Abstract
Hybrid ion exchangers are of recent origin in the field of ion exchange chemistry. They have shown excellent chemical, mechanical and thermal stability conversant to both organic and inorganic counterparts. Very recently, new class of ion exchangers has been studied by combining surfactants and inorganic exchangers. This study highlights the salient features of ion exchangers, various development stages with the modifications with an emphasis on the recent developments in the field of analytical chemistry, particularly surfactant based hybrid fibrous and non-fibrous ion exchangers.

Surfactants or surface-active agents when present in the matrix of inorganic ion-exchangers not only enhance their ion-exchange capacity but also the selective adsorption of metal ions. Therefore, these materials are of great importance in industrial and environmental applications.

Keywords: Analytical chemistry, Hybrid ion exchangers, Surfactants, Inorganic ion exchangers, Adsorption, Environmental applications.

Introduction
Analytical chemistry, broadly conceived, underlines and contributes to almost all branches of chemistry as an experimental science. It plays an important role in nearly all aspects of chemistry such as agricultural, clinical, environmental, forensic, manufacturing, metallurgical and pharmaceutical chemistry. The goal of a chemical analysis is to provide information about the composition of a sample of matter.

The discipline of analytical chemistry consists of qualitative and quantitative analyses. The former deals with the identification of elements, ions or compounds present in a sample while the latter deals with the determination of how much of one or more constituents is present; whether the sample is solid, liquid, gas, or a mixture. Analytical methods are ordinarily classified according to the property that is observed in the final measurement process. Some more important of these properties as well as the names of the methods based upon these properties, are given in table 1.

Prior to chemical analysis, separations are extremely important in analytical chemistry. The aim of an analytical separation is, usually, to eliminate or reduce interferences so that quantitative analytical informations can be obtained about complex mixtures. There is a variety of separation methods that are in common use including precipitation, distillation, solvent extraction, crystallization, dialysis, ion-exchange, chromatography, electrophoresis, field flow fractionation etc.

Of all the different types of separation methods, chromatography has the unique position of being applicable to all types of problems in all branches of science. This technique provides a very efficient method for the identification, separation, determination and purification of chemical compounds. It has undergone explosive growth in the last thirty-forty years. The chromatographic technique was first invented by a Russian botanist Mikhail Tswett in 1906, at the University of Warsaw. He coined the term ‘Chromatography’ from the Greek words ‘Chromatos’ and ‘graphy’ which mean ‘color’ and ‘to write’ respectively. The International Union of Pure and Applied Chemists (IUPAC) has drafted a recommended definition of chromatography: “Chromatography is a physical method of separation in which the components to be separated are distributed between two phases, one of which is a stationary phase, while the other is a mobile phase”.

Since its discovery, this technique has undergone tremendous modifications and nowadays various types of chromatographic techniques have been developed for separating almost any kind of a given mixture, whether coloured or colourless into its constituents and to test the purity of these constituents. The applications of chromatography have extensively been used in the last fifty years, owing not only to the development of several new types of chromatographic techniques, but also due to the growing needs of the scientists for better methods of separating the complex mixtures or metal ions. The different chromatographic methods are summarized in table 2.

Out of these several chromatographic methods, ion-exchange has gained great attention by analysts in practice. The phenomenon of ion-exchange is not of a recent origin. It has an interesting historical background. Various time spans may be identified for the development of ion-exchange technique. Figure 1 summarizes the various stages of the development of ion-exchangers and sorbents.

Initially, the ion-exchangers were mostly used for water softening, but later on they were widely employed in various fields such as syntheses and some preparative works. The use of ion-exchangers provided the new
methods for analysts, which not only met the requirements of modern laboratories but also led to the solution of previously insolvable problems. Thus, the ion-exchange process has been established as an analytical tool in laboratories and industries.

An interest in ion-exchange operations in industries is increasing day by day as their field of applications is expanding and today, it is an extremely valuable supplement to other procedures such as filtration, distillation and adsorption. All over the world, various plants are in operation, accomplishing tasks that range from the recovery of metals from industrial wastes to the separation of rare earths and from catalysis of organic reactions to decontamination of water in cooling systems of nuclear reactors.

Ion-exchangers are insoluble solid materials or immiscible liquids (in case of liquid ion-exchangers) containing exchangeable ions. These ions can be exchanged for a stoichiometrically equivalent amount of other ions of the same sign on contacting with an electrolyte solution. Depending upon their ability of exchanging cations, anions or both, the ion-exchangers may be categorized as ‘cation’, ‘anion’ or ‘amphoteric’ ion-exchangers respectively. A cation-exchanger comprises a matrix with negative charge while an anion-exchanger comprises a matrix with positive charge. The negative or positive charge on the matrix is compensated by the oppositely charged counter ions which are mobile in nature. A typical ion-exchange reaction may be represented as follows:

\[
R - A + B (aq) \rightleftharpoons R - B + A (aq)
\]

where ‘A’ and ‘B’ are the replaceable counter ions, ‘R’ is the structural unit (matrix) of the ion-exchanger and ‘aq’ stands for the aqueous phase. This process is reversible i.e. it can be reversed by suitably changing the concentration of the ions in solution.

The actual utility of an ion-exchanger depends chiefly on its ion-exchange characteristics such as ion-exchange capacity, pH-titration, concentration, elution and distribution behaviour. The ion-exchange capacity depends on hydrated ionic radii and selectivity. The selectivity of any ion-exchanger, in turn, is influenced by the nature of its functional group and degree of its cross linking. Ion-exchangers, having 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.

The elution of H\(^+\) ions from a column of ion-exchanger depends on the concentration of the eluant while an optimum concentration of the eluant, necessary for maximum elution of H\(^+\) ions depends on the nature of ionogenic groups present in the exchanger, which depends upon the pKa values of the acids used in preparation. The efficiency of an ion-exchanger depends on the following fundamental exchange reactions:

- Equivalence of exchange.
- Selectivity for one ion relative to another including the cases in which the varying affinities of the ions are modified by the use of complexing and chelating agents.
- Donnan exclusion – the ability to exclude ions but not, in general, undissociated substances.
- Screening effect – the inability of very large ions or polymers to be adsorbed to an appreciable extent.
- Differences in migration rates of adsorbed substances down a column – primarily a reflection of differences in affinity.
- Ionic mobility restricted to the exchangeable ions and counter ions only.
- Miscellaneous – swelling, surface area and other mechanical properties.

On the basis of the nature of matrix, an ion-exchanger may be ‘organic’ or ‘inorganic’ in nature.

**Organic ion-exchangers:** Organic ion-exchangers, commonly known as ‘ion-exchange resins’ are well known for their uniformity, chemical and mechanical stability and for the easy control over their ion-exchange property through synthetic methods. Organic resins have wide applications in analytical chemistry because of their high stability in the wide range of pH and reproducibility in the results, but their instability under the conditions of high temperature and strong radiation led to a major switch for the development of inorganic ion-exchange materials. The matrix of inorganic ion-exchanger is more reactive than that of organic resins and hence, the selectivity for the metal ion depends both on adsorption characteristics of the matrix and the nature of the ionogenic groups attached to the matrix.

**Inorganic ion exchangers:** Inorganic ion exchangers are capable of being stable at elevated temperatures and in the presence of strong radiations and hence they have wide ranging applications in nuclear researches such as radioisotope separations, nuclear waste treatments etc. They are used in the determination and detection of metals in pharmaceutical and biological products, analysis of alloys and rocks, as ion selective electrodes, as packing materials in ion-exchange chromatography and as catalysts. They also find applications in environmental analysis. The widespread importance of inorganic ion-exchangers in practical applications and scientific interest in their nature and properties, has precipitated a wealth of published literature on the subject.

Important advances in this field have been reviewed by a number of workers/researchers at various stages of its development, such as Fuller, Qureshi et al, Vesely and...
Inorganic ion-exchangers are generally the oxides, hydroxides and insoluble acid salts of polyvalent metals, heteropolyacid salts and insoluble metal ferrocyanides. These materials are generally produced by combining the oxides of elements of III, IV, V and VI groups of the periodic table. A large number of such materials have been synthesized by mixing phosphoric, arsenic, molybdc, antimonic and vanadic acids with titanium, zirconium, tin, thorium, cerium, iron, antimony, chromium, niobium, tantalum, bismuth, nickel, cobalt etc. However, the majority of work has been carried out on zirconium, titanium, tin, niobium and tantalum. They can be prepared both in crystalline and amorphous forms having good chemical stability, reproducibility in ion-exchange behaviour and selectivity for certain metal ions.

**Hybrid ion exchangers:** Since organic ion-exchangers were found to be unstable at elevated temperatures and under strong radiations, inorganic ion-exchangers were taken as alternatives for such cases. However, the main drawback of inorganic ion-exchange materials has been that they are not very much reproducible in ion-exchange behaviour. Further, they are found not to be chemically and mechanically very stable perhaps due to their inorganic nature. Thus, to overcome these shortcomings, an interest was developed to obtain some organic based inorganic ion-exchangers. These exchangers were termed as “hybrid ion-exchangers” as they consist of both the organic and inorganic counterparts and having the properties not seen in purely organic or purely inorganic materials. This new class of ion-exchangers has been prepared in these laboratories by incorporating a polymeric or monomeric organic species into the inorganic ion-exchange matrix.

The hybrid ion-exchangers have shown an improvement in a number of ways. One of them is its granulometric properties that make it more suitable for the application in column operations. The binding with an organic species also introduces better mechanical properties in the end product i.e. hybrid ion-exchange materials. 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.

The reactivity of both organic and inorganic precursors is usually quite different and phase separation tends to occur. The properties of hybrid materials do not depend only on organic and inorganic components but also on the interface between both phases. The general tendency is therefore, to increase interfacial interactions by creating an intimate mixing, or interpenetration between organic and inorganic networks. Moreover, the formation of chemical bonds between organic and inorganic species would prevent phase separation, allowing the synthesis of molecular composites or organic-inorganic copolymers. Hybrid materials can thus, be divided into two classes:

- Class I corresponds to hybrid systems in which weak interactions such as van der Waals forces or hydrogen bonds or electrostatic interactions are created between organic and inorganic phases. This class involves mainly small organic species embedded within an oxide matrix.
- Class II corresponds to hybrid compounds where both organic and inorganic components are bonded through strong covalent chemical bonds.

Hybrid organo-inorganic materials open up a land of opportunities in materials science. These nanocomposites bridge high temperature materials such as glasses and ceramics with very fragile species such as organic compounds or biomolecules. In last ten-fifteen years, some hybrid ion-exchange materials have been synthesized in the laboratories, such as acrylamide and pyridine based zirconium and tin phosphates. These materials have shown promising ion-exchange characteristics and having utilization in the separation of metal ions due to their selectivity towards different metals ions. Table 3 summarizes their ion-exchange capacities and selectivity towards metal ions.

**Surfactants:** Surfactants constitute the most important group of detergent components. ‘Surfactant’ is an abbreviation for surface-active agents, which literally means ‘active at the surface’. The surface can be between solid and liquid, between air and liquid and, between two different immiscible liquids. The unique property of surfactants is “adsorption” which occurs at liquid/solid, liquid/liquid and at air/liquid interfaces which is shown in figure 2. At air–water interfaces and in water, or similarly strongly hydrogen-bonded solvents, they self-associate at concentrations above the critical micelle concentration (CMC) to form association colloids, known as ‘micelles’.

Thus, “surfactants, surfactant agents” or, detergents are amphiphilic, organic or organo-metallic compounds which form association colloids or micelles in solution.

Amphiphilic substances or amphiphiles comprised of a hydrophobic portion, usually a long alky1 chain, attached to hydrophilic or water solubility enhancing functional groups. Actually, surfactant molecule consists of 2 parts: a water–hating (hydrophobic) part and a water–loving (hydrophilic) part. Figure 1 shows the basic structure of a surfactant molecule.
A hydrophilic part – water loving

A hydrophobic part – water hating

![Surfactant monomer](image)

**Figure 1: Surfactant Molecule**

### Table 1
**Analytical techniques and principal applications**

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Technique</th>
<th>Property measured</th>
<th>Principal areas of application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Gravimetry</td>
<td>Weight of pure analyte or compound of known stoichiometry</td>
<td>Quantitative for major or minor components</td>
</tr>
<tr>
<td>2.</td>
<td>Titrimetry</td>
<td>Volume of standard reagent solution reacting with the analyte</td>
<td>Quantitative for major or minor components</td>
</tr>
<tr>
<td>3.</td>
<td>Atomic and molecular spectrometry</td>
<td>Wavelength and intensity of electromagnetic radiation emitted or absorbed by the analyte</td>
<td>Qualitative, Quantitative or, structural for major down to trace level components.</td>
</tr>
<tr>
<td>4.</td>
<td>Mass spectrometry</td>
<td>Mass of analyte or fragments of it</td>
<td>Qualitative or structural for major down to trace level components isotope ratio</td>
</tr>
<tr>
<td>5.</td>
<td>Chromatography and electrophoresis</td>
<td>Various physico-chemical properties of separated analytes</td>
<td>Qualitative and quantitative separations of mixtures at major to trace levels</td>
</tr>
<tr>
<td>6.</td>
<td>Thermal analysis</td>
<td>Chemical/physical changes in the analyte when heated or cooled</td>
<td>Characterization of single or mixed major/minor components</td>
</tr>
<tr>
<td>7.</td>
<td>Electro-chemical analysis</td>
<td>Electrical properties of the analyte in solution</td>
<td>Qualitative and quantitative for major to trace level components</td>
</tr>
<tr>
<td>8.</td>
<td>Radiochemical analysis</td>
<td>Characteristic ionizing nuclear radiation emitted by the analyte</td>
<td>Qualitative and quantitative at major to trace levels</td>
</tr>
</tbody>
</table>

### Table 2
**A classification of the principal chromatographic techniques**

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Technique</th>
<th>Stationary phase</th>
<th>Mobile phase</th>
<th>Format</th>
<th>Principal sorption mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>Thin layer chromatography (TLC)</td>
<td>Silica, cellulose, ion-exchange resin, controlled porosity solid</td>
<td>Liquid</td>
<td>Planar</td>
<td>Adsorption (partition, ion-exchange, exclusion)</td>
</tr>
<tr>
<td>3.</td>
<td>Gas-liquid chromatography (GLC)</td>
<td>Liquid</td>
<td>Gas</td>
<td>Column</td>
<td>Partition</td>
</tr>
<tr>
<td>4.</td>
<td>Gas-solid chromatography (GSC)</td>
<td>Solid</td>
<td>Gas</td>
<td>Column</td>
<td>Adsorption</td>
</tr>
<tr>
<td>5.</td>
<td>High performance liquid chromatography (HPLC)</td>
<td>Solid or bonded phase</td>
<td>Liquid</td>
<td>Column</td>
<td>Modified partition (adsorption)</td>
</tr>
<tr>
<td>6.</td>
<td>Size-exclusion chromatography (SEC)</td>
<td>Controlled porosity solid</td>
<td>Liquid</td>
<td>Column</td>
<td>Exclusion</td>
</tr>
<tr>
<td>7.</td>
<td>Ion-exchange chromatography (IEC)</td>
<td>Ion-exchange resin or bonded-phase</td>
<td>Liquid</td>
<td>Column</td>
<td>Ion-exchange</td>
</tr>
<tr>
<td>8.</td>
<td>Ion chromatography (IC)</td>
<td>Ion-exchange resin or bonded-phase</td>
<td>Liquid</td>
<td>Column</td>
<td>Ion-exchange</td>
</tr>
<tr>
<td>9.</td>
<td>Chiral chromatography (CC)</td>
<td>Solid chiral selector</td>
<td>Liquid</td>
<td>Column</td>
<td>Selective adsorption</td>
</tr>
</tbody>
</table>
There are 3 basic concepts which need to be well understood in order to explain the majority of observed phenomena; these are solubility, adsorption of a surfactant at a surface and the formation of micelles in solution. These three phenomena differentiate a surfactant from other chemical entities. It is the abnormal solubility characteristics of surfactants that give adsorption and form micelles. Surfactants reduce surface tensions when dissolved in water or water solutions, reduce interfacial tensions between two liquids, or between a liquid and a solid.\(^4^9\)

When a surfactant molecule is introduced into water, the water-hating part tends to escape by attaching itself to any available surface other than water. At the same time, the water-loving part tries to remain in water. As a result, surfactants get strongly “adsorbed” to many surfaces such as fabric, soil, glass and where the water and air meet (i.e. water/air interface). This tendency of surfactants is useful:

- In the removal of the soils from surfaces,
- In holding soil particles in suspension form and preventing them from redepositing onto the surface,
- In reducing surface tension of water and allow the water to spread out.

The unusual properties of aqueous surfactant solutions can be ascribed to the presence of a hydrophilic head group and a hydrophobic chain (or tail) in the molecule. The polar or ionic head group usually interacts strongly with an aqueous environment, in which case it is solvated via dipole-dipole or ion-dipole interactions. Depending on the chemical structure of the hydrophilic moiety bound to the hydrophobic portion, the surfactants may be categorized into following types:

- Anionic surfactants\(^5^0\)
- Cationic surfactants\(^5^1\)
- Nonionic surfactants\(^5^2\)
- Amphoteric surfactants\(^5^3\)
- Gemini surfactants\(^5^4,5^5\)

### Table 3

Some hybrid ion-exchangers prepared so far and their selectivity for metal ions

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Name of the materials</th>
<th>Ion-exchange capacity for Na(^+)(meq/dry g)</th>
<th>Selectivity</th>
<th>X-ray nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Styrene Zirconium(IV) Phosphate(^3^0)</td>
<td>2.18</td>
<td>Pb(II)</td>
<td>Semi crystalline</td>
</tr>
<tr>
<td>2.</td>
<td>Acrylamide Zirconium(IV) Phosphate(^3^2)</td>
<td>2.26</td>
<td>Hg(II)</td>
<td>Crystalline</td>
</tr>
<tr>
<td>3.</td>
<td>Pyridine Zirconium(IV) Phosphate(^3^3)</td>
<td>2.00</td>
<td>Hg(II)</td>
<td>Poorly crystalline</td>
</tr>
<tr>
<td>4.</td>
<td>Acrylonitrile Zirconium(IV) Phosphate(^3^5)</td>
<td>2.08</td>
<td>Sr(II)</td>
<td>Semi crystalline</td>
</tr>
<tr>
<td>5.</td>
<td>Pyridine Tin(IV) Phosphate(^3^3)</td>
<td>2.10</td>
<td>Pb(II)</td>
<td>Poorly crystalline</td>
</tr>
<tr>
<td>6.</td>
<td>Acrylamide Tin(IV) Phosphate(^4^4)</td>
<td>2.10</td>
<td>Hg(II)</td>
<td>Poorly crystalline</td>
</tr>
<tr>
<td>7.</td>
<td>Polyacrylonitrile Thorium(IV) Phosphate(^3^6)</td>
<td>3.90</td>
<td>Pb(II)</td>
<td>Microcrystalline</td>
</tr>
<tr>
<td>8.</td>
<td>Polystyrene Cerium(IV) Phosphate(^3^7)</td>
<td>2.95</td>
<td>Hg(II)</td>
<td>Microcrystalline</td>
</tr>
<tr>
<td>9.</td>
<td>Polystyrene Thorium(IV) Phosphate(^3^8)</td>
<td>4.52</td>
<td>Cd(II)</td>
<td>Crystalline</td>
</tr>
<tr>
<td>10.</td>
<td>Acrylonitrile Cerium (IV) Phosphate(^3^9)</td>
<td>2.86</td>
<td>Hg(II)</td>
<td>Poorly crystalline</td>
</tr>
<tr>
<td>11.</td>
<td>Acrylamide Cerium(IV) Phosphate(^4^0)</td>
<td>2.60</td>
<td>Hg(II)</td>
<td>Crystalline</td>
</tr>
<tr>
<td>12.</td>
<td>Acrylamide Thorium(IV) Phosphate(^4^1)</td>
<td>2.00</td>
<td>Pb(II)</td>
<td>Poorly crystalline</td>
</tr>
<tr>
<td>13.</td>
<td>Pectin Cerium(IV) Phosphate(^4^2)</td>
<td>1.78</td>
<td>Hg(II)</td>
<td>Amorphous</td>
</tr>
<tr>
<td>14.</td>
<td>Pectin Thorium(IV) Phosphate(^4^2)</td>
<td>2.15</td>
<td>Pb(II)</td>
<td>Amorphous</td>
</tr>
<tr>
<td>15.</td>
<td>Cellulose acetate Thorium(IV) Phosphate(^4^3)</td>
<td>1.70</td>
<td>Pb(II)</td>
<td>Amorphous</td>
</tr>
<tr>
<td>16.</td>
<td>Pyridine Cerium(IV) Phosphate(^4^4)</td>
<td>2.00</td>
<td>Hg(II)</td>
<td>Amorphous</td>
</tr>
<tr>
<td>17.</td>
<td>Pyridine Thorium(IV) Phosphate(^4^5)</td>
<td>2.10</td>
<td>Pb(II)</td>
<td>Amorphous</td>
</tr>
<tr>
<td>18.</td>
<td>n-Butyl acetate Cerium(IV) Phosphate(^4^6)</td>
<td>2.25</td>
<td>Hg(II)</td>
<td>Amorphous</td>
</tr>
</tbody>
</table>
Micelle formation and critical micelle concentration (CMC): The formation of micelles in aqueous solution is generally viewed as a compromise between the tendency for alkyl chains to avoid energetically unfavorable contacts with water and the desire for the polar part to maintain contact with aqueous environment. In dilute aqueous solution, at concentration generally less than $10^{-3}$ M, the behaviour of ionic surfactants parallels that of strong electrolytes while the behaviour of nonionic surfactants often resembles that of the simple organic molecules. At higher surfactant concentrations, however, a pronounced deviation from “ideal” behaviour in dilute solution occurs. This deviation is generally being considerably large than that exhibited by simple strong electrolytes. Thus, the adsorption of a surfactant from solution onto a surface depends upon the concentration.53

Each surfactant has a characteristic CMC value. The most obvious evidence of micellar growth is probably the dramatic increase in viscosity with increasing concentration which is observed in several surfactant solutions. Micellar growth is favored by decreasing the temperature, adding electrolyte and lengthening the surfactant chain length and is, furthermore, very sensitive to the nature of the counter ion. The physico-chemical properties of surfactants vary significantly below and above the CMC value.54-60 Below the CMC value, the physico-chemical properties of ionic surfactants resemble those of a strong electrolyte. Above the CMC value, these properties change dramatically, indicating a highly co-operative association process. The general way of obtaining the CMC value of a surfactant micelle is to plot an appropriate physico-chemical property versus the surfactant concentration and observe the break in the plot.61-63

Depending upon the chemical structure of the surfactant, its micelle can be cationic, anionic, zwitterionic, or nonionic. The electrostatic character of the micelles depends in some cases on the pH of the aqueous solution due to protonation equilibria. Zwitterionic surfactants, of course, also can become either cationic or anionic and several types of nonionic surfactants can also form anionic or cationic micelles in the appropriate pH range. Micelles are not static species but rather exist in a dynamic equilibrium. The micelle may be represented as a globular, cylindrical or ellipsoidal cluster of individual surfactant molecules in equilibrium with its monomer.37,57 The reverse orientation of the hydrophilic and hydrophobic part of the surfactant in a hydrocarbon medium leads to the formation of reversed micelles.65

Surfactant adsorption and surface properties: The effectiveness of surfactant adsorption is mainly determined by surfactant concentration, surfactant functional group, alkyl hydrocarbon chain length, environment etc. When the surfactant concentration is well below the CMC value, individual surfactant molecules tend to adsorb on exposed interfaces to reduce surface tension. As the concentration of surfactant approaches the CMC value, surfactant molecules form dimers and multiple molecules aggregate micelles. Once the CMC is reached, any additional surfactant molecules added to the system will be incorporated into new or existing aggregates. Thus, further increase of surfactant concentration above the CMC value, results in bilayer or multilayer formation at interface.

The adsorption tendency of the surfactants at the surfaces imparts the properties of foaming, wetting, emulsification, dispersing of solids and detergency. The adsorption increases the concentration of surfactant at the surfaces. Surfactant adsorption is a consideration in any application where surfactants come in contact with a surface or interface. It is from solutions that surfactants then preferentially adsorb to interfaces and because of their amphiphilic nature, preferentially segregate at interfaces. There are a number of areas of applications where surfactant adsorption is important including ore flotation, improved oil recovery, soil remediation, detergency, surfactant-based separation processes and wetting. Surfactant adsorption may occur due to electrostatic interactions, van der Waals interaction, hydrogen-bonding, and/or solvation and desolvation of adsorbate and adsorbent species.56

The hydrophobic forces that drive surfactants to segregate at air-water interfaces are essentially the same that drive surfactant adsorption onto solid surfaces. However, they can be differing in the chemical forces associated with the solid surfaces. Ionic surfactants tend to adsorb onto oppositely charged solid surfaces due to electrostatic forces while adsorption of ionic surfactants on a like charged substrate, being less understood, can occur via hydrogen-bonding or attractive dispersion forces as is the case for nonionic surfactants.

The number of industrial applications of surfactants is huge. However, in analytical chemistry, surfactants have been recognized as being very useful in improving analytical technology e.g. in chromatography and luminescence spectroscopy.59 The use of surfactants in chromatography, particularly in ion-exchange is of our interest. It is well-known that surfactants are composed of two parts – hydrophobic and hydrophilic, which are oppositely charged and the surfactants also act as ion-exchangers. When their solutions are kept in contact with solid material, they are adsorbed on the solid surface remaining their hydrophilic part in the solutions due to their surface-active property and they make that surface ‘active’. It is clear from the above discussion that they play an important role in the adsorption behaviour of the molecules.

Surfactant based hybrid ion exchangers: The widespread utility of surfactants in practical applications and scientific
interest regarding their nature and properties have precipitated a wealthy literature on the subject. One of the predominant reasons for the ubiquitous applications of surfactants has been their remarkable ability to influence the properties of the surfaces and interfaces. Surfactants are widely used in various industrial applications such as petroleum, pharmaceuticals, agro-chemicals, processing of foods, paints, coatings, adhesives, lubricants, in photographic films, personal care and laundry products.

Varshney et al. used surfactants as media in the adsorption studies of some alkaline earths and heavy metal ions on inorganic and hybrid ion exchangers and observed that the presence of surfactants in aqueous media increases the adsorption of metal ions on the surface on ion exchange materials. Hence, exceptional high adsorption of the said metal ions has opened the doors in the field of material science. It was thought worthwhile to incorporate the surfactants in the matrix of inorganic ion exchangers to see how they could change the characteristics of the ion exchangers. Very recently, some hybrid fibrous and non-fibrous ion exchange materials have been synthesized by combining surfactants and inorganic ion exchangers by the researchers.

Somya et al. have used surfactants in the synthesis some of novel hybrid fibrous and non-fibrous ion exchangers by introducing surfactants (anionic, cationic and non-ionic) in the matrix of inorganic ion exchangers. They have explored the ion exchange studies such as, ion exchange, concentration, elution and thermal behavior in addition to adsorption studies for some alkaline earths and heavy metal ions. Those materials were found to be selective for certain metal ions (table 4) and on that basis some binary separations have been performed in the laboratory. The introduction of surfactants in the matrix of inorganic ion exchangers has been characterized by some physico-chemical studies like IR, X-ray diffraction, elemental, SEM and TGA/DTA/DTG studies.

Later on, Iqbal have synthesized the same class of hybrid ion exchange materials by combining sodium dodecyl benzene sulphonate and sodium bis (2-ethylhexyl) sulfosuccinate in the matrix of cerium (IV) and tin (IV) phosphates. They have explored some ion exchange studies in addition to physico-chemical characterization like, IR, XRD, SEM, TGA/DTA/DTG, elemental studies and differential pulse polarography. These materials have shown selective adsorption for certain metal ions. Hence, binary separations have been done by using columns of the synthesized materials.

The anionic [sodium dodecyl sulphate, sodium dodecyl benzene sulphonate, sodium bis (2-ethylhexyl) sulfosuccinate], cationic (N-dodecyl pyridinium chloride) and non-ionic (triton X-100) surfactants based various fibrous and non-fibrous ion exchange materials, with their respective ion exchange capacities, selectivity for metal ions, X-ray nature are depicted in table 4.

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Name of the materials</th>
<th>Ion-exchange capacity for Na⁺(meq/dry g)</th>
<th>Selectivity</th>
<th>X-ray nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>N-dodecyl pyridinium chloride-tin(IV) phosphate</td>
<td>2.39</td>
<td>Cd(II)</td>
<td>Amorphous</td>
</tr>
<tr>
<td>2.</td>
<td>N-dodecyl pyridinium chloride-cerium(IV) phosphate</td>
<td>3.15</td>
<td>Hg(II)</td>
<td>Amorphous</td>
</tr>
<tr>
<td>3.</td>
<td>Sodium dodecyl sulphate-cerium(IV) phosphate</td>
<td>2.92</td>
<td>Pb(II)</td>
<td>Amorphous</td>
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<tr>
<td>4.</td>
<td>Triton X 100-cerium(IV) phosphate</td>
<td>3.00</td>
<td>Hg(II)</td>
<td>Amorphous</td>
</tr>
<tr>
<td>5.</td>
<td>Triton X 100-tin(IV) phosphate</td>
<td>2.75</td>
<td>Fe(III), Hg(II) and Pb(II)</td>
<td>Amorphous</td>
</tr>
<tr>
<td>6.</td>
<td>Sodium dodecyl benzene sulphonate-cerium(IV) phosphate</td>
<td>2.17</td>
<td>Pb(II)</td>
<td>Semi-crystalline</td>
</tr>
<tr>
<td>7.</td>
<td>Sodium dodecyl benzene sulphonate-tin(IV) phosphate</td>
<td>2.20</td>
<td>Cu(II), Cd(II), Pb(II) and Hg(II)</td>
<td>Amorphous</td>
</tr>
<tr>
<td>8.</td>
<td>Sodium bis (2-ethylhexyl) sulfosuccinate basedtin (IV) Phosphate</td>
<td>2.40</td>
<td>Cd(II), Zn(II) and Hg(II)</td>
<td>Semi-crystalline</td>
</tr>
<tr>
<td>9.</td>
<td>Sodium bis (2-ethylhexyl) sulfosuccinate basedcerium (IV) Phosphate</td>
<td>3.02</td>
<td>Cu(II), Pb(II), Cd(II), Zn(II) and Hg(II)</td>
<td>Amorphous</td>
</tr>
</tbody>
</table>
Continued rapid development of artificial organic ion-exchangers and by a renaissance in inorganic ion-exchange sorbents.

Rapid development of organic materials. Complete elimination of inorganic ion-exchange sorbents.

Use of inorganic ion-exchange sorbents and modified natural organic materials.

First experimental observation and informations. The principle of ion-exchange had not yet been discovered.

Discovery of the principles of ion-exchange and the first experiment in the technical utilization of ion-exchangers.

Latest development in the synthesis of hybrid (organo-inorganic) ion-exchangers and their practical applications.

**Figure 1:** Stages of development of ion-exchangers and sorbents

**Figure 2:** Adsorption of surfactants at various interfaces
Conclusion
As per the studies done, so far, it is clearly indicated that surfactants have played a key role in synthesis of new class of hybrid ion exchange materials. They have not only enhanced the ion exchange capacities of the inorganic ion exchangers when present in their matrix but also the adsorption of metal ions. Hence, these materials open a door with ample opportunities for the researchers in the field of material and environmental science where they may be used in water pollution control.

Acknowledgement
The author is thankful the Chairman, Presidency University, Bengaluru and the Chairman, Department of Applied Chemistry, A.M.U., Aligarh for providing research facilities.

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(Received 25th April 2018, accepted 05th June 2018)