

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

185,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



# Hybrid Ion Exchangers

*Amita Somya*

## 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 classes of ion exchangers have been studied by combining surfactants and inorganic metal phosphates. This article highlights the salient features of metal phosphates as 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 metal phosphates as ion exchangers. Surfactants or surface-active agents when present in the matrix of inorganic metal phosphates 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:** hybrid ion exchangers, stability, surfactants, metal phosphates, inorganic metal phosphates

## 1. 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 information 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 30–40 years. The chromatographic technique was first invented by a Russian

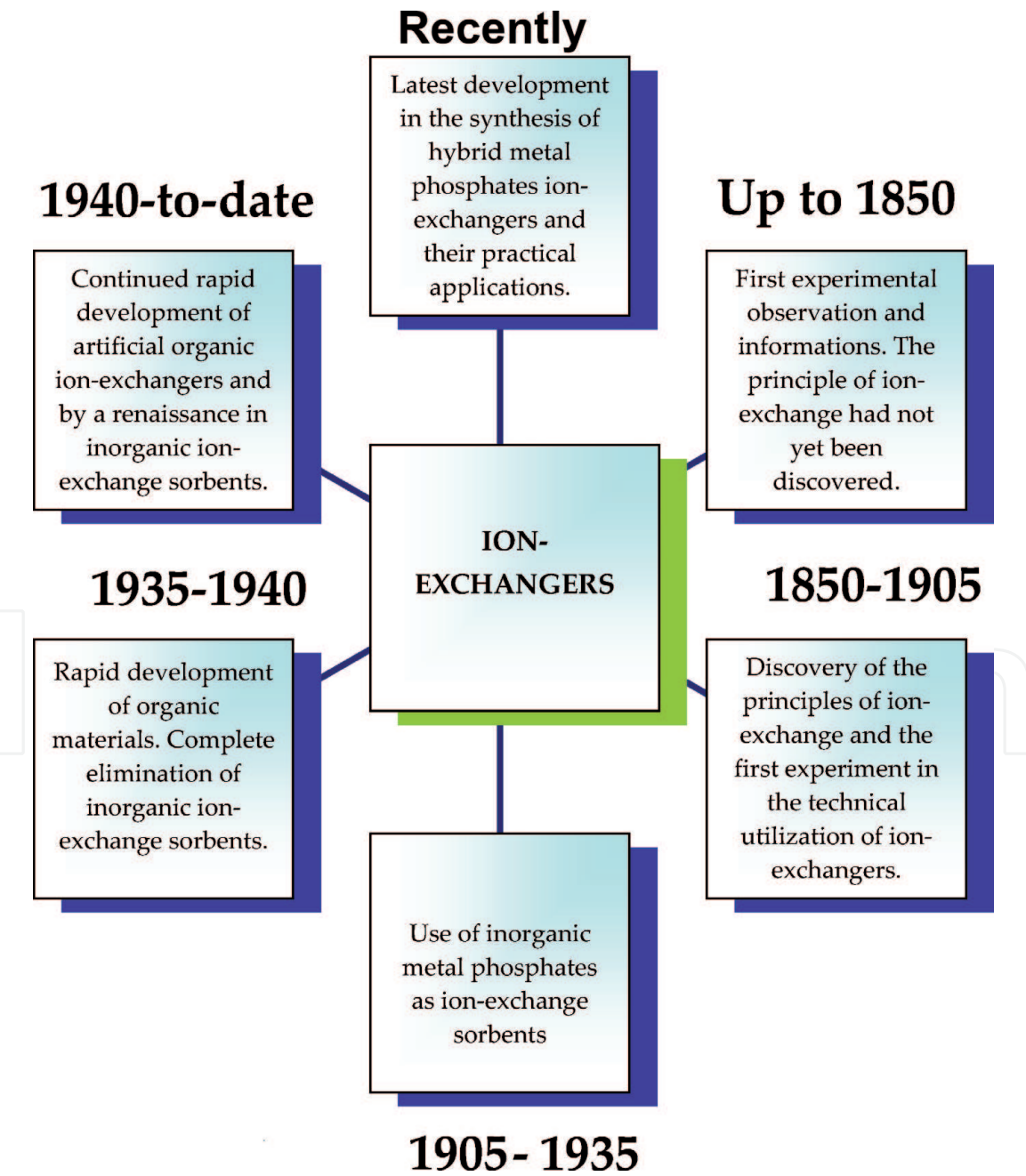
S.N.	Technique	Property measured	Principal areas of application
1.	Gravimetry	Weight of pure analyte or compound of known stoichiometry	Quantitative for major or minor components
2.	Titrimetry	Volume of standard reagent solution reacting with the analyte	Quantitative for major or minor components
3.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

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

S.N.	Technique	Stationary phase	Mobile phase	Format	Principal sorption mechanism
1.	Paper chromatography (PC)	Cellulose-water complex	Liquid	Planar	Partition (adsorption, ion-exchange, exclusion)
2.	Thin layer chromatography (TLC)	Silica, cellulose, ion-exchange resin, controlled porosity solid	Liquid	Planar	Adsorption (partition, ion-exchange, exclusion)
3.	Gas-liquid chromatography (GLC)	Liquid	Gas	Column	Partition
4.	Gas-solid chromatography (GSC)	Solid	Gas	Column	Adsorption
5.	High-performance liquid chromatography (HPLC)	Solid or bonded phase	Liquid	Column	Modified partition (adsorption)
6.	Size-exclusion chromatography (SEC)	Controlled porosity solid	Liquid	Column	Exclusion
7.	Ion-exchange chromatography (IEC)	Ion-exchange resin or bonded-phase	Liquid	Column	Ion-exchange
8.	Ion chromatography (IC)	Ion-exchange resin or bonded-phase	Liquid	Column	Ion-exchange
9.	Chiral chromatography (CC)	Solid chiral selector	Liquid	Column	Selective adsorption

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

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’ [1]. 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 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 50 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 [2]. The different chromatographic methods are summarized in **Table 2**.



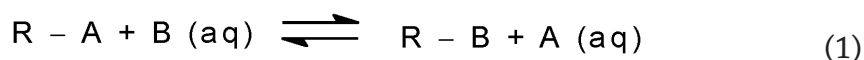
**Figure 1.**  
*Stages of development of ion exchangers and sorbents.*

Out of these several chromatographic methods, ion-exchange has gained great attention by analysts in practice. The phenomenon of ion-exchange is not of 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.

## 2. Ion exchangers

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:



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, that is, 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  $pK_a$  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 properties—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.

## 2.1 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.

## 2.2 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 [3]. 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. Good starting points for further basic information are classic books like those of Clearfield [4], Amphlett [5] and Qureshi and Varshney [6]. These books have provided a complete picture and thorough insight into this field and

widespread importance of inorganic ion exchangers. Important advances in this field have been reviewed by a number of workers/researchers at various stages of its development, such as Fuller [7], Qureshi et al. [8], Vesely and Pekarek [9], Clearfield [10, 11], Alberti et al. [12, 13], Alberti and Costantino [13], Marinsky [14], Varshney [15–20], Ivanov [21] and Terres-Rojas [22]. Dyer [23–25] has dealt with the theories involved zeolite molecular sieves, which have principles underlying the inorganic ion exchangers. Alberti (Italy) and Clearfield (USA) devoted most of their studies on the crystalline inorganic ion exchangers.

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, molybdic, antimonite 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. Out of the above, metal phosphates have been found to have good chemical stability, reproducibility in ion-exchange behaviour and selectivity for certain metal ions.

### 2.3 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 have 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 [26–30]. 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, that is, 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 [31].

- 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.

2.4 Hybrid metal phosphates

Hybrid organo-inorganic phosphates open up a land of opportunities in materials science and ion-exchange chemistry. These nanocomposites bridge high-temperature materials such as glasses and ceramics with very fragile species such as organic compounds or biomolecules. In last 10–15 years, some hybrid ion-exchange materials have been synthesized in the laboratories, such as acrylamide

S.N.	Name of the materials	Ion-exchange capacity for Na <sup>+</sup> (meq/dry g)	Selectivity	X-ray nature	References
1.	Polyacrylonitrile thorium(IV) phosphate	3.90	Pb(II)	Microcrystalline	[36]
2.	Polystyrene cerium(IV) phosphate	2.95	Hg(II)	Microcrystalline	[37]
3.	Polystyrene thorium(IV) phosphate	4.52	Cd(II)	Crystalline	[38]
4.	Acrylonitrile cerium (IV) phosphate	2.86	Hg(II)	Poorly crystalline	[39]
5.	Acrylamide cerium(IV) phosphate	2.60	Hg(II)	Crystalline	[40]
6.	Acrylamide thorium(IV) phosphate	2.00	Pb(II)	Poorly crystalline	[41]
7.	Pectin cerium(IV) phosphate	1.78	Hg(II)	Amorphous	[42]
8.	Pectin thorium(IV) phosphate	2.15	Pb(II)	Amorphous	[42]
9.	Cellulose acetate thorium(IV) phosphate	1.70	Pb(II)	Amorphous	[43]
10.	Pyridine cerium(IV) phosphate	2.00	Hg(II)	Amorphous	[44]
11.	Pyridine thorium(IV) phosphate	2.10	Pb(II)	Amorphous	[45]
12.	n-Butyl acetate cerium(IV) phosphate	2.25	Hg(II)	Amorphous	[46]

Table 3.  
Different types of hybrid metal phosphates and their important properties.



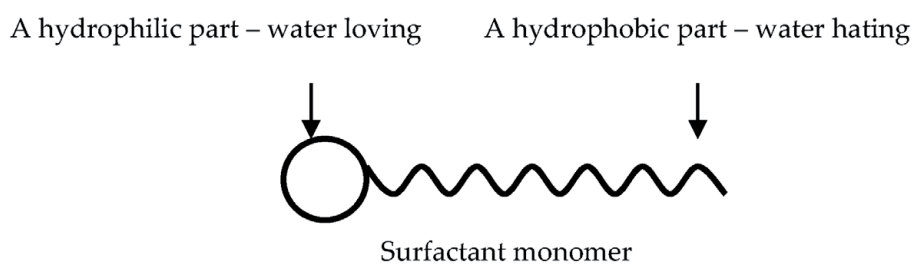
and pyridine-based zirconium and tin phosphates [32–34], acrylonitrile-based zirconium phosphate [35]. These materials have shown promising ion-exchange characteristics and have been utilized in the separation of metal ions due to their selectivity towards different metals ions. Metal phosphates, such as tin(IV) phosphate, cerium(IV) phosphate, zirconium(IV) phosphate etc. were found very good ion exchangers and intercalating agents too. The whole idea to convert them to hybrid ion exchangers has been to enhance the interlayer distances by introducing organic species in the metrics of these metal phosphates, resulting in improved ion-exchange properties. These metal-organic phosphates, or hybrid ion exchangers, correspond to metal-organic frameworks where features of organic and inorganic counterparts are revealed in terms of ion-exchange capacity, thermal, chemical and mechanical stability in addition to metal ion selectivity. However, structures of these metal-organic phosphates could not be described as these materials have been found amorphous or poorly crystalline. **Table 3** summarizes their ion-exchange capacities and selectivity towards metal ions.

### 3. Surfactants

Surfactants constitute the most important group of detergent components. ‘Surfactant’ is an abbreviation for surface-active agents (shown in **Figure 2**), 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. 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’ [47].

Thus, ‘surfactants, surface-active agents [48] or, detergents are amphiphilic, organic or organo-metallic compounds which form association colloids or micelles in solution’. Amphiphilic substances or amphiphiles are comprised of a hydrophobic portion, usually a long alkyl chain, attached to hydrophilic or water solubility-enhancing functional groups. Actually, surfactant molecule consists of two parts: a water-hating (hydrophobic) part and a water-loving (hydrophilic) part. The following figure shows the basic structure of a surfactant molecule.

There are three basic concepts that 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 which offers the adsorption on surfaces/interfaces and formation of 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 [49]. When a surfactant molecule is introduced into water, the water-hating



**Figure 2.**  
*Structure of Surfactant monomer.*

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 allowing 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 [50]
- Cationic surfactants [51]
- Nonionic surfactants [52]
- Amphoteric surfactants [53]
- Gemini surfactants [54]

### 3.1 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 unfavourable 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  $10^{-4}$  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 generally being considerably larger 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 favoured 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 [55]. 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 [56–58].

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 [59] of individual surfactant molecules in equilibrium with its monomer. The reverse orientation of the hydrophilic and hydrophobic part of the surfactant in a hydrocarbon medium leads to the formation of reversed micelles [60].

### 3.2 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 floatation, 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 [61].

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 [62], as in the case for nonionic surfactants.

The number of industrial applications of surfactants is huge, and represents the subject of several book series. However, in analytical chemistry, surfactants have been recognized as being very useful in improving analytical technology, for example, in chromatography [63] and luminescence spectroscopy [64]. 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 with their hydrophilic part remaining 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.

### 3.3 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 [65, 66] 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 [67–70] such as petroleum, pharmaceuticals, agro-chemicals, processing of foods, paints, coatings, adhesives, lubricants, in photographic films, personal care and laundry products.

Varshney et al. [71, 72] 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 metal phosphates have been synthesized by combining surfactants and inorganic ion exchangers (metal phosphates) [73–81] by the researchers. Surfactants based ion exchangers also correspond to metal organic frameworks as surfactants being an organic counterpart introduced in the inorganic metal phosphates by the bonding in between the layers of metal phosphates. At this level too, structure could not be explained, reason being the amorphous and poorly crystalline nature of these materials.

Somya et al. [73–75] have probably first used surfactants in the synthesis some novel hybrid fibrous and non-fibrous metal phosphates by introducing surfactants (anionic, cationic and nonionic) in the matrix of inorganic metal phosphates. They have explored the ion-exchange studies such as ion-exchange, pH-titration, concentration, elution and thermal behaviour in addition to adsorption studies for some alkaline earths and heavy metal ions. Those materials were found to be selective for certain metal ions and, on that basis, some binary separations have been performed in the laboratory providing their potential role in environmental and analytical chemistry. 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 [78–81] have synthesized the same class of hybrid metal phosphates by combining sodium dodecyl benzene sulphonate and sodium bis (2-ethyl-hexyl) sulposuccinate 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. Most of the surfactant based metal phosphates were found amorphous or poorly crystalline.

## 4. 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 metal phosphates as ion-exchange materials. They have enhanced not only the ion-exchange capacities of the inorganic metal phosphates when present in their matrix but also the adsorption of metal ions. These metal-organic hybrid materials have shown selectivity towards



certain metals. Hence, these materials open a door with ample opportunities for the researchers in the field of analytical and environmental science where they can be used in water pollution control.

## **Acknowledgements**

The author (A. Somya) is highly thankful to the Department of Applied Chemistry, Aligarh Muslim University, Aligarh for providing the research facilities. The author is also thankful to the Council of Scientific and Industrial Research, New Delhi for providing funds under Senior Research Fellowship scheme [09/112(0408)2K8-EMR-I]. The author wants to express special thanks to the Chancellor, Pro-Chancellor, Vice-Chancellor and Dean, School of Engineering, Presidency University, Bengaluru for giving enthusiastic and constant support.

## **Author details**

Amita Somya  
Department of Chemistry, School of Engineering, Presidency University,  
Bengaluru, Karnataka, India

\*Address all correspondence to: [somya.amita@gmail.com](mailto:somya.amita@gmail.com)

## **IntechOpen**

© 2020 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 



## References

- [1] Ettre LS. Nomenclature for Chromatography. Pure and Applied Chemistry. 1993;**65**(4):819
- [2] Qureshi M, Zafar S, Ahmad TS, Rahman N. Chemia Analityczna. 1992;**37**(1):21
- [3] Varshney KG. New development in ion-exchange. In: Abe M, Kataoka T, Kodansha ST, editors. Proceeding Int. Conf. Ion-exchange (ICEE-91). Tokyo: Elsevier; 1991. p. 413
- [4] Clearfield A. Inorganic Ion-exchange Materials. Boca Raton, Florida: CRC Press, Inc.; 1982
- [5] Amphlett CB. Inorganic Ion-Exchangers. Amsterdam: Elsevier; 1964
- [6] Qureshi M, Varshney KG. Inorganic Ion-exchangers in Chemical Analysis. Boca Raton, Florida: CRC Press, Inc.; 1991
- [7] Fuller MJ. Inorganic ion-exchange chromatography on oxides and hydrous oxides. Chromatographic Reviews. 1971;**14**:45
- [8] Qureshi M, Qureshi SZ, Gupta JP, Rathore HS. Recent progress in ion-exchange studies on insoluble salts of polybasic metals. Separation Science. 1972;**7**:615
- [9] Vesely V, Pekarek V. Synthetic inorganic ion exchangers-1: Hydrous oxides and acidic salts of multivalent metals. Talanta. 1972;**19**:1245
- [10] Clearfield A. Role of ion exchange in solid-state chemistry. Chemical Reviews. 1988;**88**:125
- [11] Clearfield A. Inorganic ion exchangers: A technology ripe for development. I and EC Research. 1995;**34**:2865
- [12] Alberti G, Casciola M, Costantino U. Inorganic ion-exchange membranes made of acid salts of tetravalent metals. A short review. Journal of Membrane Science. 1983;**16**:137
- [13] Alberti G, Costantino U. Recent progress in the field of synthetic inorganic exchangers having a layered or fibrous structure. Journal of Chromatography. 1974;**102**:5
- [14] Marinsky JA. Reactive and Functional Polymers. 1995;**27**(2):107
- [15] Varshney KG, Gupta U. Tin(IV) antimonate as a lead-selective cation exchanger: Synthesis, characterization, and analytical applications. Bulletin of the Chemical Society of Japan. 1990;**63**:1515
- [16] Varshney KG, Mohammad A. Chemical and Environmental Research. 1992;**1**(4):353
- [17] Varshney KG. In: Sinha AK, Srivastava KN, Sinha BK, Pandey SK, Agarwal NK, editors. Environment Management in Developing Countries, Water and its Managements. Vol II; 1993. p. 64
- [18] Varshney KG. Chemical and Environmental Research. 1994;**3&4**:301
- [19] Varshney KG. In: Srivastava MM, Srivastava S, editors. Recent Trends in Chemistry. New Delhi: Discovery Publishing House; 2003. p. 467
- [20] Varshney KG. Solid State Phenomena. 2003;**90-91**:445
- [21] Ivanov VA, Timofeevskaya VD, Gorshkov VI, Drozdeva NV. Journal of Radioanalytical and Nuclear Chemistry. 1996;**208**(1):23
- [22] Terres-Rojas E, Dominguez JM, Sales MA, Lopez E. Chemical Industries. 1997;**69**:567

- [23] Dyer A. An Introduction to Zeolite Molecular Sieves. Avon: Bath Press Ltd.; 1988
- [24] Dyer A, Townsend RP. The mobility of cations in synthetic zeolites with the faujasite framework — V: The self-diffusion of zinc into X and Y zeolites. *Journal of Inorganic and Nuclear Chemistry*. 1973;**35**:3001
- [25] Dyer A, Hudson MJ, Williams PA. Progress in ion-exchange: Advances and applications. In: *Proceedings of the Ion-Ex '95 Conference*. Vol. 196. Special Publication by Royal Society of Chemistry; 1997. p. 498
- [26] Chetverina RB, Boichinova ES. *Zhurnal Prikladnoi Khimii*. 1977;**50**:1181
- [27] Malik WU, Srivastava SK, Kumar S. Ion-exchange behaviour of pyridinium tungstoarsenate. *Talanta*. 1976;**23**:323
- [28] Chetverina RB, Baichinova ES. *Ibid*. 1977;**50**:1183
- [29] Niwas R, Khan AA, Varshney KG. Synthesis and ion exchange behaviour of polyaniline Sn(IV) arsenophosphate: A polymeric inorganic ion exchanger. *Colloids and Surfaces, A: Physicochemical and Engineering Aspects*. 1999;**150**:7
- [30] Varshney KG, Pandith AH. *Chemical and Environmental Research*. 1996;**5**(1-4):141
- [31] Sanchez C, Ribot F. Design of hybrid organic-inorganic materials synthesized via sol-gel chemistry. *New Journal of Chemistry*. 1994;**18**:1007
- [32] Varshney KG, Jain V, Tayal N. Synthesis and ion-exchange behaviour of acrylamide zirconium(IV) phosphate: A novel crystalline and Hg(II) selective hybrid inorganic ion exchanger. *Indian Journal of Chemical Technology*. 2003;**10**:186
- [33] Varshney KG, Jain V, Agrawal A, Mojumdar SC. Pyridine based zirconium(IV) and tin(IV) phosphates as new and novel intercalated ion exchangers. *Journal of Thermal Analysis and Calorimetry*. 2006;**86**:3,609
- [34] Varshney KG, Gupta P. Synthesis and characterization of a mercury selective phase of acrylamide tin(IV) phosphate hybrid ion exchanger: Separation of Hg(II) from Cd(II), Pb(II) and Sr(II). *Indian Journal of Chemistry*. 2003;**42A**:2974
- [35] Varshney KG, Pandith AH. Synthesis and ion exchange behavior of acrylonitrile-based zirconium phosphate - A new hybrid cation exchanger. *Journal of the Indian Chemical Society*. 2001;**78**:250
- [36] Varshney KG, Tayal N, Khan AA, Niwas R. Synthesis, characterization and analytical applications of lead (II) selective polyacrylonitrile thorium (IV) phosphate: A novel fibrous ion exchanger. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2001;**181**:123
- [37] Varshney KG, Tayal N, Gupta P, Agrawal A, Drabik M. Synthesis, ion-exchange and physico-chemical studies on a polystyrene cerium(IV) phosphate hybrid fibrous ion exchanger. *Indian Journal of Chemistry*. 2004;**43A**:2586
- [38] Varshney KG, Tayal N. Polystyrene thorium(IV) phosphate as a new crystalline and cadmium selective fibrous ion exchanger. Synthesis characterization and analytical applications. *Langmuir*. 2001;**17**:2589
- [39] Varshney KG, Tayal N, Gupta U. Acrylonitrile based cerium (IV) phosphate as a new mercury selective fibrous ion-exchanger. *Colloids and Surfaces A: Physico-chemical and Engineering Aspects*. 1998;**145**:71

- [40] Varshney KG, Gupta P, Tayal N. Synthesis, characterization and applications of a new phase of crystalline and mercury selective acrylamide cerium(IV) phosphate: A novel fibrous ion exchanger. *Indian Journal of Chemistry*. 2003;**42A**:89
- [41] Mojumdar SC, Varshney KG, Agrawal A. Hybrid fibrous ion exchange materials: Past, present and future. *Research Journal of Chemistry and Environment*. 2006;**10**(2):85
- [42] Varshney KG, Agrawal A, Mojumdar SC. Pectin based cerium (IV) and thorium (IV) phosphates as novel hybrid fibrous ion exchangers synthesis, characterization and thermal behaviour. *Journal of Thermal Analysis and Calorimetry*. 2005;**81**:183
- [43] Varshney KG, Drabik M, Agrawal A. Cellulose acetate based thorium(IV) phosphate as a new and novel hybrid fibrous cation exchanger: Synthesis, characterization and thermal analysis. *Indian Journal of Chemistry*. 2006;**45A**:2045
- [44] Varshney KG, Agrawal A, Mojumdar SC. Pyridine based cerium(IV) phosphate hybrid fibrous ion exchanger. *Journal of Thermal Analysis and Calorimetry*. 2007;**90**(3):731
- [45] Varshney KG, Agrawal A, Mojumdar SC. Pyridine based thorium(IV) phosphate hybrid fibrous ion exchanger. *Journal of Thermal Analysis and Calorimetry*. 2007;**90**(3):721
- [46] Varshney KG, Rafiquee MZA, Somya A, Drabik M. Synthesis and characterization of a Hg(II) selective n-butyl acetate cerium(IV) phosphate as a new intercalated fibrous ion exchanger: Effect of surfactants on the adsorption behaviour. *Indian Journal of Chemistry*. 2006;**45A**:1856
- [47] Tanford C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*. 2nd ed. New York: Wiley; 1980
- [48] Rosen MJ. *Surfactants and Interfacial Phenomena*. New York: Wiley; 1978
- [49] Cullum DC. *Introduction of Surfactant Analysis*. 1st ed. UK: Chapman and Hall; 1994
- [50] Linfield WM, editor. *Anionic Surfactants*. New York: Dekker M; 1973
- [51] Jungermann E, Dekker M. *Cationic Surfactants*. New York; 1970
- [52] Schick MJ, editor. *Nonionic Surfactants*. New York: Dekker M; 1967
- [53] Porter MR. *Handbook of Surfactants*. 2nd ed. UK: Chapman and Hall; 1994
- [54] Menger FM, Littau CA. Gemini surfactants: A new class of self-assembling molecules. *Journal of the American Chemical Society*. 1993;**115**:10083
- [55] Mukerjee P, Banerjee K. A study of the surface pH of micelles using solubilized indicator dyes. *The Journal of Physical Chemistry*. 1964;**68**:3567
- [56] Preston WC. Some correlating principles of detergent action. *The Journal of Physical and Colloid Chemistry*. 1948;**52**:84
- [57] Shinoda K, Nakagawa T, Tamamushi BI, Isemura T. *Colloidal Surfactants, Some Physico-Chemical Properties*. New York: Academia Press; 1963
- [58] Mukerjee P, Mysels KJ. *Critical Micelle Concentrations of Aqueous Surfactant Systems*. Washington, DC: National Bureau of Standards, NSRDS-NBS 36; 1971



- [59] Dill KA, Flory P. Molecular organization in micelles and vesicles. *Proceedings of the National Academy of Sciences*. 1981;**78**:676
- [60] Luisi PL, Straub B. *Reverse Micelles—Technological and Biological Relevance*, Plenum Press New York; 1984:143
- [61] Harwell JH, Haskins IC, Schecter RS, Wad WH. *Langmuir*. 1985;**1**:251
- [62] Rosen MJ. *Surfactants and Interfacial Phenomena*. 2nd ed. New York: Wiley; 1989
- [63] Hearn MT, editor. *Ion-Pair Chromatography*. New York: Dekker M; 1985. p. 251
- [64] Hoffmann H, Ebert G. *Surfactants, micelles and fascinating phenomena*. *Angewandte Chemie*. 1988;**100**:933
- [65] Rosen MJ. *Surfactants and Interfacial phenomenon*. 2nd ed. New York: Wiley; 1989
- [66] Myers D. *Surfactant Science and Technology*, VCH New York; 1988: 351
- [67] Karsa DR, editor. *Industrial Applications of Surfactants*. Cambridge, UK: Royal Society of Chemistry; 1987
- [68] Karsa DR. *Industrial Applications of Surfactants*. 2nd ed. Heidelberg, Germany: Springer-Verlag; 1990
- [69] Karsa DR. *Industrial Applications of Surfactants*. 3rd ed. Heidelberg, Germany: Springer-Verlag; 1992
- [70] Karsa DR. *Industrial Applications of Surfactants*. 4th ed. Cambridge, UK: Royal Society of Chemistry; 1999
- [71] Varshney KG, Rafiquee MZA, Somya A. Effect of surfactants on the adsorption behaviour of cerium (IV) phosphate, cation exchanger for alkaline earths and heavy metal ions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2007;**301**:69
- [72] Varshney KG, Rafiquee MZA, Somya A. Effect of surfactants on the adsorption behaviour of tin (IV) phosphate, cation exchanger for alkaline earths and heavy metal ions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2007;**301**:224
- [73] Somya A, Upadhyaya V. Synthesis, characterization and adsorption behaviour of N-dodecyl pyridinium chloride based Tin (IV) phosphate: A new surfactant based hybrid ion exchanger. *Research Journal of Chemistry and Environment*. 2017;**21**(1):18
- [74] Somya A, Rafiquee MZA, Varshney KG, Al-Lohedana HA. Synthesis, characterization and analytical applications of N-dodecyl pyridinium chloride cerium (IV) phosphate fibrous ion exchanger: Selective for Hg(II) and its binary separations. *Desalination and Water Treatment*. 2015;**56**:638
- [75] Somya A, Rafiquee MZA, Varshney KG. Synthesis, characterization and analytical applications of sodium dodecyl sulphate cerium (IV) phosphate: A new Pb (II) selective, surfactant-based intercalated fibrous ion exchanger. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2009;**336**:142
- [76] Varshney KG, Rafiquee MZA, Somya A. Triton X-100 based cerium(IV) phosphate as a new Hg(II) selective, surfactant based fibrous ion exchanger: Synthesis, characterization and adsorption behaviour. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2008;**317**:400
- [77] Varshney KG, Rafiquee MZA, Somya A. Synthesis, characterization and adsorption behaviour of TX-100

based Sn(IV) phosphate, a new hybrid ion exchanger. *Journal of Thermal Analysis and Calorimetry*. 2007;**90**:663

[78] Iqbal N, Rafiquee MZA. Synthesis and characterization of lead (II) selective sodium dodecyl benzene sulphonate-cerium (IV) phosphate ion exchanger. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2010;**364**:67

[79] Iqbal N, Mobin M, Rafiquee MZA, Al-Lohedana Hamad A. Removal of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  ions by the synthesized sodium dodecyl benzene sulphonate-based tin (IV) phosphate (SDBS-SnP) cation exchanger. *Desalination and Water Treatment*. 2013;**51**:6688

[80] Iqbal N, Mobin M, Rafiquee MZA. Synthesis and characterization of sodium bis (2-ethylhexyl) sulfosuccinate based tin (IV) phosphate cation exchanger: Selective for  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$  ions. *Chemical Engineering Journal*. 2011;**169**:43

[81] Iqbal N, Mobin M, Rafiquee MZA, Al-Lohedana Hamad A. Characterization and adsorption behavior of newly synthesized sodium bis(2-ethylhexyl) sulfosuccinate–cerium (IV) phosphate (AOT–CeP) cation exchanger. *Chemical Engineering Research and Design*. 2012;**90**:2364