometric titration of Cu$^{2+}$ with EDTA. Recently, Fakhari et al. [705] reported a Cu(II) ion-selective membrane electrode based on $2,2'$-[1,2-ethandiyl-bis(nitrilomethylidene)-bis]meta cresole(I), $2,2'$-[1,2-ethandiyl-bis(nitrilomethylidene)-bis] ortho cresole(II), and $2,2'$-[1,2-ethandiyl-bis(nitrilomethylidene)-bis] para cresole(III) as excellent neutral ion carriers.

In measuring the heavy metal ions like Cd$^{2+}$ in the industrial wastewater, the ion-selective electrodes are very convenient because of simplicity and selectivity. Ross et al. [706,707] have reported the precipitate based solid state CdS-Ag$_2$S mixture membrane by stoichiometric reaction. Also, Hirata et al. [708] have developed the ceramic solid-state CdS-Ag$_2$S mixture membrane by baking the CdS-Ag$_2$S mixed powder or its pressed membrane at 700 °C. Hopertenam and Cosma [709] have reported some preparation methods for mixtures of cadmium and silver sulfides with Cd$^{2+}$-selective electrode properties. Sodium sulfide, thioacetamide and sodium thiosulfate were used for simultaneous precipitation of CdS and Ag$_2$S.

The selectivity of the Cd$^{2+}$ ion-selective electrode is affected by Cu$^{2+}$, Pb$^{2+}$ and Fe$^{3+}$ ions co-existed in industrial wastewater. Also, it interfered by an oxidizer such as chlorine or hypochlorite ion. The detection limit and the calibration curve were slightly changed by pH of samples as in basic solutions Cd$^{2+}$ ion becomes cadmium hydroxide Cd(OH)$_2$. In the acidic solution, the detection limit becomes inferior owing to the increasing of solubility of CdS. All sample measurements should be performed in the best pH region. Therefore, the buffer solution for Cd$^{2+}$ ion measurement such as Orion TISAB (total ion strength adjustment buffer) [710] for the fluoride ion measurement, which could mask the interfering substances, was
developed for the practical use. Loginova and Chernysheva [711] have also reported the Cd\(^{2+}\)-buffer for potentiometry with ion-selective electrodes in micellar media.

Srivastava et al. [712] have reported a plasticized PVC based membrane of benzo-15-crown-5, which exhibited a good response for Cd\(^{2+}\) in a wide concentration range \((3.16 \times 10^{-5} - 1.00 \times 10^{-1} \text{ M})\) with a slope of 20 mV/decade of [Cd\(^{2+}\)]. The electrode was used at one stretch, for a period of 2 months and is played good selectivity for Cd\(^{2+}\) over alkali, alkaline earth and transition metal ions. The membrane sensor was also used as an indicator electrode in potentiometric titration involving Cd(II) ions. Parez-Marin and coworkers [713] have used 2-furoyl-3-benzyl-3-phenylthiourea, which was deposited on an epoxy resin and employed as neutral barrier for the ion detection of cadmium. The sensor exhibited a Nernstian slope of 29.8 mV/decade. Potential response of Cd(II) ion-selective electrode based on cyanocopolymer matrixes and 8-hydroxyquinoline as ionophore was evaluated by Gupta and D'Arc [714]. The cyano groups of the copolymers contributed significantly to enhance the selectivity of the electrode. The electrode showed an appreciable average life of 6 months without any significant drift in the electrode potential, which is explained considering phase boundary model based on thermodynamics considerations.

Shamsipur and coworkers [715] have developed a cadmium(II) ion-selective membrane electrode based on newly synthesized \([1,1'\text{-bicyclohexyl}]1,1'2,2'-\text{tetrol}\) as membrane carrier. The proposed membrane sensor showed excellent discrimination ability towards Cd\(^{2+}\) ion with regard to several alkali, alkaline earth, transition and heavy metal ions. It was successfully applied for the direct determination of Cd\(^{2+}\) in
solution and as an indicator electrode in potentiometric titration of cadmium ions. Singh et al. [716] have reported a polystyrene based membrane of 3,4,12,13-dibenzo-2,5,11,14-tetraoxo-1,6,10,15-tetracyclooctadecane as a membrane carrier for Cd\(^{2+}\) ions. It was found that some amounts of surfactants do not disturb the functioning of the sensor and also used to estimate Cd\(^{2+}\) ions in real samples.

Because of the increased industrial use of lead, at one hand and its serious hazardous effect to human health, on the other [717], the electrochemical properties and preparation of the Pb(II) ion-selective membrane electrodes have been extensively studied by using different active materials. Thind et al. [718] have developed Pb\(^{2+}\) ion-selective membrane using lead antimonate as an electroactive phase and araldite as a polymer binder. Khan et al [314,315,355-357] have published their finding for the determination of Hg(II), Cd(II), Pb(II), by potentiometric titration using polypyrrole/polyantimonic, polyaniline Sn(IV) tungstoarsenate, polyaniline Sn(IV) arsenophosphate, polypyrrole Th(IV) phosphate, polyaniline Sn(IV) phosphate and poly-o-toluidine Zr(IV) phosphate electrically conducting organic-inorganic composite based ion-selective membrane electrodes.

Gupta et al. [719] have published their results on the studies of araldite based Zr(IV) tungstophosphate (ZWP) membrane as Pb(II) ion-selective electrode. ZWP is a cation-exchanger has been used as an electroactive phase. Besides the solid-state membranes [720-725,] and liquid ion-exchange membranes [726,727], there has been increasing interest to the use of ionophore ligands as sensing materials for neutral carrier type Pb(II) ion-selective electrodes, mainly due to the unique selectivities of
these compounds. Most of the about 20 Pb\(^{2+}\)-selective ionophores described so far have been characterized in ISEs [728].

In 1986, Shpigun et al. [729] used five macrocyclic ligands as Pb carriers in PVC membranes plasticized with 66% dioctylphthalate or o-nitrophenyl octyl ether. Dibenzo-18-crown-6 and diazadibenzo-18 crown-6 was found to be good carriers for Pb\(^{2+}\)-selective electrodes for potentiometry in solutions containing 2 \(\times\) 10\(^{-6}\) – 1 \(\times\) 10\(^{-2}\) M Pb(II) ions. In 1987, Navikov et al. [730] used dibenzo-18-crown-6 and 3,17-diazadibenzo-18-crown-6 as carriers for lead selective electrodes. Lead in environmental samples was determined using an ISE by Li and Liu [731]. In 1995, a PVC-based membrane of 15-crown-5 was used by Srivastava et al. [732] for a lead selective electrode. Tavakkoli and Shamsipur [733] had reported a Pb-ISE based on dibenzopyridino-18-crown-6 as membrane carrier. This lead selective electrode exhibited comparatively good selectivities with respect to alkali, alkaline earth and some transition and heavy metal ions. Malinowska et al. [734] have reported a lead selective membrane electrode containing ionophores based on diaza-18-crown-6 units possessing amide and sulfonamide functions. Malinowska et al. have also reported polymeric membrane ion-selective membrane electrodes based on thioamide functionalized calix[4] arenes for which the selectivity coefficients for Pb\(^{2+}\) relative to Cu\(^{2+}\) were 10\(^{-3}\)-10\(^{-4}\) [735]. While Ohki et al. [736] have made solvent polymeric membrane ISEs by using 12 kinds of N,N\(_2\)-dialkylamide derivatives of the dibenzopolyether dicarboxylic acids as Pb\(^{2+}\) selective neutral carriers. Potentiometric selectivities of the ISEs for the Pb\(^{2+}\) over other heavy metal cations, alkali metal cations and alkaline earth metal cations have been assessed. Another Pb\(^{2+}\)-selective
membrane electrode based diaza-18-crown-6 was reported by Mousavi et al. [737]. They constructed a PVC membrane lead(II) ion selective electrode using 1,10-
dibenzy1-1,10-diaza-18-crown-6 as membrane carrier. This electrode was employed as an indicator electrode in potentiometric titration of EDTA with lead ions and used for direct determination of lead in wastewater. Bis(2-ethylhexyl) phosphate is quite suitable for making a Pb$^{2+}$ selective electrode. Thus an electrode constructed using bis(2-ethylhexyl) phosphate and bis(1-butylpentyl) adipate as a solvent mediator in a PVC membrane matrix showed high selectivity and sensitivity [727]. When (2-ethylhexyl) group was replaced by benzyl group, the sensitivity and selectivity to Pb$^{2+}$ were considerably improved. Thus, Xu and Katsu [738] employed dibenzyl phosphate and bis(1-butylpentyl) adipate as a solvent mediator in a PVC membrane matrix exhibited a near-Nernstian response to Pb$^{2+}$ in the concentration range from 3 × 10$^{-6}$ to 1 × 10$^{-2}$ M with a slope of 30.1 mV per concentration decade. They have also employed tetrabenzyl pyrophosphate and biphenyl phosphinic anhydride with two phosphoryl groups as liganding sites, which can be used as novel ionophores to make Pb$^{2+}$-selective membrane electrodes. A good result was obtained with tetrabenzylpyrophosphate and the electrode based on this ionophore and the electrode membrane matrix with PVC exhibited a near-Nernstian response to Pb$^{2+}$ in the concentration range of 1 × 10$^{-5}$ – 1 × 10$^{-2}$ M with a slope of 28.7 mV/concentration decade in a solution containing 0.1 M Mg(NO$_3$)$_2$. Addition of potassium tetrakis(p-chlorophenyl) borate (40% mol relative to tetrabenzyl-pyrophosphate) caused a drastic change in the response slope (53.3 mV/concentration decade), probably due to
the formation of PbA\(^+\), where A stands for anions present in the sample solution, and decreased significantly the electrode selectivity to other metal cations [739].

9,10-Anthraquinones are the largest group of natural quinines and have significant chemical importance. In addition to a wide variety of chemical and industrial applications [740], recently synthetic derivatives of anthraquinones have employed as a lead carrier in PVC membrane. Shamsipur et al. [741] used four different 9,10-anthraquinone derivatives to characterize their abilities as lead(II)-ion selective electrodes in PVC matrix membrane. The electrode based on 1,8-dihydroxy-2,7-bis(prop-2'-enyl)-9,10-anthraquinone exhibited a Nernstian response for Pb\(^{2+}\) ions over a wide concentration range (2.0 \times 10^{-3} - 2.0 \times 10^{-6} \text{ M}). Another 9,10-anthraquinone derivatives e.g., bis[(1-hydroxy-9,10-anthraquinone)-2-methyl] sulfide [742] and 1,4-bis(prop-2'-enyloxy)-9,10-anthraquinone [743] have also been used as lead(II) membrane carrier.

The derivative of quinaldic acid, 8-(dodecyl oxy-quinoline-2-carboxylic acid), was used as an ionophores in the development of a Pb(II) selective electrode by Casado et al. [744]. Solvent extraction studies showed that this compound is selective for Pb(II) and Cu(II) over a variety of divalent and monovalent metals. The electrode is selective for Pb\(^{2+}\) over Cu\(^{2+}\), Al\(^{3+}\), Ni\(^{2+}\), Co\(^{2+}\), Zn\(^{2+}\), Mg\(^{2+}\), Ca\(^{2+}\), Na\(^{+}\) and K\(^{+}\) with Hg\(^{2+}\) and Cu\(^{2+}\) the most interfering metal ions. Mousvi et al. [745] studied a PVC-based capric acid membrane potentiometric sensor for lead(II) ions. The optimum composition of the membrane was 30 wt.% PVC, 60 wt.% NPOE as plasticizers, 5 wt.% ionophore and 5 wt.% potassium tetrakis(p-chlorophenyl)borate as lipophilic salt. The electrode was used for the potentiometric titration of chromate ions with Pb\(^{2+}\) ions.
Sadeghi and Shamsipur [746] has reported a PVC membrane electrode for Pb\(^{2+}\) ions based on tetraphenylporphyrin. The sensor exhibited a Nernstian response for Pb\(^{2+}\) ions over a wide concentration range (1 \times 10^{-5} - 1 \times 10^{-2} \text{ M})\). The proposed electrode showed a fairly good discriminating ability towards Pb\(^{2+}\) ions in comparison to some alkali, alkaline earth, transition and heavy metals ions and was used as an indicator electrode in potentiometric titration of Pb\(^{2+}\) ions. They have also reported ion-selective membrane electrode for the determination of Pb\(^{2+}\) ions based on a non-cyclic ion-carrier, piroxicam [747]. In competition to PbS-based Pb(II) electrodes, the piroxicam-lead(II) ISE demonstrated the advantage of virtually no interference from some common transition metal ions such as Fe\(^{3+}\), Co\(^{2+}\), Ni\(^{2+}\), Cd\(^{2+}\), Zn\(^{2+}\), Hg\(^{2+}\) and only slight interference from alkaline earth metal ions is observed.

Ganjali et al [748] have employed 5,5'-dithiobis-(2-nitrobenzoic acid) as a suitable ion carrier to construct a lead selective electrode PVC based membrane which exhibited significantly high selectivity to lead ion over alkali, alkaline earth and several transition metal ions.

Ganjali et al. [749] have reported a PVC membrane electrode for Pb\(^{2+}\) ion based on recently synthesized dimethylbenzotetrathiafulvalene as membrane carrier. The electrode has found a very low limit of detection of 8 \times 10^{-6} \text{ M} and can be used as an indicator electrode in potentiometric titrations of Pb\(^{2+}\) ions in both H\(_2\)O and 90\% MeOH solutions.

Kulapina et al. [750] proposed lead selective electrode from tetraphenylborates of lead(II) complexes of polyhydroxyethylated nonylphenols with various number of hydroxyethyl groups. Parez-Marin et al. [751] studied the 1-furoyl-3-(2-
hydroxyethyl)thiourea as ionophores for lead(II) in electrode of liquid membrane of neutral carrier. This PVC polymeric membrane was deposited drop wise directly into a composite graphite-epoxy support. The sensor exhibited a Nernstian slope at 29.17 mV/decade and a linear response range between $4 \times 10^{-5}$ – $6.9 \times 10^{-3}$ M.

Isidak [752] has reported the solid state lead(II) ion selective PVC membrane electrode using dimethylene bis(4-methylpiperidinethiocarbamate) as a neutral ionophore and nitrophenyloctyl ether or dioctylsebacate as plasticizers. They found that the response properties of solid state contact PVC membrane electrode prepared with nitrophenyloctyl ether was better that those of the membrane electrode prepared with dioctylsebacate.

Ensaf et al. [753] have prepared the lead(II)-selective membrane electrode by incorporating cryptland(222) as the neutral carrier into a plasticized PVC membrane. The electrode was used as an indicator electrode in the potentiometric titration of Pb$^{2+}$ with EDTA. In this connection, more recently they have also reported the use of 1-phenyl-2-(2-quinolyl)-1,2,-dioxo-2-(4-bromo) phenylhydrazone (PQDBP) as an excellent neutral carrier in construction of a lead-PVC membrane electrode [754]. The membrane electrode was also applied to the titration of Pb$^{2+}$ solution with potassium chromate as well as determination of lead in mineral samples. Vardhan and Singh [755] have reported a lead(II)-selective electrode having a chelating ion-exchange resin (salicylaldoxime-formaldehyde polymer) containing nitrogen and oxygen donor atoms, as electroactive material. The characteristics of two ion-selective electrodes based on PVC and polystyrene membrane in the presence of interfering ion has been studied. The ion-exchange coefficients and diffusion of
Pb(II) in Nafion-modified electrodes were determined by Liu et al. [756] in the process of ion-exchange. Yang et al. [757] have reported the use of diazacrown ethers bearing double armeed thenoyl and thipheneacetyl groups as potential selective agents for Pb$^{2+}$ ion-selective membranes. Acyclic amides oxamides have also been investigated as potential inophores for lead [758,759]. Kamata and Onoyama [760,761] used acyclic dithiocarbamates as inophore for Pb$^{2+}$ ion-selective electrodes. Jabar et al. [762] have introduced liquid ion-exchange membranes incorporating the tetraphenylborate salts of nonionic surfactant polyoxylates for the preparation of lead selective sensor. Shamsipur et al. [763] reported the use of hexathia-18-crown-6-tetraone (HT-18C6TO) as an excellent neutral carrier in construction of lead PVC membrane electrode. Ganjali et al. [764] introduced a high selective and sensitive lead ion selective membrane coated on a graphite (CGISE) for potentiometric monitoring of ultra trace amount of Pb$^{2+}$ in environment samples by using N,N,N- dimethylcyano diaza-18-crown-6 (DM-CDA18C6) as an excellent ionophore. Jeong et al. [765] described the fabrication and characterization of new lead ion-selective electrode based on $N,N$-bis(salicylidene)-2,6-pyridinediamine as an ionophore. The coordinating effect for the selective response of lead ion was also investigated by using PVC membrane.

Lee at al. [766] have reported the lead(II)-selective electrodes based on porphyrin atropisomers tetrakis(2-hydroxy-1-naphthyl). The membrane electrode displayed a good Nernstian response (29.2 mV/decade) to Pb$^{2+}$ over the linear range of $3.2 \times 10^{-5}$ to $1 \times 10^{-1}$ M. Most of metal ions would not affect the selectivity of the lead electrode seriously. Jain et al. [767] studied in detail a comparative study of
Pb\textsuperscript{2+}-selective sensors based on the membrane of 2,12-dimethyl-7,17-diphenyltetrapyrazole (I) and 5,11-dibromo-25,27-dipropoxycalix[4]arene (II).

Mahajan et al. [768] reported a mercury ion selective electrode based on the \( p \)-tert-butyl calix[4] crown derivatives with imine units as an inophore. The electrode exhibited a good response for mercury(II) ions over a concentration range of \( 5.0 \times 10^{-5} - 1.0 \times 10^{-1} \) M with a near Nernstian slope of 27.3 mV per decade. The electrode showed high selectivity for Hg(II) ions over most of the alkali, alkaline earth and transition metal ions. Fe\textsuperscript{3+} and Ag\textsuperscript{+} ions were found to be the interfering ions. Mashhadizadeh et al. [769] reported the use of Schiff base ligand recently synthesized in his laboratory [770] of bis[5-((4-nitrophenyl)azo salicylaldehyde)](BNAS) as an excellent neutral carrier in construction of mercury(II)-PVC membrane electrode. The electrode was utilized as a potentiometric sensor for the titration of mercury(II) solution with EDTA.

Gupta et al. [771] reported the electroanalytical applicability of a diamine donor ligand as mercury ion sensor. The results presented in this paper showed that the sensor developed for Hg(II) ion using the above system as electroactive phase in a PVC matrix has a wide working concentration range and a fast response time with reproducible results.

The construction, performance, and applications of coated-wire mercury(II) selective electrodes based on 2-mercaptobenzimidazole (MBIM) and hexathiacyclooctadecane (IIT18C6) carriers, in plasticized PVC matrix, were described by Mazloum et al. [772]. The influences of membrane composition and pH on the potentiometric response of the electrodes were investigated. The electrodes
exhibit near Nernstian responses for Hg$^{2+}$ ions over a wide concentration range (4 to 5 decades of the concentration), and a detection limit of about $6 \times 10^{-7}$ M. The response time of the electrodes is between 20 and 100 s, depending on the concentration of mercury, and they can be used for about 2 months without any considerable divergence in potential. The proposed sensors revealed good selectivity for Hg$^{2+}$ in the presence of several metal ions. The best selectivity was observed for the electrode based on MBIM carrier. They were used as indicator electrodes in the potentiometric titration of Hg$^{2+}$ with EDTA and for the determination of mercury in wastewater samples.

Mahajan et al. [773] reported mercury(II) ion-selective electrode based on alicylaldehyde thiosemicarbazone (I) as an ionophore. Thiosemicarbazones are an important class of ligands with enormous biochemical applications [774]. The electrode exhibited high selectivity for mercury(II) ions over alkali, alkaline and some transition metals (Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Ba$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Pb$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Cd$^{2+}$, Fe$^{3+}$, Ag$^+$). This is the first report on use of a thiosemicarbazone as ionophore for metal ions [775-777]. The membrane electrode was also applied in the titration of Hg$^{2+}$ with I$^{-}$ ion.

Lu et al. [778] reported the hitherto unknown selective complexation of the (1-thiazole) azo-functionalized calix[6]arene derivative as a novel ionophore used in a mercury ion-selective PVC membrane electrode. In this work, the effect on the response of changing the acidity and the anionic site and the response characteristics of the electrode produced were investigated. The results showed that the proposed electrode could be applied in real samples.
Dithiazone [779], dithia crown ethers [780], hexathia-18-crown-6-tetraone [781] and 2-mercaptobenzimidazole were also used as potential selective agents for Hg$^{2+}$ PVC membrane electrodes having a good Nernstian response and high ion selectivity. Recently, 1,3-diphenylthiourea [782] has been reported as a very selective ionophore for the Hg$^{2+}$ ISE, but the applicability has not been described.

Mercury (II) ion-selective PVC membrane sensor based on ethyl-2-benzoyl-2-phenylcarbamoyl acetate (EBPCA) as novel nitrogen containing sensing material was developed by Hassan et al. [783]. The sensor exhibited good linear response of 30 mV per decade within the concentration range $1 \times 10^{-6} - 1 \times 10^{-3} \text{ M Hg(II)}$. The sensor shows good selectivity for mercury(II) ion in comparison with alkali, alkaline earth, transition and heavy metal ions. The proposed sensor was also applied as a sensor for the determination of Hg(II) content in some amalgam alloys. Jain et al. and Srivastava et al. have also fabricated polystyrene supported heterogeneous ion-exchange membrane electrode of heteropolyacid salts (e.g. Ce(IV) selenite), which were found to be selective for Hg$^{2+}$. Recently, Abbas et al. [784] have reported a new triiodomercurate-modified carbon paste electrode for the potentiometric determination of Hg(II) ions. Potentiometric determination of Hg(II) was also reported by some other workers [785-787].

Potentiometric membrane sensors for uranium(IV) were commonly prepared using phosphate esters [788-790], phosphites [791], phosphine oxides [792], diphosphine oxide [793], acyclic oligoethers with terminal phosphonate groups [794], butyl calixarene [795] and macrocyclic [796] ionophores. Bifunctional chelating agent O-methylidihexylphosphine oxide O'-hexyl-2-ethyl phosphoric acid
has also been proposed as a single molecular unit which combines the overall properties of the synergetic properties of phosphine oxide and ester of phosphoric acid [797] and has been used as an electroactive material in a membrane sensor. Hydroxy-acetophenone oxime-thiourea-trioxane resin [798], dihydroxy propiophenone oxime formaldehyde resin [799], tertiary ion association complexes of uranyl ion with ethyl violet-benzoic acid [800] and binary complexes with 2-thenoyl trifluoroacetone [801] have also been used in polymeric membrane based uranyl sensors. Many of these sensors, however, suffer from the disadvantages of a narrow range of response [794], interference from associated anions [788,799] and some common cations [796,798] and the need for several time consuming steps for ionophore preparation [798,799,802].

Although bis(ethylhexyl) phosphate ester (BEIIP) has been used in PVC membrane sensors responding to uranyl ions [788], the more lipophilic derivative tris(ethylhexyl)phosphate (TEHP) has never been examined. On the other hand, a literature survey showed that O-(1,2-dihydro-2-oxo-1-pyridyl)-N,N,N',N'-bis(tetramethyl)uranium hexafluorophosphate (TPTU) has no analytical applications despite the presence of four active chelating centers in its structure [803]. Both reagents are commercially available and are used either as a solvent or as a peptide-coupling agent. Therefore, DTP A and TPTU reagents were examined by Hassan et al. [804] as novel ionophores in PVC based membrane sensors for uranyl ions. Sensors with optimized membrane composition displayed enhanced selectivity, stability, fast and linear response for a wide concentration range of uranyl ion.
Characterization and applications of these sensors for quantification of uranium in certified and naturally occurring ores are also described.

A less attention has been made for determining tripositive metal ions. Very few potentiometric devices have been designed for aluminum [805-809]. Saleh et al. [810] have reported a novel potentiometric membrane sensor for selective determination of Al(III) ions. In this PVC matrix membrane sensor incorporating 7-ethylthio-4-oxa-3-phenyl-2-thioxo-1,2 dihydropyrimido[4,5]pyrimidine ionophore has been used as membrane carrier for Al$^{3+}$ ions. This electrode has a minimum interference of Pb$^{2+}$ and Hg$^{2+}$ ions and successfully applied for the potentiometric titration of HPO$_4^{2-}$ with Al$^{3+}$ and for direct potentiometry of Al$^{3+}$ content of some rock samples. A novel Fe(III)-selective PVC membrane electrodes based on formylsalicyclic acid derivatives were also reported by Saleh [809]. Fe$^{3+}$ ion-selective membranes sensor based on the use of coated wire anionic membrane incorporating tetrachloroferrate(III)-aliquate suffered from significant interference from many cations such as Sn$^{2+}$, Hg$^{2+}$ and Zn$^{2+}$ [811]. These difficulties also arise on using a heterogeneous solid-state cation-exchanger membrane with stannic arsenate dispersed in epoxy resin [812]. Volkov et al. [813] have developed a Fe(III) selective solid phase electrode with an ion-sensitive material Fe(III) metavanadate.

A literature survey revealed that very little work has been done on the development of ISEs for Cr(III) ion, the first report on Cr(III) was in 1980 [814], in this study a PVC based chromium(III)-wire electrode was made by incorporating (Aliquat 336$^-$–Cr(SCN)$_4^-$) ion pair, and the electrode gave a fully linear response in the Cr(SCN)$_4^-$ concentration range of 10$^{-5}$–10$^{-2}$ M and has the Nernstian slope of 58
mV per decade of Cr(III) concentrations.

In 1983 [815], a Cr(VI) selective electrode with PVC membrane based on triheptyldodecylamonium iodide was described. The response of the electrode was Nernstian for Cr(VI) concentration down to $2 \times 10^{-6}$ M in 0.03–0.13 M HF solution with limit of detection of $5 \times 10^{-7}$ M. In 1984 [816], PVC matrix membrane Cr(VI) selective electrodes based on ethyl violet or victoria blue were prepared at pH 3.5 and in concentration range of $2.5 \times 10^{-5} - 1 \times 10^{-1}$ M of Cr(VI). The detection limit of this electrode was $1.1 \times 10^{-5}$ M.

In 1987 an ion selective electrode for determination of chromium(III) was reported. In this electrode 8-quinoline-dithiocarboxylate was used as a membrane-active substance [817]. In 1989 an ion-selective electrode based on chromium dithizonate was built that was a precipitate based selective electrode [818]. Almost 10 years ago it was estimated that more than 7000 papers on ISEs had been published [819]. Numerous ISEs based on PVC membrane were reported for many inorganic ions [820], but very little was published on PVC-based trivalent ions. A PVC-based Cr(III) ion selective electrode which was recently been prepared is based on a macrocyclic compound with a concentration range of $1.77 \times 10^{-6} - 0.1$ M and a Nernstian slope of 20 mV per decade [821]. Abbaspour and Izadyar [822] reported a PVC matrix ion selective electrode for chromium(III), which is based on 4-dimethylaminoazobenzene with a concentration range of $1.66 \times 10^{-6} - 1 \times 10^{-2}$ and limit of detection $8.0 \times 10^{-7}$ M and also possessed the advantages of simplicity of the design in membrane preparation.
A poly(vinyl chloride) membrane based on glyoxal bis(2-hydroxyanil) as membrane carrier was prepared by Gholiyand et al. [823] and investigated as a Cr(III)-selective electrode. The electrode has a linear dynamic range of $3.0 \times 10^{-6} - 1.0 \times 10^{-2}$ M with a Nernstian slope of 19.89 mV per decade and a detection limit of $6.3 \times 10^{-7}$ M. It has a fast response time of 20 s and can be used for at least 3 months without any considerable divergence in potential. The membrane sensor has been used very successfully for the analysis of some food materials and alloys for the determination of Cr(III) ion. A polystyrene based membrane of tetraazacyclododecane-1,4,9,12-tetraene macrocyclic ionophore was used as Cr(III) ion-selective electrode by Singh et al. [824]. The electrode has been found to be chemically inert and of adequate stability with good reproducibility over a period of 100 days. The membrane electrode worked satisfactorily in a partially non-aqueous medium up to a maximum 30% (v/v) content of methanol and ethanol. The selectivity coefficient values indicated that the membrane electrode is highly selective for Cr(III) ions over a number of monovalent, diivalent and trivalent cations.

Few reports on Ce(III)-selective electrodes based on 1,2,3-trithiane [825,826] sulfonamide [827], azomethine of pipronylidine-4-[2.2]paracyclophenylamine [828] and aminobenzothiazol [829] as ionophores were developed as sensors for Ce(III) ions. The selectivity coefficients recorded by these electrodes showed interferences of some cations such as Hg(II) and Fe(III).

A novel ion-selective PVC membrane sensor for cerium(III) ions based on [4-(4'-nitrobenzyl)-1-phenyl-3,5-pyrazolidinedion) (NBPP) as a new ionophore has been prepared and studied by Saleh et al. [830]. This electrode has a wide linear
dynamic range from $10^{-1}$ to $2.5 \times 10^{-6}$ M with a Nernstian slope of 29.5 mV per decade and low detection limit of $1.6 \times 10^{-6}$ M. It has a fast response time (<10 s) and good selectivity with respect to different metal ions. The proposed electrode has also been used successfully as an indicator electrode in potentiometric titration of phosphate and oxalate in aqueous media and carbonate, fluoride and acetylsalicylate in some drugs.

1.8.4. Applications of ion-exchanger based membranes and ion-selective electrodes

The membrane separation technology occurred more than a quarter century ago when Srinivasa Sourirajan, a physical chemist working at the University of California, Los Angeles, announced the development of the first synthetic symmetric membrane that could be used for “surface skimming” of sea water or brackish water for the production of pure water by ion-exchange membranes. Besides these, the membrane technology has been in practice in water treatment to provide potable water. Neosepta type ion-exchange membranes prepared by Mizutani et al. [831] were used mainly for chemical utilization of desalination of seawater in Japan.

Recently, polymer based inorganic ion-exchanger membranes have become a research target because the exchangers act as an electroactive phase and polymers (i.e., cellulose acetate, polysulfone, polypropylene, polyvinylidene, regenerated cellulose, polyacrylonitrile, polyamide, polycarbonate, organic conducting polymers, etc.) provide binding support to these material to shape into membrane. These membranes are being investigated towards their employment as biosensors, chemical
sensors and ion-selective electrodes. These ion-exchange membranes having some charge over them therefore may be utilized for the recovery of selective ionic species from industrial effluents in better way and may be helping tool to solid waste management. Thus, ion-exchange membranes have been extensively employed in various applications i.e., in fuel cells, acid recovery, stabilization baths, such as aluminum anodizing, steel pickling etc., substitution reactions-adjustment of acid in juice production of inorganic and organic chemicals, chloralkali cells, electrodialysis, purification of $\text{H}_2\text{SO}_4$ and $\text{HCl}$, recovery of $\text{HNO}_3$ and $\text{HF}$, extraction of transition metals by using liquid ion-exchange membranes, and in a number of environmental pollution abatement processes like solid waste management, etc.

Nowadays, many efforts have been taking to improve the method of preparations of different kind of ion-exchange membranes. Recently, Towe and Yagar [833] have reported the different method of manufacture and its uses of ion-exchange membrane. Terada et al. [834] prepared polyolefin based heterogeneous ion-exchange membranes with low electrical resistivity and high mechanical strength comprising ion-exchange resins (e.g., Diaions SK-18, Diaion SA-10A), and binder polymers containing LDPE and EPR or EPDM.

Sata [835] reviewed with 24 references on the preparation of the composite ion-exchange membranes. The composite membranes have applications to lithium battery, ferric and ferrous ion redox cell and humidity sensors. While Sengupta et al. [836] made the selective removal of heavy metals from sludges or soil using composite ion-exchange membranes. Xu et al. [837] manufactured the ion-exchange membranes with microporous polypropylene having a thickness of 15-50 $\mu$m.
Wang et al. [838] made the selection of inorganic ion-exchangers for removing cesium. They studied the properties of five series and twenty types of inorganic ion-exchangers for removing Cs(I) from acidic high-level radioactive liquid waste. The results showed that Ti[Fe(CN)₆]/K₄[Fe(CN)₆] prepared by sol-gel technique had high mechanical property, excellent ion-exchange property and their selection as the ion-exchanger for removing Cs(I) from high level radioactive liquid waste. Xu et al. [839] also reviewed with 37 references on the development and applications of ion-exchange membranes in the treatment of industrial wastewaters.

Determination of Ca²⁺ and Mg²⁺ by potentiometric titration using ion-selective electrode as the indicator electrode, and EGTA and EDTA as the titrants were reported by Fang and Dan [840]. The method was used to determine the amount of Ca²⁺ and Mg²⁺ in mineral water and silicate samples with satisfactory results. Similarly, Agarwal et al. [841] determined the water hardness directly by using Mg(II) ion-selective electrodes comprising Mg(II)-N-phenylbenzohydroxamate complex as an electroactive material. This membrane electrode exhibited almost equal selectivities for Ca²⁺ and Mg²⁺, thus can be used for the simultaneous determination of both ions. Recently, Gupta et al. [842] have also reported the amount of hardness of water using heterogeneous inorganic ion-exchanger based Mg(II)-selective electrode. Stephen et al. [843] used the immobilized molten salt membrane based magnesium sensor for aluminum-magnesium melts. The activity of magnesium in the aluminum-magnesium melt was determined with respect to a pure magnesium reference contained in the inside of the thimble and sealed from the surrounding atmosphere and melt by zirconia based cement. Measurements were
conducted in various commercial aluminum-magnesium alloys under inert atmosphere as well as in air.

A short review on the application of membrane technology in food technology has been reported in the literature [844]. Lee et al. [845] investigated many PVC membrane electrodes for the determination of basic drugs like chlorpromazine, amityline, nortiptyline, etc. Wen et al. [846] have reported a methylene blue PVC membrane electrode based on methylene blue-phosphotungstate ion pair complex as electroactive material and its successful use in the determination of methylene blue in injection. A good agreement for the results of methylene blue content in injection between the potentiometric method and the United State Pharmaceutical standard procedure are found. An anticancer drug e.g., tetracycline hydrochloride was successfully determined by using both coated wire and the conventional polymer membrane types electrodes by Issa et al. [847]. These electrodes are based on incorporating the tetracycline-phosphotungstate ion association in plasticized PVC film. Recently, Sirkar [848] reviewed the application of membrane technologies in the pharmaceutical industry with 29 references. This review covers the most recent application of membrane technologies in blood range of separation, concentration and purification needs. A number of technologists and scientists have also found the new areas to employ the ion-selective electrodes in various types of analyses of blood, plasma serum and of surfactants.

A heterogeneous membrane in which Zr(IV) tellurite gel was embedded in polystyrene and used to prepare an electrode that was used by Srivastava et al. [849] for the estimation of Cr(IV) in water, and in tannery and plating wastes. Recently,
Pareau et al. [850] have developed a novel procedure for purification of liquid industrial effluents by eliminating the heavy metals ions. In this, an emulsion liquid membrane extraction process was developed to recover lead and cadmium from industrial effluents. The best carrier was found to be the Cyanex 301 or a mixture of cyanex 301 and Aliquat 336. Similarly, Pradelle and Cueille [851] focused on the inorganic membrane-innovation process for the chemical industries.

Zhou et al. [852] determined the aluminum powder content of propellant powder (Type-71-25) with a fluoride ion-selective electrode. Sakurai et al. [853] determined the Fe(III) ion concentration in acidic solution for the treatment of steel, stainless steel and special steel by using a copper ion electrode or a redox electrode. Similarly, Ion et al. [854] have reported the potentiometric determination of Fe(III) in fertilizers using ion-selective electrode with liquid membranes, which is based on the complex crystal violet-tetrachloroferrate(III). Li and coworkers [855] have reported the fast determination method of free calcium in human milk with ion-selective electrode. Wang [856] have developed the principle and method for determining the lime concentration in soil with pH glass electrode and PVC membrane calcium ISE. The neutral carrier ETH 1001 is used as the electroactive material for the calcium ion-selective electrode.
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