Chapter 1

Introduction
1.0 GENERAL INTRODUCTION

1.1 Fundamentals of Ion-Exchange Process

Chromatography is a physical method of separation in which the components to be separated are distributed between two phases, one of which is stationary phase, while the other is mobile phase [1]. Since its discovery in 1960 the chromatography technique has undergone tremendous modifications and is being used for separation of almost any kind of mixture. The principal chromatographic techniques include: Paper chromatography (PC), Thin layer chromatography (TLC), Gas liquid chromatography (GLC), Gas solid chromatography (GSC), High performance chromatography (HPLC), Size-exclusive chromatography (SEC), Ion-exchange chromatography (IEC) and chiral chromatography (CC). Out of these techniques, ion exchange is probably the most frequently used chromatographic technique [2-7] which is used for the separation and purification of charged species including metal ions, proteins, polypeptides, nucleic acids, and other charged biomolecules. The reasons for the wide use of ion-exchange materials for the separation and purification are owing to their widespread applicability, high resolving power, high capacity, and the simplicity and control ability of the method. The separation in ion-exchange chromatography depends upon the reversible adsorption of charged solute molecule to immobilized ion-exchange groups of opposite charge. If the immobilized ion is an anion, it requires positive exchangeable charged ions or if immobilized ion is a cation, it requires negative exchangeable charged ions (Figure 1.1). These exchangeable counter ions (charged ions) play most imperative role because they are mobile in nature and may be replaced by other ions depending on their relative concentrations and affinities for the sites.
The technique of ion-exchange chromatography is based on interaction between solute molecules and ligands immobilized on a chromatography matrix. Different substances have different degrees of interaction with the ion-exchanger due to differences in their charges, charge densities and distribution of charge on their surfaces and, therefore, these interactions can be controlled by varying the conditions for better separation such as ionic strength and pH. When the exchanger comes in contact with an electrolyte, these ions can be exchanged stoichiometrically with an equivalent amount of other ions of same sign (Figure 1.2). In ion-exchange chromatography one can choose whether to bind the substances of interest and allow the other species to pass through the column, or to bind the species and allow the substance of interest to pass through. A good ion-exchanger must be highly cross-linked with negligible solubility in the medium. It should be chemically stable, must contain sufficient number of accessible ion-exchange groups and should be sufficiently hydrophilic to permit diffusion of ions through the structure at a finite and efficient rate.

Effectiveness of an ion-exchanger depends on ion-exchange characteristics such as ion-exchange capacity, pH, concentration, elution and distribution behavior. The ion-exchange capacity depends on hydrated ionic radii and selectivity of ion-exchanger. The selectivity of ion-exchanger, in turns, is influenced by the nature of its functional group and degree of its cross linking. Ion-exchanger, having the groups that are capable of complex formation with some particular ions, will adsorb these ions more strongly. As the degree of cross linking increases, the exchanger becomes more selective towards ions of different sizes [8 -11]. The efficiency of an ion-exchanger depends on the following fundamental of exchange reactions:
• Equivalence of exchange.
• Selectivity for any species relative to other species, including the cases in which the varying affinities of the ions are modified by the use of complexing and chelating.
• Donnan exclusion the ability to exclude ions but, in general, undissociated substances.
• Screening effect - the inability of very large ions or polymers to be adsorbed to an appreciable extent.
• Difference in migration rates of adsorbed substances down a column-primarily a reflection of difference in affinity.
• Ionic mobility restricted to the exchangeable ions and counter ions only.
• Miscellaneous-swelling, surface area and other mechanical properties.

Separation and purification of charged species especially metal ions, metal complexes, proteins, polypeptides, nucleic acids, polynucleotides, charged biomolecules etc., have been the chief and oldest objective of an ion-exchange chromatography [12-15]. Ion-exchange chromatography is very horary but it is still used because of its special properties such as exchange of ions and separation of different ions. Separation depends upon the reversible adsorption of charged molecules to restrain ion-exchange groups of opposite charges. Since different substances possess different charges, charge densities and distribution of charge on their surfaces, consequently they have different degrees of interaction with ion-exchanger. These interactions can be controlled by varying conditions such as ionic strength and pH. To understand the mode of separations, it is classified into 5 main stages (Figure 1.3).
• **Equilibrium** is the first stage of separation in which an ion-exchanger is conveyed to a starting state. Ionic strength and pH which allow the binding of the desired solute molecules are adjusted for the proper adsorption/separation of desired species. At this stage exchanger groups are associated with exchangeable counter-ions.

• **Adsorption** is the second stage of separation in which solute molecules carrying the appropriate charge displace counter ions and bind reversible to the ion-exchanger. Unbound substances can be washed out from the exchanger.

• **Desorption** is the third stage of separation in which substance is removed from the column by changing the elution conditions i.e. by increasing the ionic strength of eluting solution or by changing its pH. In desorption process solute molecules are released from the column in the order of their strength of binding. Substances more tightly bound to the exchanger elute later and weakly bounded substance being eluted sooner.

• **Regeneration** and **re-equilibration** are the fourth and fifth stage of separation in which the same resin beads are regenerated to its initial state by treating with suitable ions. Now, the regenerated resin can be used over and over again.

### 1.2 Classification of Ion-Exchangers

#### 1.2.1 Organic ion-exchangers

The organic ion-exchangers are also known as ion-exchange resins. The matrix of the resins is a flexible indiscriminate network of hydrocarbon chains which carry fixed ionogenic groups such as \(-\text{NH}_3\), \(-\text{NH}_2\), \(-\text{N}^-\), \(-\text{S}\) etc. in anion exchangers and \(-\text{SO}_3^-\), \(-\text{COO}^-\), \(-\text{PO}_3^{2-}\), \(-\text{AsO}_3^{2-}\) etc. in cation exchangers. The resins are made by cross-linking of 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 solvent. The degree of swelling depends both on the characteristics of the solution or solvent and the exchanger itself and influenced by a number of conditions such as solvent polarity, degree of cross-linking, exchange capacity, strong or weak salvation tendency of fixed ion groups, size and extent of the salvation of counter ions, concentration of external solution and the extent of the ionic dissociation of functional groups. Organic ion exchangers may be ‘natural’ or ‘synthetic’. The synthetic organic ion-exchange resins are superior to other materials because of their high chemical, mechanical stability, ion-exchange rates, ion-exchange capacity and versatility and low cost relative to some synthetic inorganic media. Depending upon the change on the matrix and the ions taking part in ion-exchange process, exchanger may be classified as cation exchangers and anion exchangers. If both types of changed are taking part in an ion-exchange process then this type of exchanger is called amphoteric exchangers.

Cation exchangers are condensation product of phenol and aldehyde derivatives. They are further divided into strong acid cation and weak acid cation exchangers. The most important strong acid cation exchangers are sulfonation products of cross-linked polystyrene whereas the cross-linked copolymers of acrylic or methacrylic acid as the example of weak acid exchangers. The strong acid cation exchange resins split neutral salts and convert them to their corresponding acid.

\[ \text{R-SO}_3^- : \text{H}^+ + \text{NaCl} \rightarrow \text{HCl} + \text{R-SO}_3^- : \text{Na}^+ \]  \hspace{1cm} (1.1)

These resins can be regenerated with a strong acid such as H\textsubscript{2}SO\textsubscript{4}.

\[ 2\text{R-SO}_3^- : \text{Na}^+ + \text{H}_2\text{SO}_4 \rightarrow 2\text{R-SO}_3^- : \text{H}^+ + \text{Na}_2\text{SO}_4 \]  \hspace{1cm} (1.2)
The regeneration efficiency of these resins is 30-50%. The weak acid cation exchange resins cannot split neutral salts but can remove cations associated with the water alkalinity to form carbonic acid.

\[ \text{R-COO}^- : \text{H}^+ + \text{NaHCO}_3 \rightarrow \text{RCOO}^- : \text{Na}^+ + \text{H}_2\text{CO}_3 \] (1.3)

These resins can be regenerated with any acid stronger than the function group.

\[ \text{R-COO}^- : \text{Na}^+ + \text{HCl} \rightarrow \text{RCOO}^- : \text{H}^+ + \text{NaCl} \] (1.4)

The regeneration efficiency of these resins is near 100%. The commonly used cation exchangers are listed in Table 1.1.

Anion exchangers are condensation products of aromatic or aliphatic amines and aldehydes, dihaloparaffins, or haloepoxides (epichloroydrin). Most of these resins contain primary, secondary and tertiary amino groups and are weak base and polyfuctional materials. The most important anion exchangers are cross-linked polystyrenes into which strong or weak base groups have been introduced by chloromethylation and subsequent amination. The reaction with tertiary alkyl amine gives strong base quaternary ammonium group (strong base anion exchanger), and reaction with primary or secondary alkyl amine or ammonium gives weak base amino groups (weak base anion exchanger). The strong base anion exchange resins split neutral salts and convert them to their corresponding base.

\[ \text{R-NR}_3^+ : \text{OH}^- + \text{NaCl} \rightarrow \text{R-NR}_3^+ : \text{Cl}^- + \text{NaOH} \] (1.5)

These resins can be regenerated with NaOH.

\[ \text{R-NR}_3^+ : \text{Cl}^- + \text{NaOH} \rightarrow \text{R-NR}_3^+ : \text{OH}^- + \text{NaCl} \] (1.6)
The regeneration efficiency of these resins is 30-50%. The weak base anion exchange cannot split neutral salts but they can remove strong acids by adsorption.

\[ R-\text{NH}_2 + \text{HCl} \rightarrow R-\text{NH}_2\cdot\text{HCl} \]  
(1.7)

The resin is regenerated by treatment with excess 1M NaOH solution or by NH\textsubscript{3} solution.

\[ R-\text{NH}_2\cdot\text{HCl} + \text{NaOH} \rightarrow R-\text{NH}_2 + \text{H}_2\text{O} + \text{NaCl} \]  
(1.8)

The regeneration efficiency of these resins is near 100%. A list of different anion exchange resins has been presented in Table 1.1.

1.2.2 Inorganic ion-exchangers

The organic exchangers have wide applications in analytical chemistry because of their high stability over a wide range of pH, and reproducibility in results. However, their instability under conditions of high temperature and strong radiations has led to a major switch for the development of inorganic ion-exchange materials. Inorganic ion-exchangers are capable of being stable at elevated temperatures and in the presence of strong radiations and have played a vital role and established a distinguished position among the ion-exchange materials.

The inorganic ion-exchangers are generally the oxides, hydroxides and insoluble acid salts of polyvalent metals, heteropolyacid salts and insoluble metal ferrocyanides. They can be prepared both in crystalline and amorphous forms having good chemical stability, reproducibility in ion-exchange behavior and selectivity for certain metal ions. Inorganic ion-exchangers may be classified as natural and synthetic. The natural inorganic ion-exchangers are naturally occurring materials such
as minerals, clays, soils, natural zeolites, etc. The synthetic ion-exchangers which have been studied quite extensively [16-26] are created by combining the oxides of elements of III, IV, VI groups of periodic table. A large number of such materials have been synthesized by mixing phosphoric, arsenic, molybdic, antimonic and vanadic acid with Ti, Zr, Sn, Th, Ce, Cr, Nb, Bi, Ni, Co and Ta.

Synthetic inorganic ion-exchangers are further classified on the basis of the chemical characteristic of the ion-exchange species and include synthetic zeolites (aluminosilicates), hydrous oxides of metals, acidic salts of polyvalent metals, insoluble salts of heteropolyacids, insoluble hydrated metal hexacyanoferrate (II) and (III) or ferrocyanides and substance with weak exchange properties [27]. Important advances in the field of synthetic inorganic ion-exchangers have been reviewed by a number of workers at the various stages [27-49].

1.2.3 Hybrid ion-exchangers

Inorganic ion-exchangers were developed as alternative to organic exchangers owing to their thermal stability at elevated temperatures and under strong radiations. However, due to their inorganic nature they lacked chemical and mechanical stability. Further, they did not show reproducible ion-exchange behavior. The above shortcomings led to the development of organic based inorganic ion-exchangers termed as “hybrid ion-exchangers”. The hybrid ion exchanger consists of both organic and inorganic counter parts and did not exhibit the properties of purely organic or purely inorganic materials. Hybrid ion-exchangers are prepared in the laboratory by incorporating a polymeric or monomeric organic species into the inorganic matrix [50-53]. They exhibit interesting properties such as higher chemical, thermal and mechanical stability, good exchange capacity, and high selectivity for heavy metals.
and have high reproducibility. Hybrid materials can be divided into two classes, depending on the nature of the links and interaction existing at the hybrid interface [54].

- **Class I:** Included only van der Waals or hydrogen bonding and electrostatic forces. There are no covalent bonds between the organic and inorganic components. This class involves mainly small species embedded within an oxide matrix.

- **Class II:** This class show conflicting properties than class I. In this class parts of hybrid compounds i.e. organic and inorganic are linked through strong covalent bonds.

### 1.2.4 Fibrous ion-exchangers

In recent years, fibrous ion-exchangers have drawn the attention of researchers because they open unusual possibilities for new technological designs of various textile goods such as cloth, stables, net and nonwoven materials. They have high osmotic stability that allows them to be mechanically more durable in conditions of multiple wetting and drying for example at cyclic sorption or regeneration processes in treatment of gaseous media. The sorption rate is hundred times faster than that of the conventional granular exchangers due to their monofilaments diameter (5-50 µm), which is much smaller than that of the resin beads (500-1000 µm). Soldatov et al. have shown that fibrous ion-exchangers are suitable for the efficient air purification from ionized impurities in very low concentrations [55]. A number of monographs [56-58], review [59] and patents dealing with the preparations, properties, technologies and possible areas of applications of fibrous ion-exchangers have been published. Fibrous ion-exchangers may be further classified into organic fibrous ion-
exchanger, inorganic fibrous exchanger and hybrid ion exchangers. The hybrid fibrous ion-exchangers are synthesized by combining a fibrous inorganic ion-exchanger with an organic species. They have the added advantages of both components. The hybrid fibrous ion-exchangers exhibit outstanding chemical, mechanical (due to organic part) and thermal (due to inorganic part) stability in addition to metal ion selectivity. A large number of hybrid ion-exchangers have been synthesized in the laboratory by incorporating organic monomeric or polymeric species into fibrous inorganic ion-exchangers. These new materials have shown promising ion-exchange characteristics as supported by some important binary separations achieved practically. However, the main problem associated with these materials has been spinning them and to obtain mechanically strong materials with high exchange capacity. An increased ion-exchange capacity always led to decrease in the mechanical and tensile strength.

1.3 Progressive Development and Modification of Ion-Exchange Materials

The ion exchange process has been in practice with the start of civilization for obtaining soft water. But the modern study in this field started with the discovery of the process by Thomson [60] and Way [61]. They separately published papers in the Journal of the Royal Agricultural Society of England describing the phenomenon of ion-exchange as it occurs in soils. The most active period for the development of ion-exchanger has been regarded as the middle of the 20th century [62-71]. After that, only small developments are made in improvement of the exchange properties, application process and column design. The ion-exchange process is now an integral part of daily life. The current uses of ion-exchange process include treatment of water for drinking and industrial use, and wastewater treatment. Ion-exchangers can soften the water,
deionize it, and can even be used in desalination. In industrial uses, pure water is often crucial for the successful development of a product. Preparation of various acids, bases, salts, and solutions is also aided by ion-exchange process. The recovery of valuable metals is also possible with resins. Ion-exchange is used to prevent coagulation in blood stores and in dextrose.

Natural zeolites [72-75] were the first materials to be used in ion-exchange processes. The natural and synthetic sodium aluminosilicates (also called zeolites) are no longer used for water softening. The disadvantages associated with the inorganic exchangers are:

- Relatively low exchange capacities
- Relatively low abrasion resistance and mechanical durability
- Variable pore size
- Clay minerals tend to peptize into a colloidal form
- Difficult to size mechanically
- Limited chemical stability especially in acidic or alkaline solution (working pH range is 4–9).

Clay minerals and natural zeolites, although replaced by synthetics to a large extent, continue to be used in some applications, owing to their low cost and wide availability. They are still widely used as component of washing powders and for the treatment of liquid waste streams in which very high chemical cleanliness is not required.

The development of organic ion-exchangers largely replaced the use of inorganic exchangers as they possessed high ion-exchange capacity, high chemical
stability (resistant to acids and alkalis), wide applicability, low cost and more resistant to mechanical degradation [76-83]. The main limitations associated with synthetic organic ion-exchangers are their limited radiation and thermal stabilities. To overcome the problem of poor physical strength, radiation and thermal stabilities and to enhance chemical stability, methods for incorporating inorganic ion-exchangers into supporting binder materials, both inorganic and organic, have been developed. These composite materials or more appropriately ‘synthetic hybrid ion-exchanger’ has been developed in the granular form, with sufficient strength for column use and with improved ion-exchange properties. The properties of the synthetic/composite inorganic-organic exchangers depend upon:

- Solvent’s polarity
- Degree of cross-linking of organic part
- Organic and inorganic content in the exchanger
- Availability of active ion exchanging sites
- Strong or weak solvation tendency of the fixed ion groups
- Size and extent of the solvation of counter ions
- Concentration of the external solution, and
- Extent of the ionic dissociation of functional groups.

The advantages with the fibrous ion-exchangers [84-87] are that they can be produced in the form of filaments, cloths or nonwoven materials, which opens many possibilities for the ion-exchange technology. Alongside with the traditional column processes, it is possible to use ion-exchange fibers in the form of continuous conveyer belts, devices combining the functions of mechanical and ion-exchange filters, thin flat layers etc. A small diameter of the monofilaments (3-25 µm for the commercial
fibers) increases the surface area, rate of ion-exchange process and the efficiency of the ion-exchange apparatuses. The application of micro spherical ion-exchangers (granules and beads) on large scale processes is limited due to high resistance of the ion-exchange filters to the flows of liquids and gases. This difficulty is eliminated when the ion-exchange fibers are used since the resistance of a layer is easily controlled by density of the fiber packing in a filter and may be predetermined according to the engineering requirements [56–58]. The fibrous ion-exchangers are very promising in the environment protection where it is necessary to treat large volumes of water or air containing impurities in low concentrations. In spite of the valuable properties mentioned above, up till now the fibrous ion-exchangers have not found a wide application in the ion-exchange engineering and are not produced commercially in quantities. Some of the reasons are their low mechanical and chemical stability, low ion-exchange capacity and insufficient studies on the synthesis, applications and selectivity behavior.

After the intensive studies on development of methods for preparation of fibrous ion-exchangers of various types and the search for the fields of their efficient application, the preparation of fibrous sulphonylic-type cation exchangers (the analogues of Dowex-50) were developed. The strong base anion exchangers (the analogues of Dowex-1), weak base and medium base anion exchangers, and weak acid cation exchangers with complexing properties were reported [88-90]. The synthesis of strong base (conventionally named SBF) and the strong acid (SAF) fibers were based on graft copolymerization of polystyrene and polypropylene. The medium base fibre (MBF) exchangers have been synthesized by chemical modification of acrylic fibers. The ion-exchange fibers with a monofilament thickness from 20 to 40 µm were obtained. All these materials have been used in various textile forms during
a variety of experiments [91,92]. The literature shows that the most of the researches on ion-exchange fibers have been carried out in Russia and Japan [93,94].

Institute of Physico-organic Chemistry of Byelorussian Academy of Sciences reported the preparation for fibrous ion-exchangers of different types and suggested the fields of their efficient application, such as air purification from acidic and alkaline impurities [95], preparative chromatography, water purification or extraction of ions of useful elements from gaseous media. The processes of water purification and extraction of useful metals as uranium, gold etc., have also been reported [96, 97]. The methods and technology of production of fibrous ion-exchangers of all types based on styrene and divinylbenzene copolymers grafted onto the polypropylene fibre have been developed [88-91]. These fibrous ion-exchangers have registered trade mark “Fiban®” [98]. Fiban K-1 [88], a strong cation exchanger, was prepared by sulphonation of styrene divinylbenzene co-polymer grafted onto polypropylene (PP) fibre. Other fibre “Fiban A-1” [91], a strong base fibre, was developed by chloromethylation and subsequent amination of same grafted copolymer with trimethylamine. Thus, the Fiban K-1 and A-1 ion-exchangers are analogues of the common granular ion-exchange resins and can be used for the same purposes. The Fiban AK-22 [99,100], a weak base polyacrylic fibre, is a complex forming polyampholyte containing imidazoline and carboxyl groups [101]. Soldatov et al. [102] studied the ion-exchange fibres to explore the possibilities in technology for purification of air and water. Their main advantages proposed are; a high rate of ion-exchange process, low and easily controlled resistance to the flow of liquids and gases, and the possibility of using in a variety of physical forms, such as column filters, conveyer belts, thin layers etc. The fibrous exchangers have great advantages compared to traditional ion-exchange resins in having better ion-exchange properties,
osmotic, thermal and chemical stability and mechanical strength. Soldatov et al. [103] reported the use of fibrous ion-exchangers (FIBAN) for water softening and removal of Co$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Cu$^{2+}$, Pb$^{2+}$ ions from water. They studied the effect of the filtering bed height, density of the column packing corresponding to the volume capacity, solution flow rate on the efficiency of Ca$^{2+}$ removal from a model solution. A fibrous sulfonic-type ion-exchanger in shallow beds has exhibited high efficiency in removal of Ca$^{2+}$ from water, greatly exceeding efficiency of a conventional sulfostyrene resin studied in parallel. In the processes of water purification from heavy metal ions the highest efficiency was observed for chelating fibrous ion-exchanger with iminodiacetate groups. A granular resin of the same type had much lower efficiency and proposed that fibrous ion-exchangers can find a wide application in water treatment processes.

Many hydrometallurgical processes are accompanied by air pollution with volatile acids, anhydrides and aerosols. Fibrous ion-exchangers can be one of the powerful means to solve this problem. Fibrous ion-exchange materials in the form of cloth or non-woven belt with a filament thickness below 50 microns can be used for the removal of impurities from gas flow. It has been shown that the rate of sorption is one or two orders of magnitude higher than that for industrially produced resins of similar chemical structure [104]. These materials are elastic to some degree and have outstanding osmotic stability [105]. The ion-exchange fibre sheet in the form of tobacco smoke filter material [106,107] prepared by sulphonating polymers fibres, selectively remove carcinogenic and mutagenic substance from cigarette smoke, without affecting flavor and aroma. Thus, a compound containing polystyrene [90003-53-6], polypropylene [9003-07-0] and polypropylene (having 40:10:50 parts, respectively) were spun at 270 °C to yield fibres. The sheet and poly (ethylene-
terephthalate) were layered and made into cigarette filter tips. This cigarette filter tip removed more tar than a conventional one, and gave high organoleptic test scores. Fibrous ion-exchangers with good sorption properties were obtained by modifying partially carboxylated acrylic fibre with epichlorohydrin polyethylene-polyamine adduct, PAE [108]. The good sorption properties can be preserved by drying the fibres at 20 °C.

Fibrous porous composite (FPC) having good sound proofing properties were synthesized by Zosina et al. [109,110] from polyvinyl alcohol binder and HCHO, in the presence of mineral acid catalyst. Borrell et al. [111] prepared fibrous ion-exchangers by introducing basic groups (e.g tertiary amine, imidazoline, tetra-hydro pyrimidine and quaternary ammonium groups) on to cross-linked water insoluble polyacrylonitrile fibres. These fibres have higher ion-exchange capacity. Fibrous ion-exchanger based on polyacrylonitrile modified with sodium-alkyl-siloxaneshas been prepared [112,113]. The diffusion rate of the siloxane modifiers into the polyacrylonitrile fibres depended on the size and nature of the Si-bonded alkyl group in the siloxane. This increased the ion-exchange. The continuous manufacture of polyacrylonitrile based ion-exchange fibres increased their total exchange capacity and swelling and improved their sorption desorption parameters without deteriorating tenacity, compared with batch manufacture [114].

Polyacrylonitrile (PAN) based ion-exchange fibre was obtained [115] by PAN fibre or fibre structure material and reacting it with liquid amine compound having alkyl group. These ion-exchange fibres and textile were having strong adsorption ability to harmful gases and were also possessing high regeneration property. The ion-exchange fibre of multifunctional groups was synthesized by using PANF as a raw
material [116]. The structure of this material was analyzed by elemental analysis and IR spectrometry. The adsorption capacities and distribution coefficients for various metal ions such as Pd(II), Au(II), Pt(IV), Ru(IV), Os(IV), Rb(II) and Ir(IV) were determined. The ion-exchange fibre was found to have excellent adsorption and desorption properties and was used for the separation and pre-concentration of Au(III), Pd(II), Pt(IV) in the synthetic aqueous sample with the relative standard deviation 1.79-2.00% and the recovery 95.0-97.5%.

Acrylonitrile-acrylic acid copolymers [117,118] and acryl fibres [119-124] were reported to behaving high tactacity, spinning, chemical and technical application. A fibrous ion-exchanger prepared by Ergozhin et al. [125] which increased ion-exchange capacity with increasing modification temperature from 20-100 °C. Ion-exchange fibres based on polyvinyl alcohol, polyacrylonitrile containing -COOH group were used for the adsorption of insulin [126]. The -COOH group dissociation coefficient and adsorption-desorption processes depended on the fibre nature. The highest stability for insulin was observed for modified polyacrylonitrile fibre sorbents in the Na-salt forms. The absorption and desorption of insulin from modified polyacrylnitrile fibre was possible only in alkaline buffer solution.

A systematic investigation on the synthesis of insoluble crystalline acid salts of tetravalent metals has facilitated the preparation of several new crystalline fibrous inorganic ion-exchangers. The first fibrous acid salt of tetravalent metal was cerium (IV) phosphate prepared by Alberti et al. [127,128] in the year 1968. Subsequently, fibrous thorium phosphate, [129-131], titanium phosphate [132-134] and titanium arsenate [135,136] were also prepared. Fibrous inorganic ion-exchanger are very interesting from practical point of view because they can be used to prepare inorganic
ion-exchange papers or thin layers, suitable for chromatographic cation separations and ion-exchange membranes without a binder [128] with good electro-chemical behavior. Owing to their high selectivity and stability, these membranes have applications as selective electrodes, where organic membranes failed.

Improvement in the field of ion-exchange chromatography was made by the formation of hybrid fibrous ion-exchangers. When certain fibrous inorganic ion-exchangers were combined with the organic species, then a new class of ion-exchangers was developed. Hybrid ion-exchangers exposed new routes for research on ion-exchange properties just because of the unique characteristics feature. Hybrid ion-exchanger exhibited outstanding chemical, mechanical and thermal stability. Hybrid fibrous ion-exchangers were observed to be chemically and mechanically more stable due to presence of the organic part and thermal stable due to presence of inorganic part in it. A number of such ion-exchangers were reported when certain fibrous inorganic ion-exchanger like Ce(IV) phosphate and Th(IV) phosphate were combined with the organic species [137-146]. These materials were fibrous in nature. The commonly used organic compounds were monomeric (e.g acrylamide, cellulose acetate etc.), or polymeric species (e.g polyacrylonitrile, polystyrene etc.). These materials are reported to be very useful for separation and removal of heavy metals from aqueous media. They can be used in different convenient form due to its fibrous nature. The main problem associated with the hybrid fibrous ion-exchangers has been spinning of these materials and to obtain mechanically strong material with ion-exchange capacity. It is generally observed that an increase in ion-exchange always leads to a decrease in the mechanical and tensile strength. The studies on hybrid fibrous ion-exchangers are still in the stage of beginning.
1.4 Surfactants and Their Properties

Surfactants are the surface active agents [147-152] having potential ability to radically alter surface and interfacial properties and to self-associate and solubilize themselves in micelles. Surfactants adsorb (or locate) at interfaces, thereby, altering significantly the physical properties of those interfaces (e.g. lowering of the surface tension). The interfaces may be of liquid/liquid (e.g. oil/water), solid/liquid and gas/liquid (e.g. air/water) type. The unusual properties of aqueous solution of surfactants are attributed to the presence of hydrophilic ‘head-group’ and hydrophobic ‘chain’ (tail) in the same molecule. The hydrophilic (head-group) part of the molecule may be ionic or polar in nature while the hydrophobic tail is consists of usually straight or branched hydrocarbon or fluorocarbon containing 8-18 carbon atoms covalently attached to the polar/ionic ‘head-group’. Figure 1.4 depicts a typical representation of a low molar mass surfactant molecule.

In aqueous solution, the hydrophobic chain interacts weakly with the water molecules, whereas the hydrophilic head interacts strongly via dipole or ion-dipole interactions. This strong interaction between water and ‘head-group’ renders the surfactant soluble in water. However, the cooperative action of dispersion and hydrogen bonding between the water molecules tends to squeeze the surfactant chain out of the water (hence, these chains are referred to as hydrophobic). Therefore, surfactants tend to accumulate at the surface, which allows lowering the free energy of the phase boundary, i.e. the surface tension ($\sigma$). Surfactant molecules at concentrations above critical micellar concentration (CMC) aggregate together to form spherical structure called ‘micelles’. Micelles are spontaneously formed clusters of surfactant molecules (typically 40 to 200), whose size and shape are governed by geometric
and energetic considerations. They are loose, mostly spherical aggregates above their CMC in water or organic solvents [153]. The micellar aggregates are short-lived dynamic species, which rapidly disassemble and reassemble [154]. Thus, micelles are disorganized assemblies with the polar head-groups point towards water and hydrophobic chains are directed towards the interior of the aggregate (Figure 1.5). The formation of micelles is a result of a complex interplay between hydrophobic forces and weak non directional repulsive forces. Hydrophobic forces which are opposed by electrostatic repulsion among the ionic head-groups at the micelle surface drive the micellization in water. This driving force is actually related to the formation of hydrophobic hydration shells around hydrophobic surfactant moieties.

One of the most interesting properties of micellar aggregates is their ability to enhance the aqueous solubility of hydrophobic substances which otherwise precipitate in water [155,156]. The solubility enhancement originates from the fact that the micellar core can serve as compatible hydrophobic microenvironment for water-insoluble molecules. It finds numerous applications e.g. for the environment friendly solubilization of organic solvents in water or for the design of drug delivery systems, or else in detergency applications. Additional surfactants increase the micelle concentration or allow micelle growth, while the concentration of the unassociated monomers remains almost constant.

1.5 Classification of Surfactants

Surfactants are usually classified according to the nature of the hydrophilic head-group present in the molecule. Thus, surfactants may be broadly classified as ionic (i.e. anionic, cationic or amphoteric) and non-ionic surfactants.
1.5.1 Anionic surfactants

Anionic Surfactants are dissociated in water into an amphiphilic anion, and a cation, which is in general an alkaline metal ion (Na\(^+\), K\(^+\)) or a quaternary ammonium. They are the most commonly used surfactants and account for about 50% of the world production. Anionic surfactants are relatively cheap and are applied in most surfactant-based formulations and detergents. Commonly used anionic groups are alkylbenzene sulfonates (detergents), fatty acid soaps, lauryl sulfate (foaming agent), di-alkyl sulfosuccinate (wetting agent), lignosulfonates (dispersants) etc. (Figure 1.6). ‘Soap’ refers to a sodium or potassium salt of a fatty acid and a typical soap bars contains 30% water, 25% C12-C14 soaps to increase foam ability and tolerance to divalent cations (calcium and magnesium). C16-C18 soaps are also added to give the final product as water soluble, without being too quick to dissolve.

1.5.2 Cationic surfactants

Cationic Surfactants, when dissolved in water, are dissociated into an amphiphilic cation and an anion, mostly halogen type. A very large proportion of this class of molecules corresponds to nitrogen compounds such as fatty amine salts and quaternary ammoniums, with one or several long alkyl chains these surfactants are in general more expensive to produce and therefore used in more specialized applications such as in disinfectant formulations, corrosion inhibitors, fabric softeners, etc. (Figure 1.7).

1.5.3 Amphoteric (zwitterionic) surfactants

Amphoteric (zwitterionic) surfactants contain both cationic and anionic groups, and generally induce lower skin irritation and show good compatibility with
other surfactants (Figure 1.8). Some amphoteric surfactants are insensitive to pH, whereas others are cationic at low pH and anionic at high pH, with an amphoteric behavior at intermediate pH. Amphoteric surfactants are generally quite expensive, and consequently, their use is limited to very special applications such as cosmetics where their high biological compatibility and low toxicity is needed. Some of the examples are betaines, sulfobetaines, aminoacids and phospholipids.

1.5.4 Nonionic surfactants

These surfactants do not ionize in aqueous solution, because their hydrophilic group is of a non-dissociable, such as alcohol, phenol, ether, ester, or amide. A large proportion of these nonionic surfactants are made hydrophilic by the presence of a polyethylene glycol chain, obtained by the polycondensation of ethylene oxide. They are called polyethoxylated nonionics. Nonionic surfactants are ranked after the anionic in terms of industrial importance. They usually have repeating ethylene oxide units or carbohydrates as a hydrophilic group (Figure 1.9).

1.5.5 Polymeric surfactants

Polymeric surfactants are the ‘polysoaps’ formed from the association of one or several macromolecular structures exhibiting hydrophilic and lipophilic characters, either as separated blocks or as grafts. These repetitive units are amphiphilic and made from individual surfactant monomer units (hydrophilic and hydrophobic groups scattered all over the macromolecule) [157] (Figure 1.10). They are commonly used in cosmetics, paints, foodstuffs, and petroleum production additives.
1.5.6 Oligomeric surfactants

Oligomeric surfactants are a unique class of surfactants that differ from conventional surfactants in their molecular structures having several polar and ionic functional groups, distributed along a hydrocarbon chain, form the hydrophilic part of the molecule. The size of hydrophilic part is comparable with or greater than the hydrophobic counterpart. Oligomeric surfactants are of both academic and industrial interest as they exhibit an enhanced property profile and provide some unusual properties compared to conventional surfactants (Figure 1.11).

1.5.7 Gemini surfactants

Gemini surfactant molecules have two hydrophilic (chiefly ionic) groups and two tails per surfactant molecule. These twin parts of the surfactants are linked by a spacer group of varying length (most commonly a methylene spacer or an oxyethylene spacer) (Figure 1.12). Gemini surfactants exhibit remarkably a number of superior properties when compared to conventional single-headed, single-tailed surfactants. They possess lower values of critical micellar concentrations, increased surface activity and lower surface tension at the CMC, enhanced solution properties such as hard-water tolerance, superior wetting times, and lower Krafft points [158-162].

1.6 Applications of Surfactants and Their Role in Adsorption and Ion-Exchange Process

The applications of surfactants in industries are quite diverse and have great practical importance. Surfactants may be applied to advantage in the production and processing of foods, agrochemicals, pharmaceuticals, personal care and laundry
products, petroleum, mineral ores, fuel additives and lubricants, paints, coatings and adhesives, and in photographic films. They can also be found throughout a wide spectrum of biological systems and medical applications, soil remediation techniques, and other environmental, health, and safety applications. Ionic surfactants tend to adsorb onto opposite-charged solid surfaces due to electrostatic interactions. Adsorption of ionic surfactants on a like-charged substrate may occur via hydrogen bonding or attractive dispersion forces [163,164] as is the case for nonionic surfactants. The adsorption of surfactant molecules with all the head groups towards the solid surface forms hemimicelle [165]. In addition to the hemimicelle and local bilayer, or micelle, the other surfactant aggregates are surface micelles (spherical aggregates with only one surfactant monomer adhering to the solid surface) and hemicylinders and cylinders (cylindrical structures arranged with the surfactant headgroups facing outward) [166,167].

The work on the metal oxide-surfactant intercalated material started with the view to develop heterogeneous catalyst. Huo et al. [168,169] developed the surfactant inorganic precursor interaction method to extend the preparation to a variety of ionic surfactants. These interactions can be classified into four categories; (i) it involves direct co-condensation of anionic inorganic species with a cationic surfactants (S\textsuperscript{+}I\textsuperscript{-}), (ii) cooperative condensation of cationic inorganic species with a anionic surfactants (S\textsuperscript{-}I\textsuperscript{+}), (iii) and (iv) involves the condensation of ionic inorganic species with surfactants having the similar charge and the condensation is mediated by the counter ions of opposite charge of surfactant head-group (S\textsuperscript{+}XI\textsuperscript{+} and S\textsuperscript{-}M\textsuperscript{+}I\textsuperscript{-}, where X\textsuperscript{-} denotes anions such as Cl\textsuperscript{-} or Br\textsuperscript{-}, and M\textsuperscript{+} denotes cations like K\textsuperscript{+} or Na\textsuperscript{+}). They also reported the synthesis of non-siliceous mesoporous transition metal oxides and mixed oxides. Pinnavaia’s et al. [170,171] prepared mesoporous materials through S\textsuperscript{0}O\textsuperscript{0}
hydrogen bonding between polyethylene oxides (PEO) and inorganic species, which extended the synthesis to new polymer templates and larger pore sizes. The mesoporous silicas prepared using PEO have a less ordered wormhole-like structure and thermally more stable. Self-assembled monolayers on mesoporous silica (SAMMS) were synthesized by treating silicate with micelle template and developed nano-sized / rod shaped regular arrangement of pores. The removal of templates may be carried out by different ways such as adjusting the pH of solvent, heating, combustion or extraction [172]. Other method for the synthesis includes are sol-gel method or a spray drying method [173].

SAMMS have ability to alter the functional group of the monolayer and form highly sorbed materials which potentially bind a broad range of molecules. SAMMS is nanoporous materials whose surface area is in order of magnitude greater than nano particles because of the uniform internal surface area [174]. These mesoporous materials can be used as substrate for self-assembled monolayers of adsorptive functional groups that are selected to specifically adsorb heavy metals. SAMMS allows the removal of mercury and other metals such as cadmium, silver and molybdenum from soil and sludges. Thiol-SAMMS, first and most widely studied material for removal of mercury. Apart from this it can also bind other metallic cations, such as lead, silver and thallium [175]. Metal capped ethylene diamine (EDA)-SAMMS designed for the adsorption of anions, such as chromate and arsenate and can bind metals such as copper, nickel, cobalt and zinc. Shao et al. [176] grafted SDBS on Vulcan XC-72 carbon (XC-72 carbon) using a plasma technique and observed that XC-SDBS possessed higher adsorption capacity for Pb²⁺ than that of XC-72 carbon. They suggested the suitability of XC-SDBS for the immobilization of
heavy metal from large volume of aqueous solutions in environmental pollution cleaning.

The attention has been paid on ion-exchange properties of materials containing surfactant molecules and inorganic ion-exchanger in our laboratory. Varshney et al. [177-181] synthesized a series of cation-exchangers using ionic and polar surfactants. They synthesized Triton X-100- tin (IV) phosphate (i.e. TX-100-SnP) cation exchanger and characterized it by using different physico-chemical methods such as ion-exchange capacity, elution and concentration behaviour, IR, X-ray, TG/DTA and elemental analysis. Its adsorption behaviour has also been studied for some alkaline earths and heavy metal ions in different acidic media. It has been found more selective for metal ions as compared to tin (IV) phosphate prepared earlier. They reported that the material was selective for Pb(II), Hg(II) and Fe(III) ions also. They performed binary separations for these metal ions on the ion-exchanger. Thermal studies showed high stability of the material at elevated temperatures. It retains 54.54% of its ion-exchange capacity at 200 °C and 27.27% at 300 °C [177]. They also studied the adsorption behavior of the synthesized tin (IV) phosphate (SnP), a non-fibrous ion-exchanger, for alkaline earths and heavy metal ions in different acidic and surfactant media. The effect of varying concentrations of anionic (SDS, SDBS), cationic (CTAB, DPC) and nonionic (TX-100) surfactants on the adsorption of metal ions on tin (IV) phosphate were studied. It is reported that the micelles of anionic and cationic surfactants increase the adsorption of heavy metal ions (except Hg(II) ions in SDS) and alkaline earth metal ions (except Sr(II) ions in CTAB). The micelles of non-ionic surfactants also increased the adsorption of alkaline earths and heavy metal ions. These studies indicate the potential of the surfactant medium in the removal of ionic pollutants from waste water effectively [178]. Its adsorption studies have been carried
out for some alkaline earth and heavy metal ions in different acidic media. The role of anionic (SDS, SDBS), cationic (CTAB, DPC) and nonionic (TX-100) surfactants as medium to enhance the adsorption behavior of metal ions on cerium (IV) phosphate (CeP) were also studied and are reported by them. Micelles of anionic surfactants decrease the adsorption of heavy metal ions (except Hg(II)) on CeP while the adsorption of alkaline earths remains uninfluenced. The micelles of cationic and nonionic surfactants, on the other hand, increased the adsorption of alkaline earths and heavy metal ions [179]. The synthesis of triton X-100 based cerium (IV) phosphate (TX-100-CeP) material, a new phase of fibrous cation exchanger, has been reported [180]. The cation exchanger was characterized by using IR, X-ray, SEM, TGA/DTA and elemental analysis and its ion-exchange properties such as ion-exchange capacity, elution, concentration and thermal behavior was also studied. The studies on adsorption behavior of TX-100-CeP for some alkaline earths and heavy metal ions in different acidic media showed that the material is selective for Hg(II), a toxic heavy metal ion. The binary separations of Hg(II) ions from other metal ions have been performed on its column and were reported.

The sodium dodecyl sulphate (SDS) based cerium (IV) phosphate (SDS-CeP), has been reported to be Pb(II) ions selective intercalated fibrous ion-exchanger. Additionally, the prepared material has shown good ion-exchange capacity (2.92 meq/g), thermal stability and adsorption behavior [181].
1.7 Statement of the Problem

Heavy metals, such as Hg, Pb, Cu, Cd, Ni, Zn, As etc. are natural elements and components of the Earth’s crust and causes of environmental pollution and health concerns. With the increase in industrial activities human being are also responsible for the increased pollution level in environment particularly by the presence of heavy metal ions. These metal ions are non-biodegradable, their intake results in an increasing concentration as the metals accumulate in the body of an organism [182-184]. At high concentrations these elements can lead to poisoning. The metals released into the water systems slowly increase through bioaccumulation with each successive level of the food chain. The earlier studies have shown that the surfactant based materials can be employed to effective and efficient removal of metal ions. The surfactants are amphiphilic molecules with polar/ionic ‘hydrophilic’ head-group and ‘hydrophobic’ hydrocarbon chain. The unique properties of surfactants have always been matter of interest among the researchers. Huo et al. [168,169] synthesized a number of silica-surfactant mesoporous materials using cationic and anionic surfactants. The mesoporous materials were having the lamellar structure with porous metal oxide embedded in self-assembly of surfactants. The matching charge density between surfactant and inorganic surface governs the assembly process. The work on the ion-exchange behavior of inorganic surfactant material started in our laboratory to elaborate the significance of the material for waste water treatment. In continuation of earlier works, SDBS (sodium dodecyl benzene sulphonate) and AOT (sodium bis (2-ethylhexyl sulphosuccinate)) based cerium (IV) phosphate and tin (IV) phosphate cationic exchange materials were synthesized. The characterizations of these materials were done using the various physical and chemical techniques. The physical techniques employed were IR, XRD, TGA/DTA and elemental analysis. The studies
on their ion-exchange properties included the ion-exchange capacity, elution behavior, concentration behavior and thermal stabilities. The thesis has been divided in five chapters.

Chapter 1 is general introduction and is devoted to the literature survey on the proposed work. It deals with the fundamentals of ion-exchange process, its classification and progressive development in the field of ion-exchange materials. It also includes information about surfactants, classification and application and their role in adsorption and ion-exchange process. The thesis includes literature survey from selected research papers, reviews and reports published on the subject. Special emphasis has been led to the work which has direct and indirect bearing on the studies presented in this thesis. It might be possible that some results of important study have been left unquoted quite inadvertently yet there was absolutely no intension to undermine those works.

Chapter 2 gives the details of the chemicals used, methods of synthesis of ion-exchangers and the instrumentations used for characterization of the materials. This chapter also includes the procedure and methods adopted for the studies of the ion-exchange properties of the synthesized material.

Chapter 3 describes the results of the investigations concerning with the characterization and ion-exchange properties of SDBS and AOT based-cerium (IV) phosphate cationic exchangers. The synthesized cationic exchangers are characterized using IR, XRD, TG/DTA and elemental analysis. The ion-exchange properties such as ion-exchange capacity, elution behavior, concentration behavior and thermal stabilities of the material are also explained in the chapter.
Chapter 4 deals with the studies concerning with the characterization and ion-exchange properties of SDBS-SnP and AOT-SnP cation exchangers. The characterization of the exchangers have been done using the physical techniques e.g. IR, XRD, TGA/DTA and elemental analysis. The studies on their ion-exchange properties include the ion-exchange capacity, elution behavior, concentration behavior and thermal stabilities.

The studies on the adsorption behavior of SDBS-CeP, AOT-CeP SDBS-SnP and AOT-SnP ion-exchangers for alkali metal ions, alkaline earth and transition metal ions are reported in Chapter 5. The studies also include on the selectivity of the materials for preferential adsorption and separation of metal ions. The influence of acids, alkali and alkaline earth metal ions on the selectivity nature of the cation exchangers were also studied and are discussed in this chapter. The relevant references to the work are cited after Chapter 5 under the heading ‘REFERENCES’.
Table 1.1

Examples of some commonly used ion-exchangers and their trade names.

<table>
<thead>
<tr>
<th>Type</th>
<th>Matrix</th>
<th>Functional groups</th>
<th>Commercial product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weakly acidic (cation-exchangers)</td>
<td>Polyacrylic acid</td>
<td>-COO⁻</td>
<td>Amberlite IRC 50</td>
</tr>
<tr>
<td></td>
<td>Polystyrene</td>
<td>-CH₂COO⁻</td>
<td>Bio-Rex 70</td>
</tr>
<tr>
<td></td>
<td>Cellulose</td>
<td>-CH₂COO⁻</td>
<td>Zeocarb 226</td>
</tr>
<tr>
<td></td>
<td>Dextran</td>
<td>-CH₂COO⁻</td>
<td>Poros CM</td>
</tr>
<tr>
<td></td>
<td>Agarose</td>
<td>-CH₂COO⁻</td>
<td>Cellex CM</td>
</tr>
<tr>
<td>强酸性 (阳离子交换剂)</td>
<td>Polystyrene</td>
<td>-SO₃⁻</td>
<td>Amberlite IR 120</td>
</tr>
<tr>
<td></td>
<td>Dextran</td>
<td>-CH₂CH₂CH₂-SO₃⁻</td>
<td>Bio-Rad AG 50</td>
</tr>
<tr>
<td></td>
<td>Polystyrene</td>
<td>-CH₂CH₂-SO₃⁻</td>
<td>Dowex 50</td>
</tr>
<tr>
<td></td>
<td>Polystyrene</td>
<td>-CH₂CH₂CH₂-SO₃⁻</td>
<td>Zeocarb 225</td>
</tr>
<tr>
<td>Weakly basic (anion-exchangers)</td>
<td>Polystyrene</td>
<td>-CH₂NH⁺R₂</td>
<td>Amberlite IR 45</td>
</tr>
<tr>
<td></td>
<td>Cellulose</td>
<td>-CH₂CH₂NH⁺</td>
<td>Bio-Rad AG 3</td>
</tr>
<tr>
<td></td>
<td>Dextran</td>
<td>(CH₂CH₃)₂</td>
<td>Dowex WGR</td>
</tr>
<tr>
<td></td>
<td>Agarose</td>
<td>-CH₂CH₂NH⁺(CH₂CH₃)₂</td>
<td>DEAE SepacrylO</td>
</tr>
<tr>
<td></td>
<td>Polystyrene</td>
<td>-CH₂CH₂NH⁺</td>
<td>DEAE SephadexO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(CH₂CH₃)₂</td>
<td>DEAE SepharoseO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polyethyleneimine</td>
<td>Poros PI</td>
</tr>
<tr>
<td>Strongly basic (anion exchangers)</td>
<td>Polystyrene</td>
<td>CH$_2$N$^+$ (CH$_3$)$_3$</td>
<td>Amberlite IRA 401 Bio-Rad AG 1 Dowex 1 Amberlite IRA 410 Bio-Rad AG 2 Dowex 2 Cellex T QAE-Sephadex Poros QE QMA</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Cellulose</td>
<td>CH$_2$CH$_2$N+(CH$_2$CH$_3$)$_2$I Quaternized polyethyleneimine</td>
<td>CH$_2$CH(OM)CH$_3$ (O)NH(CH$_2$)$_3$N$^+$ (CH$_3$)$_3$</td>
<td></td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Figure 1.1  Representative structure of cationic and anionic exchanger.

Figure 1.2  Anion exchanger (PA) and cation exchanger (PC) in equilibrium with exchangeable anions (A\(^-\) and B\(^-\)) and exchangeable cations (M\(^+\) and N\(^+\)), respectively.

Figure 1.3  Different stages in the separation of ions: (A) Initial stage of the column; (B) Adsorption, the sample is loaded onto the column, the charged particles of the sample are therefore able to displace the mobile ions and bind to the ion-exchanger; (C) Desorption, weakly charged sample particles are no longer bound to the ion-exchanger and are eluted from the column; (D) The salt concentration in the mobile phase when increased further displaces the adsorbed charged sample particles from the ion-exchanger. The charged adsorbed particles are no longer bound to the stationary phase and are eluted from the column.

Figure 1.4  Representation of a low-molar mass surfactant molecule.

Figure 1.5  Scheme of a spherical micelle of surfactants in aqueous solution.

Figure 1.6  Structures of some anionic surfactants.

Figure 1.7  Structures of some cationic surfactants.

Figure 1.8  Structures of some amphoteric (zwitterionic) surfactants.

Figure 1.9  Structures of some nonionic surfactants.

Figure 1.10  Structures of some polymeric surfactants.

Figure 1.11  Structures of some oligomeric surfactants.

Figure 1.12  Structures of some gemini surfactants.
Figure 1.1

Figure 1.2
Figure 1.3
Figure 1.4

Figure 1.5
Figure 1.6
Figure 1.7
Figure 1.8

- Betaine
- Amidobetaine
- 'Imidazoline'
- Amine oxide
Figure 1.9

- Fatty alcohol ethoxylate
- Alkylphenol ethoxylate
- Fatty acid ethoxylate
- Fatty amide ethoxylate
- Fatty amine ethoxylate
- Alkyl glucoside
- Sorbitan alkanoate
- Ethoxylated sorbitan alkanoate
Figure 1.11
Figure 1.12