Review

Review on Composite Cation Exchanger as Interdicipilinary Materials in Analytical Chemistry

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Green chemistry and technology is the design of chemical manufacturing systems to minimize their adverse affects on the environment. Thus, a primary goal of green chemistry and technology is to reduce the environmental impact of chemical processes and chemical manufacturing while simultaneously enhancing the overall process performance. Although it is beneficial to simply reduce the use of organic solvents in chemical processes, green chemistry and technology goes further, in that it evaluates the entire thing to identify techniques that can be applied to minimize the overall process hazard, while maintaining economic practicality. Evaluation of the environmental impacts of the manufacturing process requires a systematic approach and appropriate metrics that permit quantitative assessment of environmental hazards. Thus, this review begins with a introduction of cation-exchange materials the drivers for green technology and the metrics through which processes can be started. Then, the cation-exchange materials have so many applications described in this review and their many derivative and we describes inorganic to nanocomposite cation exchange materials and their technological improvement from old era to latest age of nano because green chemistry can be applied to real processes. Two elements are specifically highlighted: (*a*) the use of new materials to facilitate active and selective chemistry and the use of said materials within removal of environment hazardous.

1. INTRODUCTION

Organic polymers showed the properties of chemical stability through synthetic methods [1]. The inorganic ion-exchange materials based on polyvalent metals have been established now with an excellent recognition in various disciplines, i.e. metal ion separation, catalysis, environmental studies, medical science (kidney dialysis), ion-selective electrodes preparation, heterogeneous solid state membranes formation and in ion-exchange fibers preparation, etc. Besides other advantages, these materials are important in being more stable to high temperature radiation field than the organic one [2].

In order to obtain associated organic and inorganic materials as ion-exchangers, attempts have been made to develop a new class of composite ion-exchangers by the incorporation of electrically conducting organic polymers (polyaniline, polypyrrole, polythiophene, poly-o-toluidine, poly-o-anisidine etc.) into the matrices of inorganic precipitates of multivalent metal acid salts. These composite materials are attractive for the purpose of creating high performance or high functional polymeric materials that are expected to provide many possibilities, termed as 'organic-inorganic' hybrid ion-exchangers [3-7] with better chemical, mechanical, and thermal stabilities, reproducibility and possessing good selectivity for heavy metals indicating its useful environmental applications. Many 'organic-inorganic' composite ion-exchangers have been developed earlier by incorporation of organic monomers into inorganic matrix, by way of pillaring or non-pillaring methods [8-12]. Few such excellent ion-exchange materials have been developed and successfully being used in environmental analysis [13-16].

Inorganic precipitate ion-exchanger based on organic polymeric matrix must be an interesting material, as it should possess the mechanical stability due to the presence of organic polymeric species and the basic characteristics of an inorganic ion-exchanger regarding its selectivity towards some particular metal ions [17-20]. In this regard, a number of 'organic-inorganic' composite cation-exchanger samples such as poly-o-toluidine Th(IV) phosphate and poly-o-anisidine Sn(IV) phosphate were prepared by mixing poly-o-toluidine and poly-o-anisidine into inorganic precipitate gels of Th(IV)phosphate and Sn(IV) phosphate under varying conditions. In order to determine the composition, size, structural and thermal properties of these materials several physico-chemical investigations were carried out by elemental analyses, atomic absorption spectrophotometry (AAS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), spectral analyses (FTIR), thermal analyses (simultaneous TGA-DTA) and X-Ray analysis. Their thermal stabilities were studied at various temperatures and chemical stabilities of the composite in various acidic, alkaline and organic media. This review represents the preparative conditions and physico-chemical properties of these composite cation-exchange materials.

Analytical chemistry is a measurement science consisting of various ideas and methods that are useful in all fields of science, medicines and industry. Today everyone has to know. What is in the food? What is in the water? What is in the air? Quantitative analysis establishes the chemical identities of the species in the sample. Quantitative analysis determines the selective amounts of these species in numerical terms. We can classify analytical methods according to the nature of the measurement used. Gravimetric method determines the mass of the analyte and some component chemically related to it.

In a volumetric method, the volume of a solution containing sufficient reagent to react completely with the analyte is measured. Electyroanalytical method involves the measurement of such electrical properties as potential, current, resistance and quantity of electrical charge. Spectroscopic methods are based on measurement of the interaction between electromagnetic radiation and analyte atoms and molecules or on the production of such radiations by analyte.

Methods of separation are important for detection and determination for different kinds of species present in a sample. Chromatographic methods are important and useful in the modern techniques of chemical analysis. Different type of chromatography include such as size exclusion chromatography, in which molecules are separated based on their size by passing through a porous structure stationary phase; ion-exchange and ion chromatography, in which ion are separated based on their charge; and gas chromatography, in which gaseous solutions are separated based on their adsorption on stationary phase. High performance liquid chromatography is a modern development based on the above principle but using micrometer-sized particles for the stationary phase so that equilibrium is achieved rapidly and separations are performed rapidly. Supercritical fluid chromatography uses a mobile phase that is intermediate between gas and liquid, exhibiting advantages of both in solute solubility. Various types of plane chromatography are described in which the stationary phase is in the form of sheet or flat surface.

2. ION-EXCHANGE CHROMATOGRAPHY

This separation method is based on ion-exchange process occurring between the mobile phase and ion-exchange groups bonded to the support material. In highly polarize ion, additional non-ionic adsorption processes contribute to the separation mechanism. In inorganic ion-exchange materials, the stationary phase consists of polystyrene, ethylevinylbenzene, or methacrylate series co-polymerized with divinylbenzene and modified with ion-exchange groups.

Inorganic-cation exchangers with much more satisfactory properties have been prepared by combining group IV oxides with the more acidic oxides of group V and VI. For example, Zirconium Phosphate with variable $ZO_2:P_2O_3$ ratios have been obtained by precipitation with alkali phosphates or phosphoric acid from the solution of zirconyl chloride. Organic-inorganic ion-exchange materials are the new development of composite ion-exchange materials.

Ion-exchange chromatography is used for the separation of both inorganic and organic amines and cations.

3. ION-EXCHANGE PROCESS AND ITS MECHANISM

The ion-exchange process became established as an analytical tool in laboratories and in industries, as chiefly practical chemists interested in effects and performance etc studied it. The primary condition of an ion-exchange process is the stoichiometry. In organic resins, it is an established fact [17]. 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:

$$\overline{AB} + B\ (aq) \ \leftrightarrows \ \overline{BX} + A\ (aq) \tag{1}$$

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 equilibrium 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, it was the first time when quantitative formation of ion-exchange equilibrium had been made by Gane by using the mass action law in its simplest form without involving the concept of activity coefficients. This concept was further accounted by Kielland [18] and finally, a suitable choice of general treatment was given by Gaines and Thomas [19]. Many workers have studied the thermodynamics of cation-exchange on zirconium (IV) phosphate [20-22]. 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 were examined. Ion-exchange isotherms and calorimetric heats of exchange were determined on samples varying from amorphous to highly crystalline [23-26].

However, from the practical point of view, the mass action approach is simpler. Nancollas and coworkers [27,28] have interpreted the thermo dynamical 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 [29] who calculated the equilibrium constants and other thermo dynamical parameters viz. ΔG^o, ΔH^o and ΔS^o. Similar studies have been made on anion-exchanger also [30]. Ion-exchange equilibria of alkaline earth metal ions on different inorganic ion-exchangers such as tantalum arsenate [31], iron (III) antimonate [32], antimony (V) silicate [33], zirconium (IV) phosphosilicate [34] and alkali metal ions on iron (III) antimonate [35] and α -cerium phosphate [36]. Other interesting thermodynamic studies relate to the adsorption of pesticides on inorganic and composite ion-exchangers have also been studied in these laboratories [37,38]. 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 [39] 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 solid ion-exchangers or conversely the rate with which the exchangeable ions are released from the exchanger. Later on Boyd et al. [40] 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. Reichenberg had studied the kinetic of metal ions on sulphonated polystyrene. 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).

4. ION-EXCHANGE MATERIALS: AN INTRODUCTION AND LITERATURE REVIEW

4.1. Inorganic ion-exchange materilas

Creating chemical compounds with the desired physical and chemical properties produces synthetic ion-exchangers. On the basis of chemical characteristics of 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) (Ferro cyanides)

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 inorganic ion-exchangers prepared so far are given in Table 1 [41-86].

4.2. Organic ion-exchange materials

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: $-SO_3^-$, $-COO^-$, $-PO_3^{2-}$, $-AsO_3^{2-}$ etc. in cation-exchangers, and $-NH_3^+$, $-NH_2^+$, $-N^+$, $-S^+$ 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 salvation tendency of the fixed ion groups,
- The size and extent of the salvation 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 (10 to 100% capacity loss), owing to physical degradation at both the molecular and macroscopic leval.

Table 1. Various inorganic ion-exchange materials based on Tin(IV) and Th(V) prepared so far and their silent features.

S. No.	Material	Nature	Composition	Empirical formula	Selectivity	Ref.
(I) Tin based exchangers						
1.	Stannic phosphate	Amorphous	P:Sn = 1.25 – 1.50	$SnO_2.0.62P_2O_5.nH_2O$	Na(I), Li(I), K(I), Rb(I), Cs(I), Cu(II), Zn(II), Ni(II), Co(II)	[41] [42]
		Crystalline	---	$SnO_2.P_2O_5.2H_2O$	Zr(IV)	
2.	Stannic tungsto-phosphate	---	Sn:W:P 2:1:3.2	---	---	[43]
3.	Stannic EDTA	Amorphous	---	---	---	[44]
4.	Stannic molybdo-phosphate	---	Sn:Mo:P 1:0.33:2.0	---	---	[45]
		Semi-crystalline	Sn:Mo:P= 40:26.5:0.7	---	Cs^+, Sr^{2+}	[46]
5.	Tin oxide (hydrated)	Amorphous	---	---	$[Fe(CN)_6]^{4+}$, $[Fe(CN)_6]^{3+}$-SCN⁻	
6.	Stannic arsenate	Amorphous	Sn/As = 1.84	---	Pb(II), Fe(III), Al(III), Ga(III), In(III)	[47] [48]
		Crystalline	---	$SnO_2.As_2O_5.2H_2O$	Li(I), Na(I), K(I)	
7.	Stannic antimonate	Amorphous	Sb/Sn = 1.0	$SnO_2.Sb_2O_5.nH_2O$	Cu(II), Ni(II), Co(II)	[49]
8.	Stannic molybdate	Amorphous	Sn/Mo = 1.0	---	Pb(II)	[50]
9.	Stannic selenite	Amorphous	Sn/Se = 1.33 Sn/Se = 1.0	$[(SnO_4)(OH)_2 (SeO_3)_3.6H_2O]$	Li(I), Na(I), K(I), Cu(II), Fe(III), Sc(III), La(III)	[51]
10.	Stannic tungstate	Amorphous	Sn/W = 1.33	---	Co(II), Ba(II), Ni(II), Pb(II), Mn(II), Cu(II), Sr(II)	[52]
11.	Stannic vanadate	Amorphous	Sn/V = 1.0	$[(Sn(OH)_3 V_3O_9.4H_2O]_n$	K(I), Na(I), Li(I)	[53]

12.	Stannic vanado pyrophosphate	Micro-crystalline	---	---	Ag(I), Cu(II), Pb(II), Bi(III), Zr(IV)	
13.	Stannic ferro-cyanide	Amorphous	Sn/Fe = 3.0	$[(SnO)_3(OH)_3.HFe(CN).3H_2O]_n$	K(I), Ba(II), Na(I)	[54]
14.	Stannic silicate	---	---	---	---	[4]
15.	Stannic hexametaphosphae	---	---	---	Ag(I), Pb(II)	
16.	Stannous ferrocyanide	Amorphous	Sn/Fe = 1.0	$[SnO.H_4Fe(CN)_6.2.5H_2O]_n$	Cu(II), Ni(II), Mg(II), Mn(II), Y(III)	[55,56]
17.	Stannic arsenophosphate	Amorphous	Sn :As :P 1 :1 :1	$(SnO_2)_5.(H_3PO_4)_3(H_3AsO_4).nH_2O$	Th(IV), Zr(IV), K(I)	[57,58]
		Crystalline	---	$Sn(HAsO_4)(HPO_4).H_2O$	---	
18.	Stannic molybdo arsenate	Amorphous	Sn:Mo:As 2:1:1	---	---	[59]
19.	Stannic pyrophosphate	Amorphous	$Sn:PO_4^{3-}$ 1:2	---	Zr(IV), Th(IV), Y(III), Bi(III)	
20.	Stannic sulfide	Amorphous	---	---	Cu(II)	[60]
21.	Stannic phosphosilicate	Amorphous	Sn:Si:P 2:2:3	$(SnO_2)_2 (SiO_2)_2 (H_3PO_4). nH_2O$	Hg(II)	[61]
22.	Stannic pyroantimonate	---	---	---	---	
23.	Stannic selenophosphate	Amorphous	Sn:Se:P 1:1:1	---	---	[62]
		Crystalline	Sn:Se:P 4:1:6	$[(SnO)_4 (OH)(HSeO_3)(H_2PO_4)_6]_n.4H_2O$	---	[63]
24.	Stannic selenopyrophosphate	Amorphous	$Sn:Se:PO_4^{3-}$ 1:1:1	$(15SnO.8OH)(10H_2P_2O_7.O_2HSeO_3).5nH_2O$	Ag(I), Pb(II), Sr(II), Zr(IV)	
25.	Stannic tungstoarsenate	Amorphous	Sn:W:As 12:5:2	---	Ba(II), Cu(II)	[64]
26.	Stannic antimonophosphate	Amorphous	---	---	Pb(II), Ce(III), Sm(III)	
		Crystalline	---	---	Pb(II), Sm(III), La(III)	
27.	Stannic vanadoarsenate	Amorphous	Sn :V :As 1.94 :1.14 :1	---	Ba(II)	[65]
28.	Stannic fungstoselenate	Crystalline	Sn :Se :W 7 :1 :18	$[(SnO_2)_7.HSeO_3(HWO_4)_{18}.45H_2O]$	Th(IV), Ce(IV)	[66]
29.	Stannic vanadophosphate	Crystalline	---	---	Ba(II), Cu(II)	[67]
30.	Stannic tungstovanadophosphate	Amorphous	Sn :W :V :P 1 :1 :1 :1	---	---	[68]
31.	Stannic vanadotungstate	Amorphous	Sn :V :W 2 :1 :1	---	Al(III)	[68]
32.	Stannic arsenosilicate	---	---	---	---	[69]
33.	Tin(IV) antimonite	Amorphous	Sn :Sb = 2 :11	$Sn_2[Sb(OH)_6]_{11}.8H_2O$	Pb(II)	[70]
34.	Tin(IV) vanadopyrophosphate	Amourphous	---	---	---	[4]
35.	Tin(IV) sulphosilicate	Crystalline	---	---	---	[71]
36.	Stannic hexacyano ferrate(III)	Amourphous	---	---	---	[72]
37.	Stannic setenoarsenate	Amourphous	Sn :Se :As 1 :1 :1.02	---	Hg(II)	[73]

No.	Name	Form	Ratio	Formula	Ions	Ref.
38.	Stannic iodophosphate	---	---	---	Hg(II)	[75]
39.	Stannic bortophosphate	Amourphous	---	---	---	[76]
40.	Stannic hexacyano Ferrate (II)	---	---	---	Tl(I), Ba(II), Pb(II), Ce(IV), Th(IV)	
41.	Amine bored stannic hexacyano-ferrate (II)	---	---	---	Cd(II), Cu(II), Hg(II)	[77]
42.	Silica based stannic hexacyano-ferrate (II)	Amorphous	Sn:Fe:Si 5:4:2	---	---	[78]
43.	Stannic silicomolybedate					[89]
44.	Sodium stannosilicate	-----	Sn:Si = 1:1	$Na_2(SnO_2)x(SiO_2)y.zH_2O$	Ag(I)	[80]
45.	Stannic vanadophosphate	Crystalline	Sn:V:P = 3:3:10	-------	------	[81]
(II) Thorium based exchangers						
1.	Thorium phospahte	Amorphous	P/Th = 1.9-2.1	-------	Pb(II), Fe(III), Bi(III)	[82]
		Crystalline	$Th/PO_4 = 0.50$	$Th(HPO_4)_2.2H_2O$	Ca(II), Sr(II), Ba(II)	
		Fibrous	------	$ThO_2.P_2O_5.2H_2O$	------	
2.	Thorium arsenate	Crystalline	As/Th = 1.53	$Th(HAsO_4)_2. H_2O$	Li(I)	
3.	Thorium antimonate	Amorphous	Sb:Th = 3.67: 4.27	------	------	[83]
4.	Thorium molebedate	Crystalline	------	------	Fe(III), Zr(IV)	
		Amorphous	Th/Mo = 0.50	-------	Fe(III), Zr(IV), Pb(II)	[84]
5.	Thorium tungstate	Crystalline	Th/W = 2.0	$Th(OH)_2(HO_{42}.nH_2O$	Cs(I), K(I), Na(I)	[85]
			-------	-------	-------	
		Amorphous	------	-------	Bi(III), Hg(II)	[86]
6.	Thorium oxide	Amorphous	-------	$Th(OH)n.nH_2O$	Na(I), Rb(I), Ca(II), Sr(II)	
7.	Thorium tellurite	-------	Th:Te = 1:2	-------	Pb(II), Co(II), Cu(II)	
8.	Thorium phosphosilicate	Amorphous	Th:P:Si = 1:1.2: 8:1.12	$(ThO_2.H_3PO_4H_4SiO_4).6H_2O$	Hg^{2+}	
9.	Thorium iodate	-------	Th:I = 1:1	$ThO_2.I_2O_5.nH_2O$	-------	

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 precooked substantially before their introduction to the ion-exchange media.

4.3. 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. These types of chelating ion-exchangers have been developed recently and their analytical applications explored [87].

Complexions have been used for the preparation of new chelating resins for separating metal ions on the basis of complex formation [88]. A number of such ion-exchangers have been prepared by the incorporation of ligands on resins [89]. 8-hydroxy quinoline [90] sobbed on porasil is capable of separating metal ions at trace level. Ferrochrome black–T modified graphite columns have been used for the separation of metal ions [91]. A PAN [1-(2-pyridylazo-2-napthol)] sobbed zinc silicate [50] has been used for the recovery of precious metal ions Pt^{4+} and Au^{3+}, and ammonium-molybdophosphate [92], has been used for the quantitative separation of Cs^+ ions. Separation and retention behavior of metal ions have been achieved on tetracycline hydrochloride coated alumina [93] and zirconium(IV) selenomolybdate, while tetracycline hydrochloride sobbed zirconium(IV) tungstophosphate chelating exchanger has been employed in the separation of La^{3+} ions [94]. An important feature of chelating ion-exchangers is the greater selectivity, which they offer compared with 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.

4.4. 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. 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. 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 between the sheets of a layered insoluble compound.

Alberti et al. [95] have reported the synthesis and characterization of a new type of zirconium phosphate by the name of zirconium phosphate hemihydrate [α -Zr (HPO$_4$)$_{0.5}$. H$_2$O]. A large number of other new materials have also been prepared on zirconium phosphate by pillaring methods. Alberti and coworkers [96] have intercalated α-Zr(IV)(RPO$_3$)$_2$.H$_2$O by phenyl containing –SO$_3$H groups and γ - Zr(IV)(PO$_4$)(H$_2$PO$_4$).2H$_2$O by crown ether. U. Costantino [97] has given a detailed description of intercalation of alkanols and glycols into α -Zr(HPO$_4$). H$_2$O and also developed zirconium phosphate-phosphite [98]. Clearfield and Tindwa [99] have studied in detail the uptake of n-phenyl amine, n-butyl amine and ethylene diamine on α–Zr(HPO$_4$)$_2$.H$_2$O. Dines et al. [100] 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 α, ω - diphosphonic acids. Varshney et al., Rawat

et al., Singh et al. and Qureshi et al. have also studied on amine tin(II) hexacyanoferrate(II) [101], tin(IV) diethanol amine [8], iron(III) diethanol amine [102] and zirconium(IV) ethylene diamine [103] respectively.

Recently, some intercalation ion-exchangers have been developed and reported in the literature. Hudson et al. [104] have reported the intercalation of monoamine into α- $Sn(HPO_4)_2.H_2O$ and investigated the ion-exchange behavior of amine in the presence of transition metal ions. Wang et al. have reported the selective separation of Cs^+ on zirconium phenyl diphosphonate [105]. Chudasama et al. [106] 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. Malik et al. [107] have reported pyridinium tungstoarsenate, selective for Rb^+ and Cs^+ and Singh et al. intercalated aniline into tin(IV) phosphate [108] and Zr(IV)phosphate, $[(ZrO_2)_2.(C_6H_5NH_2)HPO_3. 3.7H_2O]$; selective for Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} [109]. Nabi et al. have reported the synthesis, characterization and analytical applications of Zr(IV) sulfosalicylate [110] (selective for Ag^+ and Hg^{2+}) and pyridinium-tin(IV) tungstoselenate.

5. ORGANIC-INORGANIC' COMPOSITE ION-EXCHANGE MATERIALS

Composite materials formed by the combination of organic polymers and inorganic materials are attractive for the purpose of creating high performance or high functional polymeric material termed as "organic-inorganic hybrid materials." The conversion of organic ion-exchange materials into hybrid ion exchangers is the latest development in this discipline. The preparation of hybrid ion-exchangers is carried out by the binding of organic polymers i.e. polyaniline, polyacrylonitrile, polystyrene etc. These polymer based hybrid ion exchangers showed an improvement in a number of properties viz chemical, mechanical, radiation stability, improvement in ion-exchange properties and also selective nature for the heavy toxic metal ions. One of the important properties of them is granulometric nature that makes it more suitable for the application in column operations. Hybrid ion exchangers can be prepared as three-dimensional porous materials in which layers are cross linked or as layered compounds containing sulphonic acid, carboxylic acid or amino groups. Some of the hybrid ion-exchangers prepared so far are pyridinium-tungstoarsenate [111], zirconium (IV) sulphosalisylo phosphate, styrene supported zirconium phosphate. Recently, some organic-inorganic composite ion-exchange materials have been developed in these laboratories. Khan et al. have reported polypyrrole Th(IV) phosphate, polyaniline Sn(IV) phosphate [112] polyaniline Sn(IV) arsenophosphate [113], polystyrene Zr(IV) tungstophosphate [114], poly-o-toluidine Th(IV) phosphate [115], poly-o-anisidine Sn(IV) phosphate [116], poly-o-toluidine Zr(IV) phosphate [117], and polypyrrole/polyantiminc acid [13], used for the selective separation of Pb^{2+}, Hg^{2+}, Cd^{2+}, Hg^{2+}, Hg^{2+}, respectively, and ion-exchange kinetics of M^{2+}-H^+ exchange and adsorption of pesticide [118], have also 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 [119] pectin based Th(IV) phosphate [120], with great analytical applications have been investigated by Varshney et al. These materials can be used as ion-exchange membranes and ion selective electrodes [121,122]. Polyaniline

Zr(IV) tungstophosphate has been synthesized by Gupta et al. [94], which was used for the selective separation of La^{3+} and UO_2^{2+}.

6. COMPOSITE MATERIALS

6.1. Composite theory

A combination of two or more materials (reinforcing elements, fillers, and composite matrix binder), differ in form or composition on a macroscale. The constituents retain their identities, that is, they do not dissolve or merge completely into one another although they act in concert. Normally, the components can be physically identified and exhibit an interface between one another. Examples are cermets and metal-matrix composites.

Society has always wanted and continued to seek materials that are strong, tough, and light. In this quest, it was discovered that the macroscopic combinations of two or more different materials resulting in a new material with improved properties could be described as "composite" [123]. Naturally occurring composites are bone, bamboo, feathers, natural fibers, and wood. Bone is an organic-inorganic composite of protein (collagen) and minerals (calcium apatite) and bamboo is cellulose reinforced by silica. These combinations make a hard material with high impact strength. The cellulose cell structure of wood and fiber is bound together with lignin, a natural polymeric substance.

6.2. Nanocomposite materials

Conventional, macroscopic composite materials such as adobe is a mixture of clay and straw that serves as an effective structural composite material which has been used to make bricks and wall in arid regions and these along with reinforced concrete has shaped our world during the past. Yet when it comes to the microscopic world, reduced particle size boosts the importance of the interphase in composite mixtures and this is especially important for a new class of recently developed materials named, the nano - composites.

The definition of "nanocomposite material" has broadened significantly to encompass a large variety of systems such as one-dimensional, two-dimensional, three-dimensional materials, amorphous or crystalline, made of distinctly dissimilar components which are mixed at the nanometer scale.

Nanocomposite is a distinct form of composite materials, which involves embedding nano or molecular domain sized particles into an organic polymer, metal or ceramic matrix material. In all cases, it is perceived that the intimate inclusion of these nanoparticles in these matrices can completely change the properties of these materials. The nanoparticles can serve as matrix reinforcement in order to change the physical properties of these base materials. With such small inclusions, a large amount of interfacial phase material is now included in the bulk of these nanocomposites, enabling a complete transformation of the material's chemical, mechanical and morphological domain structure. Much of today's research activity in the field of polymer based organic-inorganic hybrid nanocomposites exhibits mechanical, electrical properties superior to those of their separate components.

Nanocomposite plastics have their origin in the 1970's with the use of sol-gel technology to form homogeneous dispersions of small sized inorganic particles throughout a polymer matrix. In such systems, the inorganic phase may or may not be chemically attached to the organic phase. These first generation nanocomposites have been found to be useful in coating applications. Subsequently during 1980's, second generation nanocomposites emerged as a result of the resurgence in the use of fine particles, minerals and clay fillers for plastics. Limited compatibility between the filler and polymers as well as complex polymer processing requirements was needed to form these nanocomposites. In the 1990's and beyond, a new form of nanocomposite has emerged third generation nanocomposites where polymeric materials are reinforced with nanofibers such as carbon nanotubes (Fig. 1), SiC whiskers, colloidal silica, nano-clay particles etc. This unique ability to obtain control of the nanoscale structures via innovative "bottom-up" synthetic approaches has consequently entailed several challenges and opportunities. Undertaking this challenge provides an opportunity for developing new materials with synergic behavior leading to improved performance [124].
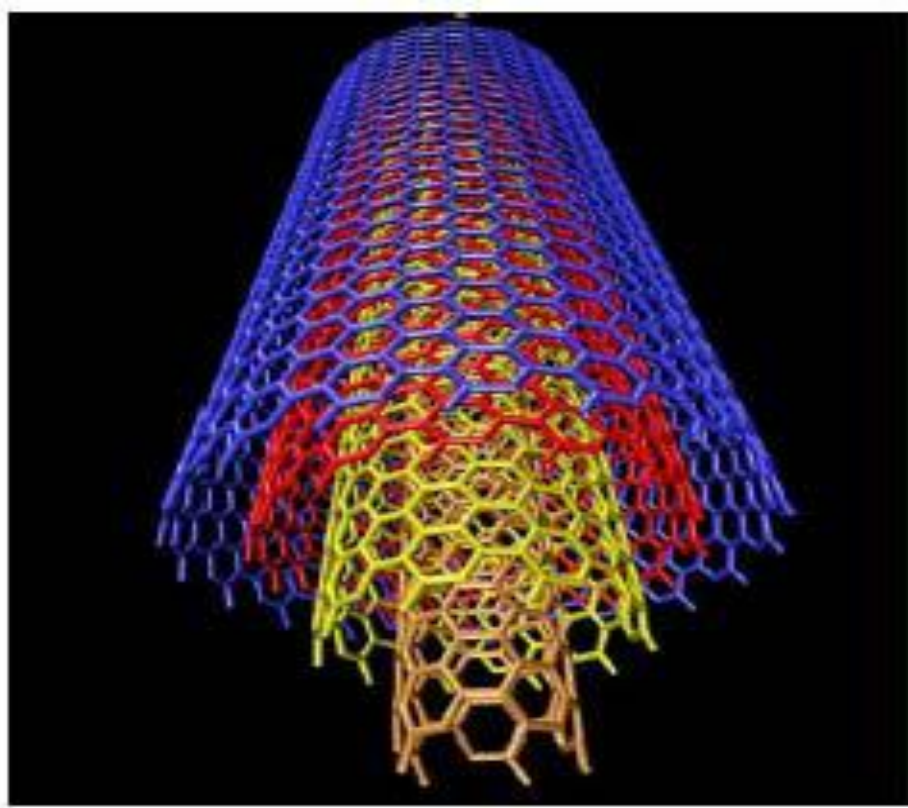

Figure 1. Representation of a multiwall carbon nanotube.

6.3. Guest-host materials interacting in nanocomposites

A great variety of nanocomposite materials can be formed by guest-host interactions between organic and inorganic species. When we consider the myriad of extended and molecular inorganic species, small organic molecules and polymers available for the design of these hybrid materials, it

becomes clear that the variety of combinations is huge. Table 2 shows the host and guest types of inorganic materials derived from different structural dimensions with various classes of organic materials as both guests and hosts and vice versa.

Table 2. Organic and inorganic guest-host materials.

Inorganic Materials	Organic Materials (Organic Conducting Polymers)	References
(Zero Dimensional, 0-D) Nano clusters- Au, Ag, Pd, Pt and CdS, CdSe, colloidal metallic/ semiconducting nanoparticles.	Polyaniline (PAni) polypyrrole (PPy)	[129-132]
One Dimensional, 1-D Materials. Metal/Metal oxide nano wires and nanotubes, nano rods: Au, Pt, SiO_2, TiO_2, MnO_2, ZrO_2, CuO, MnO_2, Ta_2O_5, CeO_2, RuO_2, γ-F_2O_3 ,WO_3, ZnO, $(Mo_3Se_3^-)n$ chains, carbon nanotubes (SWCNT, MW CNT)	Polythiophene: PTh poly(p-phenylene), PPP poly (p-phenylenevinylene):PPV	[133-141/ 88-95]
Two Dimensional, 2-D Layered Materials Transition metal oxides- V_2O_5, LixMoO$_3$, LixWO$_3$, CsxTiO$_2$, LixMnO$_2$. dichalcogenides- VS_2, VSe_2 MoS_2, $MoSe_2$, TaS_2, TiS_2, NbS_2, $NbSe_2$, WS_2 oxychlorides- FeOCl. Phosphates: α-$VOPO_4$, UO_2PO_4 inorganic layered clays	Poly(3,4-ethylenedioxythiophene): PEDOT	[143-150]
Three Dimensional, 3-D Materials zeolitic solids, LiM_2O_4, $H_3PMo_{12}O_{40}$, Fe_2O_3, γ-MnO_2 λ-MnO_2, Mn_3O_4, $FePO_4$, $LiMnVO_4$, $Li[Li_{1/3}Ti_{5/3}]O_4$	Nonconducting organic molecules and polymers. naphthalene, poly(ethylene oxide), PEO, poly(ethylenegycol), PEG biomolecules- enzymes, proteins, DNA, collagen, cellulose.	[151-155]

During last two decades, the field of organic conducting polymers (OCPs) which is also referred as synthetic metals has enjoyed a dramatic transition from chemical curiosities to revolutionary new plastic materials that continues to receive great attention in such a way that recent reviews tend to center on particular polymers or applications. The vast majority of reports dealing with

OCPs involve the study of p-doped polymers, for example polyaniline (PAni), polypyrrole (PPy), poly(p-phenylene vinylene) (PPV), polythiophene (PTh) and their derivatives. Range from their use as plastic conductor or light emitting diodes (LED), electrochromic display and smart windows, corrosion inhibitor, field effect transistors (FET), electromagnetic interference (EMI) shielding, and more significantly energy storage applications such as batteries, supercapacitors and fuel cells [125-128]. Among their properties and applications the most frequently studied systems (Table 2) [129-155] relate to their semiconducting nature and electroactivity.

The assortment would include innovative combinations of OCPs with a wide variety of available inorganic components like three-dimensional framework systems of zeolites, two-dimensional layered materials such as clays, metal oxides, metal phosphates, chalcogenides, and even one-dimensional nanowires, nanotubes, $(Mo_3Se_3^-)_n$ chains and zero-dimensional materials such as CdS, CdSe nanoclusters. Experimental work has generally shown that virtually all types and classes of nanocomposite materials lead to new and improved properties when compared to their macrocomposite counterparts. Therefore, nanocomposites promise new applications in many fields such as mechanically reinforced lightweight components, non-linear optics, battery cathodes, sensors and optoelectronics. The general class of organic-inorganic nanocomposites may also be of relevance to issues of bio-ceramics and biomineralization in which in-situ growth and polymerization of biopolymer and inorganic matrix also occurs [126-128].

6.4. Conducting polymer based nano-composites and their classification

According to the nature of the organic-inorganic interface (focusing more on the inorganic materials) these nanocomposites could be classified into two types: nanoparticles and nano-structured layered materials. Depending upon the nature of association between the inorganic and organic components, these nanocomposites can also be classified into two categories as illustrated in Table 3 [141-150]; one in which the inorganic nanoparticles are embedded in organic matrix is called "Inorganic-Organic nanocomposite" (IO-materials) to denote hybrids where the organic phase is host to an inorganic guest. The other type is "Organic-inorganic nanocomposite" (OI-materials) where the guest organic polymer is confined into inorganic host layers. In each case however, the composite formation demands some entrapment or encapsulation rather than simple blending or mixing.

6.5. Inorganic-organic (I-O) nanocomposites

In this section of inorganic-in-organic (Fig. 2) system, such nanocomposite not only bridge the world of microparticles with that of the macromolecules, but often makes successful strides towards overcoming the processing problems of OCPs, thus also enhancing their importance to a large extent. Inorganic nanoparticles can be introduced into the matrix of a host-conducting polymer either by some suitable chemical route or by an electrochemical incorporation technique. However, each synthesis opens a way to a group of materials with complementary behavior between two components. Chemical

origin as well as the special properties viz. its colloidal stability, optical, catalytic, elect the resulting composite.

6.6. Organic-inorganic (O-I) nanocomposites

A second group of nanocomposite materials is constituted by those in which the organic polymer is confined into the inorganic layers for a broad range of applications. Since the inorganic layered materials exist in great variety possessing a well defined, ordered intralamellar space potentially accessible by foreign species they can act as matrices or hosts for polymers, yielding interesting lamellar "organic-in-inorganic nanocomposite" materials. Lamellar nano-composites can be divided into two distinct classes, intercalated and exfoliated. In the former, the polymer chains alternate with the inorganic layers in a fixed compositional ratio and have a well defined number of polymer layers in the intralamellar space. In exfoliated nanocomposites the number of polymer chains between the layers is almost continuasly variable and the layers stand >100 Å apart.

Table 3. Conducting polymer nano-composites classification.

| 1. Nanocomposite with surface functional group (-NH2 , -COOH on colloidal particles, SiO_2, SnO_2, $BaSO_4$ etc as core materials)	1. Nanocomposite with functionalized structural materials with superior mechanical properties, (Claypolymer intercalative	141-143, 146
2. Nanocomposite with improved physical and mechanical properties (Fe_2O_3, ZrO_2,TiO_2 etc as incorporated materials).	2. Nanocomposite with functionalized structural materials with superior mechanical properties, (Claypolymer intercalative nanocomposite with polymer like nylon-6, PMMA, styrene, polypropylene intercalation into the layered silicates- sodium montmorillonite, hectorite etc)	14,153
3.Nanocomposites with magnetic susceptibility (using Fe_3O_4, γ-Fe_2O_3 etc magnetic particles.)		148-149
4.Nanocomposites with dielectric, piezoresistive, catalytic activities (with $BaTiO_3$, PMo_{12}, TiO_2, Pt, Pd, etc incorporation)	3. Nanocomposite with novel electronic anisotropic material and thermoelectric power, catalysis (V_2O_5, MoO_3, FeOCl, MoS_2, TiS_2, $RuCl_3$, α-VOPO$_4$, UO_2PO_4, $CdPS_3$, $NiPS_3$)	147-149
5.Naocomposites with energy storage, optical and electrochromic activities (incorporation of MnO_2, SnO_2, WO_3, SiO_2, TaO_2. $LiMn_2O_4$ Prussian blue, CdS, CdSe.	4. Nanocomposite for energy storage, enhanced electrochemical properties for lithium batteries, fuel cells, and supercapacitors (using V_2O_5, MoO_3, FeOCl, MoS_2, TiS_2, MnO_2	139,150
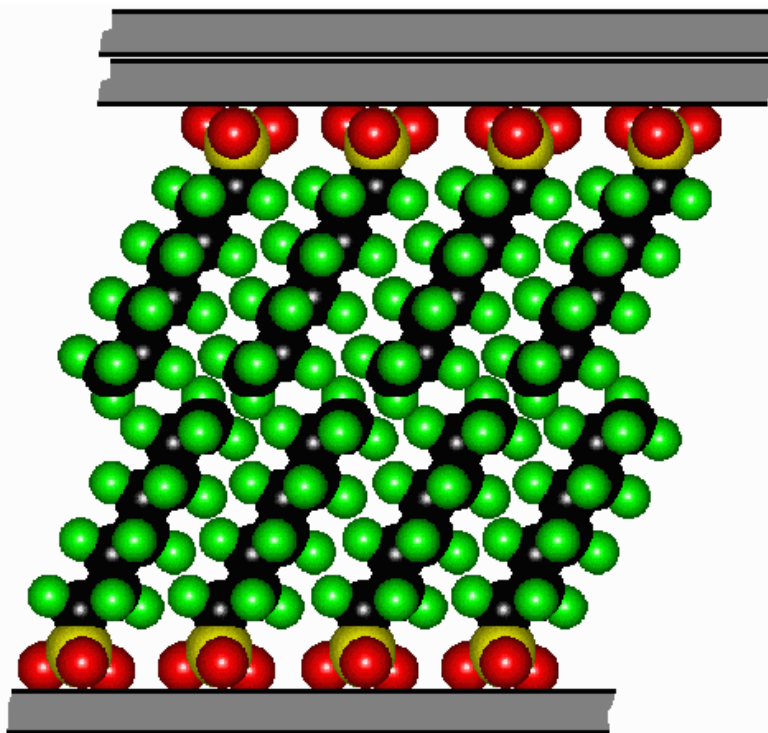
Figure 2. Simulated structure of organo-inorganic interactive nano-composite.

The intercalated nanocomposites are also more compound-like because of the fixed polymer/layer ratio, and they are interesting for their electronic and charge transport properties. On the other hand, exfoliated nano-composites are more interesting for their superior mechanical properties.

6.7. Nanocomposites prepared by exfoliative and intercalative strategies

It is well known that layered silicates have crystal structure is shown in Fig. 1. with two dimensional spacings in the nanometer range. Exchangeable cations and water usually occupies the spacings to balance the negative charges n the ionic lattice. Clay-polymer nanocomposites have recently attracted a great deal of attention as they offer enhanced mechanical and thermal properties as compared to conventional materials. For example, recently Okada et al. prepared new molecular scale nanocomposites from saturated polymers (Nylon-6 and other plastic) intercalated in clay layers. These products show extraordinary mechanical strength compared to that expected by Fig. 3. Because of these enhanced properties, they find extensive applications in automobile, and furnishing industries.

However, the enhancement of material properties has been linked to the interfacial interaction between the polymer matrix and the organically modified layered silicate filler structure. The filler particles provide a very high surface area and the polymer can be incorporated either as oligomeric species itself or via the monomer, using in situ polymerization to form polymer-clay nanocomposites.

The latter is a more successful approach although it probably limits the ultimate utility of these systems. The synthetic route of choice for making a nanocomposite depends on exfoliated hybrid (Fig. 4.). In the case of an intercalate, the organic component is inserted between the layers of clay such that

the inter-layer spacing is expanded, but the layers still bear a well-defined spatial relationship to each other. In an exfoliated structure, the layers of the clay have been completely separated and the individual layers are distributed throughout the organic matrix. Another alternative is to disperse clay particles (tactoids) completely within the polymer matrix, although this simply represents the use of the clay as conventional filler.
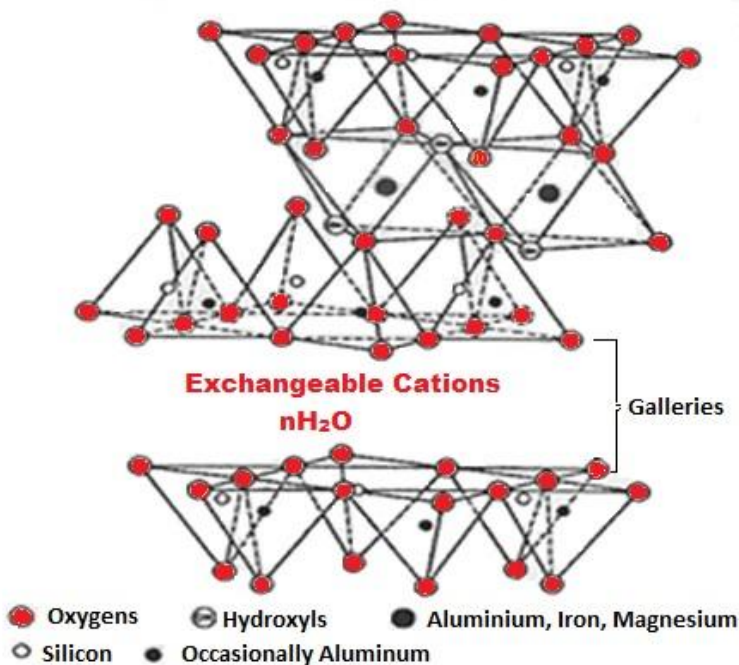

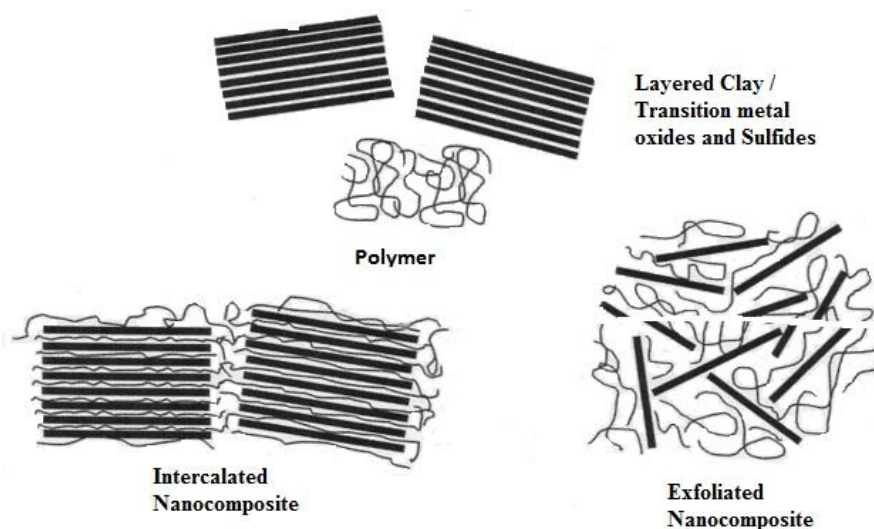**Figure 3.** Crystal structure of layered silicate

Figure 4. Schematic representations of different types of nanocomposite formation.

In recent years, there has been extensive study of the factors which control whether a particular organo-clay hybrid can be synthesized as an intercalated or exfoliated structure. Since clay nanocomposites can produce dramatic improvements in a variety of properties, it is important to understand the factors which affect the delamination of the clay. These factors include the exchange capacity of the clay, the polarity of the reaction medium and the chemical nature of the interlayer cations (e.g. onium ions). The correct selection of modified clay is essential to ensure effective penetration of the polymer or its monomer into the interlayer spacing of the clay which results in the desired exfoliated or intercalated product. Indeed, further development of the compatibiliser chemistry is undoubtedly a key to the expansion of this nanocomposite technology beyond the systems where success has been achieved to date [156,157]. Despite their relatively large molecular weights, electronically conducting polymers can play the role of intercalated guest molecules inserted within the Van der Waals gaps of layered inorganic phases resulting in a special class of intercalative nanocomposites is shown in Fig. 4 termed as "organic-in-inorganic nanocomposites". At least in principle, in these cases the structure of the inorganic host dominates the structure of the hybrid and the polymers adapt to it. The insertion of conducting polymers in layered inorganic host materials and other structurally organized environments is a topic of considerable interest.

6.8. Newly emerging applications

6.8.1. Electronic and optoelectronic devices

Nanometer-size particles possessing hybrid molecular and bulk behavior define a new class of materials with several interesting optical and electronic applications. For example, light emitting diodes have been developed recently that are based on new materials such as porous silicon [158]. By taking advantage of the developments in the preparation and characterization of direct-gap semiconductor nanocrystals and of electroluminescent polymers [159], Colvin et al. has constructed a hybrid inorganic-organic electroluminescent device [160]. Light emission arises from the recombination of holes injected into a layer of p-type semiconducting poly p-phenylene vinylene (PPV) [161] with electrons injected from n-type cadmium selinide nanocrystals. Because of the quantum size effect [162] the color of the emission can be tuned from red to yellow by changing the nanocrystals size.

6.8.2. Electrochemical energy storage

Recently, Yoneyama et al. has successfully attached oxide particles having very low isoelectric points, such as WO_3, SiO_2 and Ta_2O_5 into polypyrrole film by electrochemical oxidation of pyrrole in the presence of oxide suspensions espesially if the pH of the deposition is higher than the isoelectric point of the oxide. These composites have been found to be useful as electrode materials for batteries and electrochromic applications. Oxide particles which do not belong to this class, such as TiO_2, can also be incorporated into polypyrrole if small amount of electrolyte anions having specific adsorption to the oxide e.g., SO_4^{2-}, are added to the deposition baths containing oxide suspensions. As polypyrrole

is one of the most popular conducting polymer, its technological applications for cathode material for rechargeable lithium batteries had been widely studied. Even with the use of highly porous polypyrrole, however, the volumetric energy density is not very high, because the amount of electrolyte anions involved in the redox reaction is limited. This limitation can be improved by incorporating electrochemically active anion-adsorbed MnO_2 as a dopant. Although Manganese dioxide is one of the promising materials as a cathode material for Li-batteries, it possesses an extremely low conductivity, and it is essential to have a conducting net work for complete utilization of the active material had also for accomplishing high power density. Usually some conducting form of carbon like acetylene black or graphite powder is mixed with MnO_2 particles. If PPy films containing MnO_2 particles could be used as cathode materials, it can form PPy/MnO_2 nano composite which would not only act as conducting network for MnO_2 but also as efficient active materials. For example, Yoneyama et al. has recently, reported that MnO_2 particles incorporated into conducting polymer film works well as an active material, causing enhanced charge-discharge capacity [163]. Similarly, a new "core-shell" polypyrrole (PPy)/ maghemite (γ-Fe_2O_3) nanocomposite prepared by Kwon et al. [164] via surface modification has improved the electrochemical discharge capacity compared to that of the pristine oxide. More recently, Mastragostino and co-workers have reported the improvement in electronic conductivity, discharge capacity and open circuit voltage up to 4V for $LiMn_2O_4$ particles, after mixing with poly (3,4- ethylenedioxythiophene) PEDOT [165].

Growing demand for miniaturized power sources of high-power density has also stimulated great interest in electrochemical capacitors in recent years. For example, carbon powder and conducting polymers do possess large double layer capacitance (and also have high surface area) while oxides of multivalent metals such as ruthenium and iridium exhibit large Faradaic pseudocapacitance and hence these two classes of materials find extensive applications in supercapacitor [166]. Jongin Hong et al. has recently reported [167] the use of conducting polymers with metal oxides for electrochemical capacitors. More specifically, RuO_2 when deposited on poly(3,4-ethylenedioxythiophene), is found to exhibit large specific capacitance 420 F/g.

6.8.3. Application in electro-catalysis

Another important application of hybrid nanostructured composite material is in electro-catalysis. For example many fuel cell reactions like the electro-oxidation of methanol in principal, requires an efficient reversible redox process where catalyst need sustained stability. Since, some of the important fuel cells operate in acid medium which requires both the catalyst and support to be highly stable the building of efficient nanocomposite electrode is very important. This principle has been followed by several researchers, describing the preparation of nanocomposites in which nanoparticles of Pt, Pd, Cu, etc. are combined with PPy, PAni, PTh etc to form efficient electrocatalytic electrodes. The dispersion of Pt particles in PAni matrix and their ability for enhancing methanol oxidation has been extensively discussed by Hable et al. [168]. Similarly, the formation of a series of such mono and bimetallic electrodes using Pd, Cu, Pd/Cu and Cu/Pd catalyst in conjunction with PAni has been reported to show efficient oxidation of formic acid and methanol [169].

6.8.4. Magnetic applications

Several nanostructured materials show interesting size dependence magnetic properties like superparamagnetism and quantum tunneling of magnetization and hence some of the unique nanostructured magnetic materials have been used to form composites with promising applications for diverse area [170]. A versatile process for the preparation of maghemite/ polyaniline (γ-Fe_2O_3/PAni) nanocomposite was first reported by Ben Zhong Tang et al. [171]. In this case γ-Fe_2O_3 nanoparticles were coated with PAni chains doped by anionic surfactants. Both the coated γ-Fe_2O_3 and the doped PAni were soluble in common organic solvents, and casting of the homogeneous solutions gives free-standing nanocomposite films with good electrical conductivity ($\sigma = 82 - 237$ Scm^{-1}) much higher than that of the iron oxide/conducting polymer system prepared by mixing. The nanocomposite films were superparamagnetic, showing no hysteresis loop at 300K. Since these nanocomposites, formed by nanometer-size particles of metals or metallic compounds dispersed in OCPs constitute a good example of hybrid nanomaterials their detailed preparation and properties have been reviewed recently.

7. 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 divers.

Some need to 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 material semiconductors, and insulators. Nowadays, particular attention is given to the characteristics of semiconductors.

8. ELECTRICAL CONDUCTION IN MATERIALS

Electrical conductivity (σ) used to specify the electrical character of a material. It is simply the reciprocal of the resistivity, or

$$\sigma = \frac{1}{\rho} \qquad (2)$$

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 volatage as given by the equation

$$\sigma = qn\mu \qquad\qquad (3)$$

Where σ is electircal conductivity of material, n is the number of charge carriers, q is the charge and μ is drift mobility of charge carriers. Drift mobility characterizes the ease with which the charge carriers can move under the influence of applied material. Electrons and holes in the electronic contribute and cations 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.

9. 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 current carriers and this number is independent of temperatures. An insulator has relatively few numbers of current carriers at ordinary temperatures and semicondutor has current carries, the number of which in 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 do not find use in electrical industry because of it is expensive. The resistivity of metallic conductors at room temperature lies between 1.6×10^{-6} to 100×10^{-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 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 semiconductor however is many orders of magnitude smaller than in a conductor.

K. Onnes first oserved 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 metal and their alloys, many compounds which have zero resistance below a certain critical temperature; T^{c}.

10. 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 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 Nobel Prize has recognized the interest of these materials for the year 2000 in Chemistry to Heeger, [172] MacDiarmid 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 from of electrons or holes.

10.1. Polyaniline

In recent years, polyaniline has attracted much attention [173-174] on account of its ability, under certain conditions, to exhibit a high level of electrical conductivity [175] having potential applications such as in the fabrication of novel 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. Under appropriate conditions the so called emaraldine base form of the polymers reacts with dilute acids to give corresponding emaraldine salts, with protonation of the nitrogen atoms. This reaction is accompanied by a 9-10 order of magnitude increase in conductivity to 1×10^2 - 5×10^2 S cm^{-1}. Hence it can be used in aqueous electrolyte rechargeable batteries [176]. Key attractions of polyaniline are the relatively low cost of the route from aniline and the fact that it has very important features that distinguish it from other conductive polymers.

10.2. 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 S cm^{-1}. One of the principal advantages of polypyrrole over other doped polymers is its excellent thermal stability in air. It is thermally stable up to 250 ^{0}C. Although chemical

analysis of polyprrole varies with preparative conditions, elemental analyses have indicated that the pyrrole varies with preparative conditions, elemental analysis have indicated that pyrrole rings remain intact with each unit being connected by its ά carbons.

11. 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 [177-180]. 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 [181-185]. Special interest today is focused on composite system having high conductivity at ambient and sub-ambient temperatures, since they find unique application, 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 application, such as smart windows, toners in photocopying, conducting paints etc. [186].

12. APPLICATIONS OF ELECTRICALLY CONDUCTING POLYMERS AND COMPOSITES

12.1. Optical devices

Optics was certainly one of the first applications of hybrid materials [187]. 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 materials index as well as the thickness and therefore, the procesibility 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 those devices [188,189]. For example, photoconducting composites were prepared by the incorporation of cadmium sulfide particles in a polyvinylcarbazole martrix. The resulting materials allowed the tuning of the band gap of the particular wavelength of operation [190,191].

In terms of conductivity, the behavior ranges from insulating through semi conducting to metallic and superconducting. Many types of electrically conducting composites materials classified as electrolytes or polymer ionic have been developed and characterized in recent years 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 networks forming species should contain components that allow an interaction to the conducting ions.

12.2 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 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 [192], 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 into clay (montmorillonite) by the interaction of colloidal nanoparticles of the polymers with the colloidal layered host [193]. This method using a colloid-colloid reaction [194] might provide a general route to incorporation intractable polymers within layered host structures that can be exfoliated, such as smeccice clays [195], 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 exposiing them to NH_3 gas [196].

13. MEMBRANE 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 [197] 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 [198]. The term heterogeneous has been used to indicate the internal physical

structure and external physico-chemical performance [198-200]. 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 [201].

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.

14. 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.

14.1. 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.

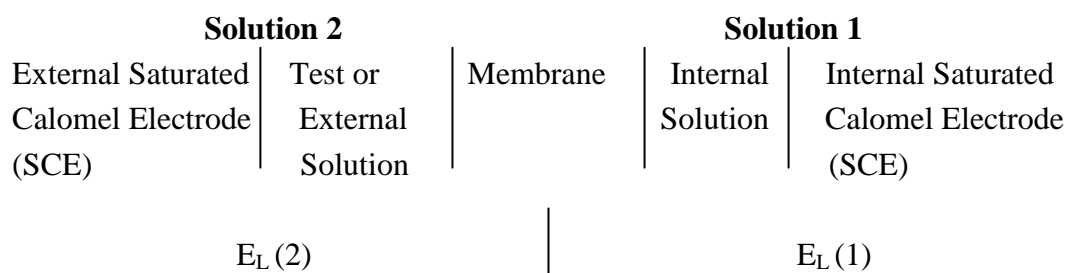### 14.1.1. Electrode response or membrane potential

The use of ion-selective electrodes depends on the determination of potentials [202]. 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 Eq. (4):

$$E_m = \frac{RT}{Z_A F}\left[\ln\frac{[a_A]_2}{[a_A]_1} - (Z_y - Z_A)\int_1^2 t_y \, d\ln a \pm\right] \tag{4}$$

Where A = counter ion, Y = co-ion, Z = charge on ions, t_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 Eq. (4) 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 ($t_y = 0$) then Eq. (4) takes the form of the well-known Nernst Equation as follows:

$$E_m = \pm\frac{RT}{Z_A F}\ln\frac{[a_A]_2}{[a_A]_1} \tag{5}$$

The Eq. (5) 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. Eq. (5) 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:

Solution 2				**Solution 1**	
External Saturated Calomel Electrode (SCE)	Test or External Solution	Membrane	Internal Solution	Internal Saturated Calomel Electrode (SCE)	
E_L (2)				E_L (1)	

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:

$$E_{cell} = E_{SCE} + E_{L(2)} + E_m + E_{L(1)} - E_{SCE} \tag{6}$$

where E_{SCE}, E_L and E_m refer to calomel electrode, junction and membrane potentials, respectively. On combining Eqs. (5) and (6), the following equation takes the form-

$$E_{cell} = E_{SCE} - E_{SCE} + E_{L(2)} + E_{L(1)} \pm \frac{RT}{Z_A F} \ln \frac{[a_A]_2}{[a_A]_1} \tag{7}$$

For cation-exchange membrane,

$$E_{cell} = E_{L(2)} + E_{L(1)} - \frac{RT}{Z_A F} \ln[a_A]_1 + \frac{RT}{Z_A F} \ln [a_A]_2 \tag{8}$$

As the activity of internal solution is kept constant and the values of $E_{L(1)}$ and $E_{L(2)}$ are also almost constant, the term in parenthesis may be taken equal to a constant, E^o. 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 Eq. (8) reduces to-

$$E_{cell} = E^o + \frac{RT}{Z_A F} \ln [a_A]_2 \tag{9}$$

Now, it is quite clear from Eq. (9) that the cell potential would change with the change in concentration (or activity) of the cation in external or test solution 2. At 25 ^{o}C, value of $RT/Z_A F$ comes out to be $0.059/Z_A$ volts. The membrane is said to give Nernstain 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 and above it, it is hyper-Nernstian. Sensors, which are outside the Nernstian range, can still be useful analytically.

14.1.2 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. 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 Eq. (10):

$$E = E^o + (2.303 \, RT/Z_i f) \log a_i \qquad\qquad (10)$$

However, Eq. (10), 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:

$$E = E^o + (2.303 \, RT/Z_i f) \log (a_i + K_{ij}^{pot} a_j^{\, Z_i/Z_j}) \qquad\qquad (11)$$

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}^{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}^{pot}, the more selective is the electrode. For ideally selective electrodes, the K_{ij}^{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 [204-206]. Various methods [207] have been suggested for determining the selectivity coefficient, however, it falls in two main groups, namely- (a) Separate-solution method and (b) Mixed-solution method.

(a) Separate-solution methods [208]: 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:

$$E_i = E^o + (2.303\ RT/Z_if)\ \log a_i \tag{12}$$

$$E_j = E^o + (2.303\ RT/Z_if)\ \log K_{ij}^{pot}\ a_j \tag{13}$$

K_{ij}^{pot} can be calculated either with the so-called equal activity or with the equal potential method. In both cases, it is actually 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 Nernstain 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 Eqs. (12) and (13), we get

$$\log K_{ij}^{pot} = \frac{E_j - E_i}{2.303RT/Z_iF} + \log \frac{a_j}{(a_j)^{Z_i/Zj}} \tag{14}$$

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}^{pot}. As such Eq. (14) takes the form.

$$\log K_{ij}^{pot} = \frac{E_j - E_i}{S} + \log \frac{a_j}{(a_j)^{Z_i/Zj}} \tag{15}$$

Thus, using Eq. (15) selectivity coefficient K_{ij}^{pot} can be calculated. The separate solution technique for determining selectivity coefficients is simple and allows a number of K_{ij}^{pot} values to be measured on the basis of different activities and potentials.

(b) Mixed solution methods [209-212]: In the mixed solution techniques, the electrode potentials are measured in solutions containing both the primary ion 'i' and the interfering ion 'j'). The procedure for determining selectivity coefficients by Mixed Solution Method is:

Procedure. In this procedure, the potentials of the electrode E_i and E_{ij} are measured in solutions of primary ion 'i' only and a mixture of primary and interfering ion 'j', respectively.

$$K_{ij}^{pot} = \log [10^{(Ei+j - Ei/m)} - 1] + \log a_i - Z_i/Z_j \log a_j \tag{16}$$

Or, in other form, it can be writen as

$$K_{ij}^{pot} = \frac{a_j}{a_j^{Z_i/Zj}} \left[\left\{ 10^{\frac{E_{i+j}-E_i}{2.303RT/Z_iF}} \right\} - 1 \right] \tag{17}$$

14.1.3. Response time

Another important factor besides linear response that recommends 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. [213-214] have discussed this aspect in details.

14.1.4. Effect of pH

The membrane electrodes with polymer binders like PVC responds 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.

14.1.5. 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.

15. MEMBRANES AND ION-SELECTIVE ELECTRODES

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 there systematic studies started after Pungor et al. in 1961. Therefore, in thus task we have reviewed heterogeneous ion-selective member electrode based on inert binder PVC and polystyrene selective for alkali, alkaline earth metals and heavy metal ions. Research in the field of ISEs was enormously stimulated by the publication by Fran and Roos [215] of their article on the floride and calcium ion-selective electrode. A number of review articles [216-219] have come across from time to time towards the work done by various eminent persons.

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) heteroployacid salt-epoxy resin membranes in their studies and they also have determined Cs^+ potentiometrically [220, 221]. Tungstoarsenate based ion-selective membranes have been developed by Malik et al. [222] and found very much suitable in the determination of Cs^+ and Tl^+ ions. However, there has been only a few reports concerning Thallium(I) ion-selective membrane electrode [223-231]. They need to improved with regard to there low selectivities against alkali metal ions linearity and pH-dependance [232]

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 Ca^{2+}-selective electrodes. The first Ca^{2+}-selective electrode was a liquid membrane electrode developed by Ross [268]. It was prepared by using a liquid membrane of didecyl -phosphate in di-n-octyl phosphonate. The useful Ca^{2+}-selective electrodes were developed by Thomas, Moody and coworkers [233] by incorporating Ca-bis[2,6-dinitro-4-(1,1,3,3-tetramethylebutyl)] phenoxide and Ca-bis[di{4-(1,1,3,3-tetramethylbutyl) phenyl}]phosphate in PVC. Chattopadhyaya and Misra [234] 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 $Na_2C_2O_4$.

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(ditolylphosphineoxide) in PVC was reported as Mg^{2+}-sensor [235]. The electrode shows good selectivity towards Mg^{2+} over Ca^{2+} and works well in the concentration range 6.0×10^{-5}- 1.0×10^{-1} M. Another electrode for Mg^{2+} has been developed by O'Donnell and coworkers [236] using various octamethylene bis(malonic acid diamides) and tris(malonic acid diamides) in PVC with 2-nitrophenyloctyl ether as solvent mediator.

First useful Sr^{2+} ion-selective electrode was developed by Baumann [237] using strontium complex of polyethylene glycol as electro active 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 [238] have reported a heterogeneous membrane using hydrous thorium oxide embedded in polystyrene while Jain et al. [239] 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.

Ba^{2+}-selective polymeric membrane electrodes have been constructed from lipophilic electrically neutral carriers [240] and neutral carboxylic poly ether antibiotic [241,242] 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-complex prepared by using an epoxy resin binder were also found suitable as Ba^{2+}-sensor [243]. These electrodes show good selectivity for Ba^{2+} and also used for the titration of Ba^{2+} against SO_4^{2-}.

Chelating ion-exchanger resins are found to possess specific selectivity for some metal ions and play an important role in separation processes. Srivastava et al. have reported the utility of salicylaldoxime-formaldehyde resin membranes for the estimation of Zn^{2+}. Recently Wardak et al. [244] studied the properties on the ion selective electrode with a chelating pseudo-liquid membrane

phase for Zn^{2+} determination. Cu(II) is an essential element and is also toxic at elevated concentration. Its reactivity and biological uptake are strongly influence by the free ion concentration that is controlled by the extent of copper complexation with ligands. 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, tungsten oxide, ion-exchangers and copper (III) complexes as electro active material have been tried as copper potentiometer sensors.

In measuring the heavy metals ions like Cd^{2+} in the industrial wastewater, the ion-selective electrodes are very convenient because of simplicity and selectivity. Ross et al. [245] have reported the precipitate based solid state CdS-Ag_2S mixture membrane by stoichiometric reaction. Also Hirata et al. [246] have developed the ceramic solid-state CdS-Ag_2S mixture membrane by baking the CdS-Ag_2S mixed powder or its pressed membrane at 700 ^{o}C. Hopertenam and Cosma 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_2S.

Srivastava et al. [247] have reported an elasticized PVC based membrane of benzo-15-crown-5, which exhibited a good response for Cd^{2+} in a wide concentration range ($3.16 \times 10^{-5} – 1.00 \times 10^{-1}$ 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.

Because of the increased industrial use of lead, at one hand and its serious hazardous effect to human health, on the other [248] , 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. [249] have developed Pb^{2+} ion-selective membrane using lead antimonate as an electroactive phase and araldite as a polymer binder. Khan et al. [254-258] have published their findings for the determination of Hg(II), Cd(II), and Pb(II), by potentiometric titration using polypyrrole/polyantimonic, polyaniline Sn((IV) tungstoarsenate, polyaniline Sn(IV)arsenophosphate, polypyrole Th(IV) phosphate, polyaniline Sn(IV) phosphate, poly-o-toluidine Th(IV) phosphate, poly-o-toluidine Zr(IV) phosphate electrically conducting organic-inorganic composite based ionselective membrane electrodes.

Gupta et al. [250] have published their results on the studies of araldite based Zr(IV) tungstophosphate (ZWP) membrane as Pb(II) ion-selective electrode. Tavakkoli and Shamsipur [251] 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. Recently, Malinowska et al. [252] have reported a lead selective membrane electrode containing ionophores based on diaza-18-crown-6 units possessing amide and sulfonamide functions. Ganjali et al. 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 8×10^{-6} M and can be used as an indicator electrode in potentiometric titrations of Pb^{2+} ions in both H_2O and 90% MeOH solutions. Ensaf et al. [253] have prepared the

lead(II)-selective membrane electrode by incorporating cryptand 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.

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. 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 .

A less attention has been made for determining tripositive metal ions. Very few potentiometric devices have been designed for aluminum. Recently, Saleh et al. have reported a novel potentiometric membrane sensor for selective determination of Al(III) ions. This electrode has a minimal 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.

Khan et al. have been reported poly-o-toluidine Th(IV)phosphate [254]; polypyrrole Th(IV) phosphate [255]; polyaniline Sn(IV) tungastoarsenate [14]; Poly-pyrrole/polyantimonic acid [256]; Nylone 6,6 Sn(IV)phosphate [257]; poly-o-anisidine Sn(IV)arsenophosphate [258] based ion selective membrane electrode for the potentiometric determination of Hg(II), Pb(II), Cd(II), Hg(II), Hg(II) and Pb(II), respectively. Ion-selective electrodes for determination of organic ammonium ions were reported by Egorov et al. [259]. Dibenzo[e,k]-2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,5,7,9,11-hexaene has been explored as an electroactive material for the fabrication of a poly(vinyl chloride)-based membrane electrode for selective determination of Ni^{2+} ions by Singh et al. [260]. A highly Ce(III) ion- selective poly vinyl chloride (PVC) membrane sensor based on N′-[(2-hydroxyphenyl)methylidene]-2-furohydrazide (NHMF) as an excellent sensing material is successfully developed by Zamani et al. [261]. A series of recently synthesized benzo- and pyridine-substituted macrocyclic diamides were studied to characterize their abilities as lead ion carriers in PVC membrane electrodes. The electrode based on 3,15,21-triaza-4,5;13,14-dibenzo-6,9,12-trioxabicycloheneicosa-1,17,19-triene-2,16-dione by Kazemi et al. [262]. Novel platinum(II) selective membrane electrode based on 1,3-bis(2-cyanobenzene) triazene was reported by Gholivand et al. [263]. New silver selective electrode fabricated from benzothiazole calyx(4)arene for the analysis of silver nanoparticles by Ngeontae et al. [264].

A new hafnium selective sensor was fabricated from polyvinylchloride (PVC) matrix membrane containing neutral carrier N,N′-bis(α-methyl-salicylidene)-dipropylenetriamine (Mesaldpt) as a new ionophore, sodium tetraphenyl borate (NaTPB) as anionic discriminator and dioctyl phthalate (DOP) as plasticizing solvent mediator in tetrahydrofuran solvent by Rezaei et al. [265]. Oxalate-selective electrode based on the complex 2,2′-[1,4-butandiyle bis(nitrilo propylidine)]bis-1-naphtholato copper(II) (CuL) as the membrane carrier was developed by Ardakani et al. [266]. Mercury ion-selective membrane electrodes based on 2-amino-6-purinethiol (I_1) and 5-amino-1, 3, 4-hiadiazole-2-thiol (I_2) were described BY Gupta et al. [267]. Mercury(II)-selective polymeric membrane electrode based on the 3-[4-(dimethylamino)phenyl]-5-mercapto-1,5-diphenylpentanone was described by Xiu Yu et al. [268].

16. MAGNETIC SUSCEPTIBILITY MEASUREMENTS

The determination of magnetic moments of transition metal complexes have been found to provide ample information in assigning their structure. The main contribution to bulk magnetic properties arises from magnetic moment resulting from the motion of electrons. It is possible to calculate the magnetic moments of known compounds from the measured values of magnetic susceptibility.

There are several kinds of magnetic phenomenon observed in chemical substances viz., diamagnetism, paramagnetism and ferromagnetism or antiferromagnetism. Mostly compounds of the transition elements are paramagnetic. Diamagnetism is associated with substances having closed shell electrons in an applied magnetic field. In the closed shell the electron spin moment and orbital moment of the individual electrons balance one another so that there is no magnetic moment. Ferromagnetism and antiferromagnetism arise as a result of interaction between dipoles of neighboring atoms. If a substance is placed in a magnetic field H, the magnetic induction B with the substance is given by

$$B = H + 4\pi I \qquad\qquad (18)$$

where I is the intensity of magnetization. The ratio B/H is called magnetic permeability of the material and is given by

$$B/H = I + 4\pi(I/H) + I + 4\pi\kappa \qquad\qquad (19)$$

Where κ is called the magnetic susceptibility per unit volume or volume susceptibility. B/H is the ratio of the density of lines of force within the substance to the density of such lines in the same region in the absence of sample. Thus the volume susceptibility in vacuum is zero by definition since in vacuum B/H 1. When magnetic susceptibility is considered on the weight basis, the term gram susceptibility (χ_g) is used instead of volume susceptibility. The μ_{eff} value can then be calculated from the gram susceptibility multiplied by the molecular weight corrected for diamagnetism:

$$\mu_{eff} = 2.84\sqrt{\chi_M^{corr}.T}\, BM \qquad\qquad (20)$$

where T is the absolute temperature at which the experiment is performed. The magnetic properties of any individual atom or ion will result from some combination of two properties that is the inherent spin moment of the electron and the orbital moment resulting from the motion of the electron around the nucleus. The magnetic moments are usually expressed in Bohr Magnetons (BM). The magnetic moment of a single electron is given by

$$\mu_S = g\sqrt{S(S+1)}\ BM \qquad\qquad (21)$$

Where S is the total spin quantum number arising from unpaired electrons and g is the gyromagnetic ratio. For Mn^{2+}, Fe^{3+} and other ions having ground states as S there is no orbital angular

momentum. While the transition metal ion in their ground state D or F being most common, do possess orbital angular momentum. The magnetic moment for such ions, e.g. Co^{2+} and Ni^{2+} is given by

$$\mu_{(S+L)} = \sqrt{4S\,(S+1) + L\,(L+1)} \tag{22}$$

where L represents the total orbital angular momentum quantum number for the ion. The spin magnetic moment is insensitive to the environment of metal ion but the orbital magnetic moment is not. In order for an electron to have an orbital angular momentum and thereby an orbital magnetic moment with reference to a given axis, it must be possible to transform the orbital into a fully equivalent orbital by rotation about that axis. For octahedral complexes the orbital angular momentum is absent for A_{1g}, A_{2g} and E_g term, but can be present for T_{1g} and T_{2g} terms. Magnetic moments of the complex ions With A_{2g} and E_g ground terms may depart from the spin-only value by a small amount. The magnetic moments of the complexes possessing T ground terms usually differ from the high spin value and vary with temperature. The magnetic moments of the complexes having a $^6A_{1g}$ ground term are very close to the spin-only value and are independent of the temperature.

For octahedral and tetrahedral complexes in which spin-orbit coupling causes a split in the ground state, an orbital moment contribution is expected. Even no splitting of the ground state appears in cases having no orbital moment contribution; an interaction with higher states can appear due to spin-orbit coupling giving an orbital moment contribution.

Practically the magnetic moment value of the unknown complex is obtained on Gouy Magnetic balance. Faraday method can also be applied for the magnetic susceptibility measurement of small quantity of solid samples. The gram susceptibility is measured by the following formula.

$$\chi_g = \frac{\Delta W}{W} \cdot \frac{W_{std}}{\Delta W_{std}} \cdot \chi_{std} \tag{23}$$

Where χ_g = Gram Susceptiblity

ΔW = Change in weight of the unknown sample with magnet on and off

W   = Weight of the known sample

ΔW_{std} = Change in weight of standard sample with magnets on and off

W_{std} = Weight of standard sample

χ_{std} = Gram susceptibility of the standard sample

17. TEMPERATURE DEPENDENCE OF MAGNETIC SUSCEPTIBILITY: *CURIE AND CURIE- WEISS* LAWS

The susceptibilities of the different kinds of magnetic material are distinguished by their different temperature dependences as well as by their absolute magnitudes. Many paramagnetic substances obey Curie Law, especially at high temperatures. This states that the magnetic susceptibility is inversely proportional to temperature:

$$\chi = \frac{C}{T} \qquad\qquad (24)$$

Where C is the Curie onstant. Often, however a better fit to the experimental data is provided by the Curie-Weiss Law:

$$\chi = \frac{C}{T} + \theta \qquad\qquad (25)$$

Where θ is the Weiss constant.

Ferromagnetic materials show a very large susceptibility at low temperatures that decreases increasingly rapidly with rising temperature. Above a certain temperature (ferromagnetic Curie Temperature, T_c), the material is no longer ferromagnetic but reverts to paramagnetic, where Curie-Weiss Law behavior is usually observed. For antiferromagnetic materials, the value of χ actually increases with rising temperature up to a critical temperature known as Neel point, T_N. Above T_N, the material again reverts to paramagnetic behavior.

The paramagnetic χ values correspond to the situation where unpaired electrons are present in the material and show some tendency to align themself in a magnetic field. In ferromagnetic materials, the electron spins are aligned parallel due to the cooperative interactions between spins of the neighboring ions in the crystal structure. The large χ values represent this parallel alignment of a large number of spins. In general, not all spins are parallel in a given material unless (a) very high magnetic fields and (b) low temperature are used.

In antiferromagnetic materials, the electrons spins are aligned antiparallel and have a canceling effect on χ. Hence small χ values are expected. For all materials, the effect of increasing the temperature is to increase the thermal energy possessed by ions and electrons. There is, therefore, a natural tendency for increasing structural disorder with increasing temperature.

For paramagnetic materials, the thermal energy of ions and electrons act to partially cancel the ordering effect of the applied magnetic field. Indeed, as soon as the magnetic field is removed, the orientation of the spins becomes disordered. Hence, for pararnagnetic materials, χ decreases with increasing temperature, in Curie/ Curie-Weiss Law fashion.

Magnetic susceptibility measurements were carried out using Faraday balance at 298°K. However, the temperature dependence of magnetic susceptibility was recorded on a quantum design. SQUID magnetometer under field cooled conditions between 298 and 4.5 K at 1000G.

18. POLYMERS RECYCLING

In search of a better material for our advancing technologies the polymer scientist have all these years invested much efforts, energy and money to develop man-made polymers that are strong, stable and durable. Polymers have become the important materials for science and technology development, and high standard of living. The modern society cannot live or progress without

polymers. Synthetic polymers have become very versatile and useful materials for modern technology. Because polymers are low cost and can be easily fabricated to consumer products by fast automated machines, they have been widely used in form of packaging materials for farm, forest, dairy products and other consumer items. The usual strength and durability of polymers, however desirable they may be create threat to environmental pollution when these are discarded after use. That the synthetic polymers, unlike natural ones, do not rust or rot or not easily degraded in the outdoor environment, they accumulate in the garbage dump site and cause litter. Thus most of the applications of synthetic polymers are based on their relative resistance to environmental degradation including biodegradation. Extensive use of polymeric materials, lead to the waste disposal management difficulties. Incineration helps produce energy but has problem of emission of toxic fumes and gases due to the decomposition of polymer chain molecules and particular additives present. Land filling of plastics is not preferred because of space constraints and land pollution. On the other hand recycled polymers are also not a permanent solution either since recycling led to the poor quality product. Due to this problem, polymer industry, both manufacturing as well as processing, poses a positive threat to the clean environment. If these industrial operations are not carefully carried out and controlled there exists a very serious problem of pollution of the environment. Polymer scientists are conscious about it and have seized the problem face to face.

The problem of disposal of waste plastics is complex, and requires active participation of industry, government and the public. Though the most important cause for recycling and reprocessing the waste plastics has arisen from the awareness and concern for environmental pollution, it is also important due to the urge of conservation of costly and scarce energy and feedstock. Also discarded polymers represent a colossal waste of energy embodied in them. If these are recovered, even partly, a large amount of scarce and costly resources for energy and chemical feed stocks can be conserved. Also polymer recycling is related to the national economy where the hydrocarbons feed stocks is both scarce and costly. The high price of virgin polymers and cheap labor are the driving forces for recycling of waste plastics. The paper reviews the problem due to the use and disposal of poly (ethylene terphthalate) to the environment. To solve this problem various method of polymer recycling has been presented.

19. POLYETHYLENETREPHTHALATE (PET)

PET is an acronym for polyethylene terephthalate, which is a long-chain polymer belonging to the generic family of polyesters [269]. PET is formed from the intermediates, terephthalic acid (TPA) and ethylene glycol (EG), which are both derived from oil feedstock. There are other polyesters based on different intermediates but all are formed by a polymerisation reaction between an acid and an alcohol. PET, in its purest form, is an amorphous glass like material. Under the influence of direct modifying additives it develops crystallinity. Also, crystallinity can be developed by heat treatment of the polymer melt. Originally patented and exploited by DuPont during the search for new fibre-forming polymers [270], polyester fibre applications have developed to such an extent that PET represents over 50% of world synthetic fibre manufacture. PET is used alone or blended with cotton or

wool to impart better wash/wear and crease resistant properties to textiles. In the late 1950s PET was developed as a film. It was first used for video, photographic and X-ray films in addition to uses in flexible packaging. Later PET was modified for use in injection moulded and extruded articles, primarily reinforced with glass fibre.

In the early 1970s PET was stretched by blow moulding techniques which produced the first oriented three dimensional structures initiating the rapid exploitation of PET as lightweight, tough, unbreakable bottles [271]. Many companies produce virgin PET globally giving it different trade name [272,273].

19.1. The physical and chemical properties of PET

PET exhibits interesting physical properties (morphology). PET, in its purest form, is an amorphous glass-like material. Under the influence of direct modifying additives it develops crystallinity. Also, crystallinity can be developed by heat treatment of the polymer melt. PET is classed as a semi-crystalline polymer and when heated above 72 ^{0}C changes from a rigid glass-like state into a rubbery elastic form where the polymer molecular chains can be stretched and aligned in either one direction to form fibers, or in two directions to form films and bottles. Because of its rather high transition temperature only a limited amount of crystallization can occur during cooling after injection molding poly (ethylene terphthalate). Such moldings are transparent and amorphous and are of little value. If the material melt is cooled quickly, while still held in the stretched state, then the chains are frozen, with their orientation remaining intact. Once set in this stretched state the material is extremely tough and confers the properties we see in a typical PET bottle. If the PET is held in the stretched form at temperatures above 72 ^{0}C it slowly crystallizes and the material starts to become opaque, more rigid and less flexible. It is then known as crystalline PET or CPET. In this form it is capable of withstanding higher temperatures and can be used for trays and containers capable of withstanding moderate oven temperatures. It is this 'heat setting' technique which also develops the erease and wash resistance properties of polyester textiles. Careful manipulation between each of these forms generates a wide range of different products, which are all variants of the same basic chemical formula of PET. The PET described so far is the simplest typical product. However, many modifications are introduced to develop specific properties for the various packaging applications and to suit particular manufacturing equipment. Usually the modifications are of a chemically nature to make manipulation of the PET between different crystalline forms easier. For example, small concentrations of an appropriate co-monomer (isophthalic acid-IPA or 1, 4-cyclohexanedimethanol) slow down the rate of crystallization and allow the manufacture of thicker bottle walls, sheets and films. A typical example would be in the heavier, thicker bottles used for refillable container systems.

There is also a requirement to extend the rate of crystallization to restrict movement and deformation at elevated temperatures, for example in oven able food trays. In this case a nucleating agent or crystallization promoter is employed and the molecular weight is increased. PET is becoming the package of choice for many food products, particularly beverages and mineral waters. The main reasons for its popularity are the properties of glass-like transparency coupled with adequate gas

barrier properties for retention of carbonation. Also it exhibits a high toughness/weight property ratio which allows lightweight, large capacity safe unbreakable containers.

19.2. Application of PET

For more than 100 years, plastic products have revolutionized the way we live. Polyethylene terephthalate, or PET, is a particularly notable example. Global consumption of PET for packaging is valued at $17 billion this year, and is forecast to reach $24 billion by 2011. Asia Pacific, central and eastern Europe, and parts of Latin America showed the strongest growth between 2001 and 2006. The United State is the largest user of PET packaging, followed by China and Mexico. Polyethylene terephthalate is a thermoplastic polymer resin of the polyester family that produced by the chemical industry and is used in synthetic fibers; beverage, food and other liquid containers; thermoforming applications; and engineering resins often in combination with glass fiber. It is one of the most important raw materials used in man-made fibers. It also used for microwave food trays and food packaging films. This is due in part to its inherent properties that are well suited for lightweight, large-capacity and shatter-resistant containers. Because it provides an excellent barrier against oxygen and carbon dioxide and due to consumer trend favoring healthier beverage options, the carbonated soft drink sector has been growing more rapidly than other applications in the past five years. Because of this wide spread application the PET waste disposal poses a serious problem to maintain a clean environment. However, the most important cause for recycle and reprocess the waste PET has arisen from the awareness and concern for environmental pollution. PET recycling represents one of the most successful and widespread examples of polymer recycling. The main driving force responsible for this increased recycling of post-consumer PET is its widespread use, particularly in the beverage industry. A very important feature of PET, decisive in the choice of its wide application in the manufacture of packaging for the food industries is that it does not have any side effects on the human beings. It should be pointed out, that PET does not create a direct hazard to the environment, but due to its substantial fraction by volume in the waste stream and its high resistance to the atmospheric and biological agents, it is seen as a noxious material. Therefore, the recycling of PET does not only serve as a partial solution to the solid waste problem but also contributes to the conservation of raw petrochemical products and energy. Products made from recycled plastics can result in 50–60% energy saving as compared to making the same product from virgin resin. The recycling of waste polymers including PET can be carried out in many ways. Four main classes have been proposed. Classification of polymer recycle can be classified into four categories e.g. primary, secondary, tertiary and quaternary recycling.

19.3. Classification of polymer recycle

Polymer recycle can be classified into four categories e.g. primary, secondary, tertiary and quaternary recycling.

(i) Primary recycling (pre-consumer industrial scrap). It is the recycling of clean, uncontaminated single-type waste which remains the most popular, as it ensures simplicity and low cost, especially when done ''in-plant'' and feeding with scrap of controlled history [274]. The recycled scrap or waste is either mixed with virgin material to assure product quality or used as a second-grade material [375]. Primary recycling of industrial scrap produced during the manufacture of food-contact articles is not expected to pose a hazard to the consumer.

(ii) Mechanical recycling (secondary recycling). In this approach, the polymer is separated from its associated contaminants and it can be readily reprocessed into granules by conventional melt extrusion. Mechanical recycling includes the sorting and separation of the wastes, size reduction, melt filtration and reforming of the plastic material. The basic polymer is not altered during the process. The main disadvantage of this type of recycling is the deterioration of product properties in every cycle. This occurs since the molecular weight of the recycled resin is reduced due to chain-scission reactions caused by the presence of water and trace acidic impurities. A secondary recycling process presents some unique problems that may cause it to be inappropriate for the production of food-contact articles, particularly if the recycler had little or no control over the waste stream entering the recycling facility [276–278].

(iii) Chemical recycling (tertiary recycling). Unlike physical recycling, chemical recycling involves transformation of polymer chain. The polymer backbone under the recycling process is degraded into monomer units (i.e. depolymerisation) or randomly ruptured into larger chain fragments (i.e. random chain scission) with associated formation of gaseous products. The chemical recycling is carried out either by solvolysis or by pyrolysis; the former through degradation by solvents including water, and the latter through degradation by heat in absence of oxygen or air, or vacuum. Chemical recycling yields monomers, petroleum liquids and gases. Monomers are purified by distillation and drying, and used for manufacture of polymers.

(iv) Energy recovery (quaternary recycling). The energy content of the plastics waste can be recovered by incineration. When the collection, sorting and separation of plastics waste are difficult or economically not viable, or the waste is toxic and hazardous to handle, the best waste management option is incineration to recover the chemical energy stored in plastics waste in the form of thermal energy. This is carried out in special type of reactors called incinerators, to burn wastes in the presence of air in a controlled manner to convert hydrocarbons of the plastic into carbon dioxide and water. The heat produced by burning plastics in the waste in the form of superheated steam can be utilized for generating electricity through turbine generators, and the residual heat from the waste stream for heating residential and industrial buildings. The melt residue from the incinerator is free from toxicity hazards and may be disposed off by landfill.

Although polymers are actually high yielding energy sources, this method has been widely accused of being ecologically unacceptable owing to the health risk from air borne toxic substances such as dioxins (in the case of chlorine containing polymers). It should admit that it is not possible to have zero-emission in the incineration of waste plastic. Apart from the aforementioned methods, direct reuse of a plastic material (i.e., PET) could be considered as a ''zero-order'' recycling technique. In a lot of countries, it is a common practice for PET bottles to be refilled and reused. However, this should

be done with great care since plastic bottles are more likely than glass to absorb contaminants that could be released back into food when the bottle is refilled.

Table 4. Some cation exchange material prepared with their analytical applications.

S. No.	Cation exchanger	Application	Reference
Inorganic ion-exchanger			
1.	Sn(IV) and Cr(III) arsenophosphate	Separation of metal ions	[57]
2.	Sn(IV) hexacyanoferrate(II)	Separation of cadmium (II) from Zn(II), manganese(II) and Aluminum(III).	[78]
3.	Sn(IV) arsenosilicate	Separation of metal ions	[279]
4.	Zirconium(IV) and Thorium(IV) arsenosilicate	Kinetic studies	[280]
5.	Antimony(V) silicate	Ion-exchange kinetics	[281]
6	Antimony(V) arsenophosphate	Adsorption of transition metal ions	[282]
7.	Chromium(III) arsenosilicate	Synthesis	[283]
8.	Antimony(V) arsenophosphate	Reverse exchange of alkaline earth metals	[284]
9.	Antimony(V) phosphate	Binary separations of metal ions	[285]
10.	Antimony(V) arsenophosphate	Forward and reverse Na(I)-H(I) and K(I)-H(I)	[286]
11.	Antimony(V) phosphate	Separation of Amino acids	[287]
12	Antimony(V) phosphate	Adsorption of phosphomidon	[288]
13.	Zirconium(IV) tungstophosphate	Synthesis, Hg(II) selective	[3]
Organic-inorganic composite cation exchanger			
1	Polyaniline Sn(IV) Arsenophosphate	Synthesis, ion exchanger behaviour	[132]
2	Tin(IV) arsenophosphate	Adsorption behaviour of carbofuran	
3.	Zirconium(IV) tungstophosphate	Synthesis, ion-exchange behavior, Pb(II) selective	[290]
4.	Polyaniline Sn(IV) tungstoarsente	Synthesis,, electrically conducting, Cd((II) selective	[14]
5.	Polypyrrole/polyantimonic acid	Synthesis,, electrically conducting, crystalline	[13]
6.	Polypyrrole Th(IV) phosphate	Preparation, electrically conducting ad Cd(II) selective	
7.	Polyaniline Sn(IV) phosphate	Preparation, electrically conducting, Hg(II) selective	[12]
8.	Poly-*o*-toluidine Th(IV) phosphate	Preparation, electrically conducting, nano particle, Hg(II) selective	[115]
9.	Poly-o-toluidine Zr(IV) phosphate	Preparation, nano composite, electrically conducting, Hg(II) selective	[117]
10.	Poly-o-anisidine Sn(IV) phosphate [POASn(IV)P]	Preparation, electrically conducting, nano composite, Sb(II) selective	[116]
11.	Nylone-66 Sn(IV) phosphate	Synthesis, Hg(II) selective, fibrous	[257]
13	Poly-o-anisidine Sn(IV) arsenophosphate:	Synthesis, Pb(II) selective	[258]

Moreover, refilling of a PET bottle with a drink with high alcohol content may lead to degradation of the macromolecular chains with unexpected results. Worldwide, the main end-use of post-consumed PET is for the production of fibers (almost 70%), with only 4% of PET recycled with

chemical methods. Among the above recycling techniques, the only one acceptable according to the principles of sustainable development (development that meets the needs of the present generation without compromising the ability of future generations to meet their needs) is chemical recycling, since it leads to the formation of the raw materials (monomers) from which the polymer is made. In this way the environment is not surcharged and there is no need for extra resources (monomers) for the production of PET. PET chemical-recycling techniques the world's most recyclable polymer is polyester. PET is polyester with functional ester groups that can be cleaved by some reagents, such as water (hydrolysis), alcohols (alcoholysis), acids (acidolysis), glycols (glycolysis), and amines (aminolysis). The recycled PET is mostly used in the form of fibres, films, foams, sheets, bottles etc. Thus, chemical-recycling processes for PET are divided as follows: (i) hydrolysis, (ii) glycolysis, (iii) methanolysis and (iv) other processes. Some cation exchangers prepared with their applications are given in Table 4 [279-290].

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