IONIC LIQUIDS:

ECO-FRIENDLY SUBSTITUTES FOR SURFACE AND INTERFACE APPLICATIONS

Editor:

Chandrabhan Verma

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Ionic Liquids: Eco-friendly Substitutes for Surface and Interface Applications

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FOREWORD 1

From the first time I met Dr. Chandrabhan Verma in July 2017, I knew he was going to be a star. He had all the qualities of a good researcher. He worked with me and published good research and review articles on highly reputed platforms. He authored and edited many books on different platforms. I believe that the book entitled "*Ionic Liquids: Eco-friendly Substitutes for Surface and Interface Applications*" is one of the best books on surface and interface applications of ionic liquids. This will be useful for students, professors, academicians and industrialists working particularly in ionic liquids and their applications. Today, as I write this foreword to his new book, I share words that I always hoped.

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FOREWORD 2

Dr. Verma joined my research team as a Ph.D student in 2012 at the Department of Chemistry, IIT-BHU Varanasi. Dr Verma is one of the best students I supervised, and I am confident that he is a well-focused and dedicated researcher. The qualities he has displayed over the years in scientific research suffice him to be a good editor. In his Ph.D. and PDF studies, Dr. Verma did outstanding research and published more than 150 research and review articles in high-impact factor international journals. He also authored and edited more than 10 books on the highly recognized platforms of ACS, RSC, Elsevier, Wiley and Bentham Science. He has total citations of over 7600, an i-10 index of 126 and an H-index of 48. Dr. Verma is ranked 46 among the top 13021 top scientists in Saudi Arabia. He is passionate about his work and I am certain that his passion, as well as his extensive knowledge, will help the institution. I am pleased to recommend this book for the wide readership, and I am happy to write the forward for this excellent book.

M. A. Quraishi
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PREFACE

The development and consumption of ionic liquids are gaining particular attention because of their various salient features, such as high polarity, negligible volatility, high thermal stability, high ionic conductivity, low melting point, and structural designability. They are well-established environmentally sustainable alternatives for different industrial and biological applications. The use of environmentally friendly ionic liquids in place of extensively used toxic and volatile solvents (Volatile) that leads to serious environmental challenges is associated with numerous advantages. Their surface and interface chemistry and related applications are also gaining significant consideration. They are widely used for various applications, such as in wastewater treatment, treatment of other industrial influents, corrosion protection, catalysts in phase transfer, surfactants, *etc.* The present book aims to collect the major and up-to-date advancements in surface and interface properties and applications of ionic liquids.

The present book is divided into two sections, section-I: Ionic Liquids: Basics, Surface/ Interface Chemistry Properties and section-II: Ionic Liquids: Surface/ Interface Applications. Section-I contains eight chapters that collectively describe ionic liquids' fundamental and eco-friendly properties. This section also reports their colloidal, surface and interface properties and the factors responsible for their abilities to behave as surface and interface active species. This also covers the interactions of ionic liquids with the metallic surface through coordination bonding. Section-II also contains eight chapters and describes the use of ionic liquids for numerous surface and interface applications. In different chapters, wastewater treatments, decontamination of toxic metals impurities, corrosion protection, tribological, phase transfer catalysis, electrolytes for photoelectrochemical cells, selective separation, medical devices and sensing applications of ionic liquids are described.

Overall, this book is written for scholars in academia and industry, working in engineering, materials science students and applied chemistry. The editors and contributors are well-known researchers, scientists and true professionals from academia and industry. On behalf of Bentham Science, I am very thankful to the authors of all chapters for their amazing and passionate efforts in making this book. Special thanks to Ms. Humaira Hashmi, editorial project manager (EPM), and Ms. Rabia Maqsood (publishing assistant) for their support and help during this project. In the end, all thanks to Bentham Science for publishing the book

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CHAPTER 1

Ionic Liquids: Fundamental Properties and Classifications

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Abstract: The ionic liquids (ILs) have been recognized as the salts of differently made anions and cations, existing in liquid form at rt or below 100 °C. They have drawn their special attention as an alternative to toxic solvents, such in organic transformations along with several other fields such as wastewater management, organic transformations, chemical transformations, synthesis of heterocycles, sensing applications, *etc*. The present work shall describe the basis of ILs, their types, structural insights, and mechanistic overview along with a brief introductory account of ILs for the general benefit of the reader of the present works.

Keywords: Applications of ILs, Catalysis, Ionic liquids, Properties of ILs, Types of ILs.

1. INTRODUCTION

Two decades ago, a few researchers were familiar with the term ionic liquids (ILs) and used them for some organic transformations. In comparison to commonly utilised volatile organic solvents, ILs have been said to be good molecular and/or green solvents, having some specific physicochemical and thermal properties. Being liquid at room temperature or less than 100 ºC temperature and composed of ions, ILs recognized as fused/ molten/ liquid organic salts, *etc* [1]. In this chapter, elemental knowledge about ILs along with their vast applications will be provided in brief for the benefit of the reader of the book chapter.

2. PROPERTIES OF ILs

Due to the structural variability of the ions, it is difficult to determine a general set of IL properties completely. To name a few, the properties of IL as a solvent can

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be amphiphilic nature, ability to form supramolecular assembly due to solvophobic property[2], Lewis acidic behaviour, *etc*. ILs possess an amphiphilic profile having both hydrophilic and lipophilic properties as observed in synthetic or natural compounds that can self-assemble into micelles, vesicles, nanotubes, nanofibers, *etc* [3, 4]. These ILs have been known to form supramolecular assemblies through noncovalent intramolecular interactions, such as hydrophobic or hydrogen bonding, and electrostatic/ π-π/ and van der Waals interactions. These interactions have been deeply involved in interactions for self-assembly, and molecular recognition applications ranging from material science to biological chemistry [5].

Ionic liquids are referred to as "green solvents" because of their better safety profile, and less flammability. They have higher thermal and electrical conductivities than typical laboratory solvents and have broader electrochemical windows. Owing to the finer tunability of anions and cations, there has been a potential scope to design a solvent with precise qualities or applications unlike that with organic solvents. Due to their behaviour as hydrogen bond acceptors/donors and possessing a higher degree of anionic charge delocalisation, they possess a high capability to solubilize the organic/ inorganic counterparts to boost the rate of the reactions and selectivity [6].

Further, ILs have been recognized as Lewis acids in organic synthesis in either stoichiometric or catalytic amounts, with varying Brønsted acidic centres. Organic cationic counterparts of ILs control their physical properties as compared to anionic counterparts [7]. Furthermore, Coutinho and co-workers have reported an increase in molecular interactions or ion speciation in a mixture of ILs under aqueous conditions in comparison with the individual ILs [8, 9].

For the several amino acid-based ILs, there have been varying properties, such as spectroscopic properties due to their aliphatic/aromatic nature, colour, viscosity, and specific rotation (negatively dependent upon the size of cation), glass transition temperature (dependent on their molecular weight). At rt, they are mostly colourless or slightly yellow-coloured liquids with a viscosity between 330 to 16,856 mPa·s, which decreases significantly with a temperature rise. ILs possess high thermal stability due to hydrogen bonding, van der Waals interactions, and the size of the amino acid anion. These ILs are soluble in polar solvents and immiscible among non-polar solvents [10].

Several attractive properties of ILs, like high viscosity, chemical stability, hydrophobicity and reusability, have rendered ionic liquids a highly used alternative in isolation studies such as (micro)extraction. The immobilized and modified ILs with solid supports have been the significant alternatives to exploit their capabilities in the adsorptive removal of emerging water contaminants [11]. Apart from these, they possess excellent properties, including low vapour pressure, sufficient stability at different pH and temperature, solubilization potential for substances or gases, such as hydrogen, carbon monoxide, carbon dioxide, *etc*., the potential for the enhancement of reaction rate for chemical transformation under microwave heating, long time stability without decomposition, *etc*. As a result, they have been sustainable alternatives to replace existing corrosion inhibitors with efficient adsorption on metallic surfaces [12].

The phrase "task-specific ILs" refers to ILs that are deemed in non-solvent applications, such as catalysts for metal or gas separation or organic synthesis. The functionalized ILs have found their applications as phase transfer catalysts (PTC). The most important subclasses of task-specific ILs, the Brønsted acidic ionic liquids (BAILs), have various advantages, including great thermal stability, high acidity, facile separation/purification and recyclability for re-runs [13]. The combination of ILs and ultrasound techniques has improved the physical effects of sonochemistry significantly [14, 15].

Metal-organic frameworks (MOFs) supported ILs can reduce the catalytic loading of ILs for their use in desired applications to optimize their properties *via* substantial interactions. The ionic conductance of ILs has been relatively low at reduced temperatures because of the significant drop in the migration of the ions owing to the creation of contacts between the molecules, which further depress them below their freezing point. These MOFs offer considerable scopes as attractive materials to control the properties of ILs due to their customized designability, which allows for customizable host-guest interactions [16, 17]. Due to the electrochromic and thermochromic attributes of magnetic ILs, they have been proposed as a potential option for energy storage applications in redox flow batteries [18].

ILs possess several properties, such as chemical and thermal stability, non-flammability, superionic/electrochemical conductance, catalytic potential, low melting point, *etc*. Further, the physicochemical properties of ILs can be customized by a finely tuned combination of cations and or anions [19]. Different strategic techniques have been used to improve the recyclability and recovery of ILs [20], *viz.* distillation, extraction with aqueous/organic solvent, adsorption, pressure-driven membrane methods (pervaporation, membrane distillation, and electrodialysis), crystallization, forcefield based separation (gravity separation, centrifugation, and magnetic separation) [21]. Techniques have improved the sustainability and greener aspects of ILs through efficient separation, isolation or purification at the end of the completion of several applications. Furthermore, there are several computational techniques to treat and predict the properties of

CHAPTER 2

Eco-friendly Nature of Ionic Liquids

Himani[1], **Anirudh Pratap Singh Raman**[1], **Pallavi Jain**[2], **Ramesh Chandra**[3,4], **Kamlesh Kumari**[5], **Vinod Kumar**[6] and **Prashant Singh**[1,*]

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Abstract: Ionic Liquids (ILs) are believed to be designer solvents, and their use has helped to speed up research in the field of chemistry properties like high viscosity and low vapor pressure. ILs are well-known for their physicochemical properties that can be modified to obtain desired functionality and improved efficiency, analyte extraction selectivity, and sensitivity. ILs have been studied through the methodologies for their synthesis, recyclability after use, reusability for different applications, toxicity against living organisms, and degradation with time. Usually, ILs have considerably better solvents than traditional solvents, but their synthesis involves harmful chemicals. ILs have also proved to be superior lubricants to other lubricants, which show high performance because friction in ILs may be regulated actively by using an external electric potential even when it is diluted in oil. ILs are proven appreciable electrolytes and have significant performance in the generation of energy. ILs are considered an alternative to the traditional solvents obtained from fossils. This chapter will concentrate on current advances in surface and interfacial applications.

Keywords: Green solvent, Ionic liquids, Organic cations and inorganic anions, Room temperature ILs.

1. INTRODUCTION

Ionic liquids (ILs) have a salt-like chemical composition and exist in a liquid state below 100°C.They possess high viscosity, wide electrochemical ability, low vapor

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pressure, poor conductivity, and others. Paul Walden reported the first IL, that is, ethylammonium nitrate, in 1914, but he was not aware that the ILs would bring a transformation in the scientific field after many decades. These characteristics of ILs have attracted researchers' attention since ILs offer a viable alternative to volatile and hazardous organic solvents [1 - 4]. ILs are well-known for their physicochemical properties to enable them to collaborate with a wide range of molecules with varying hydrophobicity, polarity and viscosity [5 - 7]. Though, there is still some debate over the applicability of ILs with the concept of toxicity, their importance in delivering effects is more impactful. As a result, efforts have been focused on substituting the most frequent IL component with bio-based materials, therefore, enhancing biodegradability and increasing renewable resources. In analytical chemistry, ILs have made significant progress in investigations of elimination, extraction, and differentiation [8, 9]. Micelles are effective drug transporters, therefore, they have a strong impact on the pharmaceutical industry, which prompted scientists to emphasize how the ILs interact with drug-like molecules [10]. Due to various properties of ILs like non-flammability, promising electrochemical and thermal stabilities, ILs have been explored as electrolytes to get Li-ion batteries [11 - 13]. Application of ILs is discovered effectively in a wide range of areas owing to their designer solvents property [14, 15]. In the oil refining industries or processes, it could also be used to substitute organic surfactants in splitting water/oil emulsions [15]. Micellization in ILs solutions allows them to operate as emulsifiers, allowing them to solubilize and disperse molecules that would otherwise be incompatible, such as oil. ILs have lately attracted attention as a green alternative to conventional emulsifiers for enhanced oil recovery (EOR) [16, 17]. ILs have the highest catalytic activity as well as unique characteristics. However, their large-scale use is hampered by their high-power consumption and inherent difficulties in output purification and catalysts recovery. Several routes to immobilize the ILs for facile extraction and processing have been presented. Numerous supportive compounds, such as carbon nanotubes (CNT), ZSM-SiO_2, chloromethyl polystyrene, and meta-organic frameworks (MOF), have been described to support ILs with the goal of refining, recovery, and segregation properties. [14] ILs gas separation is considered the most potential application to offer alternate solutions to volatile solvents [18 - 21]. Researchers discovered the solubilities of CO_2 in numerous ILs during the end of the twentieth century and the beginning of the twenty-first century. It was discovered that CO_2 solubilities with ILs are substantially greater as compared to other noble gas like N_2 and inert gas like CH_4. Despite being non-polar and linear, CO_2 has polar nature to its quadrupolar moment. As a result, it can disperse both non-polar and low polarity compounds in liquid or supercritical conditions, but it is not an effective solvent for high molecular weight, strongly polar, or ionic compounds. Since carbon dioxide has polar bonds and reacts with water to form carbonic acid, it dissolves in water much more readily than other gases. At the same pressure, cyclohexanone dissolves carbon dioxide more easily than toluene or n-butanol. An excellent solvent for a variety of organic solvents is carbon dioxide in the liquid state. Surface-active ILs with a long hydrophobic hydrocarbon chain may have surface-active qualities comparable to traditional surfactants. These may form self-assemblies in an aqueous solution to form micelle, liquid lyotropic crystals, and vesicles based on their structure and surface-active nature [22 - 24]. The pharmaceutical industry has several obstacles, including administering solid and crystalline versions of many medications due to their low solubilities in water and the conversion of polymers that can reduce bioavailability. Fortunately, the flexible features of ILs permit the customization of medicinal solvents or the production of novel drugs with specific desirable qualities that are substantially constrained when using water or molecular organic solvents [25]. Most common types of synthetic food comprise azo dyes that have -N=N- groups, considered to be toxic for humans [26]. Tartrazine (TZ) is a sulfonated azo dye commonly employed in food additives, nutritional supplements, and pharmaceuticals in very low quantities, but they cause great harm to the environment after mixing with river water. Researchers are working to create sustainable ILs to discard the harmful effect of these dyes. ILs have gotten a lot of attention in the last decade for a variety of reasons [26]. It was recently discovered that applying chitin beads with Aliquat-336, an IL improves the adsorption capacity of dye, which eventually leads to its elimination from the environment [26 - 28].

Surface-active ionic liquids (SAILs) are being used in medication delivery and are currently the subject of much investigation. Using micellization, a considerable number of researches on drug-IL interactions have been conducted to enhance the bioavailability of drugs and reduce drug toxicity [29]. In various environments, ILs with imidazolium or pyrrolidinium cations and lengthy alkyl chains clump together in micelles, vesicles, reverse micelles, microemulsions, and other fascinating molecular structures originate from such aggregations. Drug transport, gene delivery, nanocarrier, bioimaging, and photodynamic treatment are all aided by these IL-induced micro-heterogeneous aggregates [30]. ILs have recently been used in electro-deposition, electro-synthesis, lubricants, electro-catalysis, plasticizers, lithium batteries, electrochemical capacitors, solvents, solvents for manufacturing nanomaterials, extraction, gas absorption agents, ionic conductive matrix, and benign-reaction solvents, and so on. Owing to their high electrical conductivity and stability, ILs are being extensively studied as electrolytic functionalities in batteries and supercapacitors, where the dynamics, composition, phase, and structure may be changed by using applied voltage, dilution, temperature, or a change in ion chemistry. ILs have also proved to be superior lubricants to other lubricants which show high performance because friction in

CHAPTER 3

Solid (Metal)-Liquid (Ionic Liquids) Interface: Basics and Properties

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Abstract: Ionic liquids (IL) are biodegradable and green designer solvents for use in lots of vital applications *i.e.,* catalysis, CO_2 capture, green chemistry synthesis, energy storage, particle stabilization, self-assembly media and lubrication. ILs show many attractive properties in proximity to solid surfaces. ILs form well-defined interfacial layers that are tunable-electrically and thermally as well as stable- mechanically, electrically and thermally over a wide range. The structure of solid-ILs interfaces plays a basic role in these applications. In this book chapter, the recent literature is presented while future research information's discussed. In the past decade, there has been rising interest in this topic, and significant progress has been made in understanding such interfaces. It has been known that electrostatic forces self-assembly of ILs and solid-IL interfaces are two key parameters. Moreover, how the structure of the IL-interface impacts the property, *e.g*., conductivity, viscosity and friction, has yet to be understood. Surface properties of ILs are explored with techniques that probe force, such as atomic force microscopy (AFM) and surface force apparatus (SFA), with scattering techniques such as neutron (NR) and X-ray reflectometry (XRR), sum frequency generation spectroscopy (SFGS) and other techniques, as well as with molecular dynamics (MD) simulations and theory.

Keywords: Ionic liquids, Properties, Solid-ionic liquids interface.

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1. INTRODUCTION

Metal-containing ILs are a potential subclass of charged liquids that combine the features of ILs with the magnetic, photophysical/optical, or catalytic properties of the metal salts contained. In catalysis, ILs containing palladium, ruthenium, platinum, gold, and aluminum (but not iron, nickel, zinc, or copper) have proved successful. In addition to their Lewis acidity, solutions of f-element compounds in ILs are considered promising as soft luminous materials for application in photochemistry and spectroscopy, as well as prospective catalysts in synthesis. Another intriguing option is to prepare novel electrical dispositive or sensors using ILs containing metals. Finally, metals can be electrodeposited in ILs from metal salt combinations to create novel materials with specific properties (thin films, nanostructures and others).

In recent years, large quantities of co-solvents have been used for numerous chemical and biochemical processes [1 - 3]. However, because of new environmental regulations, the challenge of using non-harmful solvents has prompted a great development of an innovative product to protect the environment [4]. Ionic liquids (ILs) possess unusual physicochemical properties and a bright application potential in various fields [5 - 7]. Surface-active ILs are used as novel surfactants or designer green solvents and are of significant interest to researchers worldwide due to their self-assembling behavior [8, 9]. It is noteworthy that the ILs have analogous properties to surface active agents and are capable of forming micellar nano-aggregates in aqueous solutions [10]. ILs behave as the inorganic electrolyte (co-solvents) or as co-surfactants encouraged us to study the impact of ILs on the aggregation behavior of surfactants, bio-surfactants, proteins, cyclodextrins, amino acids, drugs, and metallic nanoparticles, *etc* [11 - 15]. The search for alternatives to the most damaging organic liquids has become a high priority for the industry and academics to develop and design cleaner or greener technologies. Fused inorganic salts are liquids containing only ions and are thus ionic liquids. The main advantages of ionic liquids are their negligible volatility, non-flammability, the control of their properties due to their composition, and their high compatibility with various organic compounds and other materials [16, 17]. Additionally, they can be easily recycled due to their immiscibility with a range of solvents [18]. Due to their fascinating and outstanding properties, ILs are often considered future solvents for catalysis [19], chemical reactions, extractions [20], electrochemical purposes [21] and many other potential applications [22, 23].

Frequently, ILs are termed “green solvents” or “designer solvents” [24 - 27]. The reputation of “green solvents” mainly arises from the fact that ILs are non-volatile under standard conditions and therefore do not create atmospheric pollution. By the choice and combination of the ions, physicochemical properties such as polarity, viscosity, solubility, melting point, and thermal and electrochemical stability can be targeted.

2. HISTORY OF IONIC LIQUIDS

Ionic liquids of the type mentioned above are not new, and some of them have been known for many years. Gabriel and Weiner [28] reported ethanol ammonium nitrate with a melting point of around 52-55ºC in the year 1888. Ethyl ammonium nitrate, which has a melting point of 12 °C, was first described in 1914 by Walden [29]. Hurley and Wier [30] reported alkyl pyridinium and chloro aluminates as electrolytes for electroplating aluminium. However, these organoaluminate ILs have high reactivity towards the water; hence, the range of applications is limited. Wilkes and co-workers [31] reported in the early 1980s, room-temperature ionic liquids (RTILs) were prepared through the mixing of 1-ethyl-3-methylimidazolium chloride ([Emim][Cl]) with aluminium trichloride. In the early 1990s, Wilkes and Zaworotoko [32] reported two new ILs such as 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF_6]). Since the middle of the 1990s, a theory modified to the rich chemistry of molten salts had to begin and continues to flourish. Research into the synthesis of these RTILs and their use as reagents, solvents, catalysts and materials will continue to be produced. As mentioned earlier, one of the advantages of 1,3-alkyl imidazolium-based ILs over conventional molten salts is that the former have melting points below 100 °C and sometimes as low as -96 ºC as compared to 614 °C for lithium chloride and 801°C for sodium chloride [33]. The low melting points are a result of the chemical composition of RTILs or ILs, which contain larger asymmetric organic cations compared to their inorganic counterpart molten salts [34]. Fig. (**1**) shows the structure of sodium chloride (packing of ions in simple symmetric) and ionic liquids (cations are asymmetrically and anions symmetrically) crystal lattice. It can be seen that the asymmetric arrangement of molecules lowers the lattice energy, and hence the melting point is low [35, 36]. Based on the emerging research and development in ILs, one can classify the cations as first and second-generation types, while anions as first, second and third-generation types represented in Scheme **3**. First ILs was discovered in the 1980s and based on their physical properties. Some cations, *e.g.*, imidazolium, pyridinium, ammonium, pyrrolidinium, sulphonium, phosphonium and anions, *e.g.*, chloride, bromide and iodide, are the first generation of ILs. The implication of IL-based research work was carried out in the year 2000, which focused on the physical and chemical properties of ILs. A variety of biological processes rely on feedback-controlled communication involving nucleic acids, proteins and polypeptides that can adapt conformational specific to their surroundings [37].

CHAPTER 4

Surfactants and Colloidal Properties of Ionic Liquids

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Abstract: The development of surface-active ionic liquids (SAILs) has gained significant interest in recent decades and has successfully replaced the currently utilized conventional surfactants. Due to the amphiphilic character of the SAILs, they have become remarkable surfactants and are particularly important for commercial and field usage. SAILs formed microemulsions and have shown potential in various sectors, including oil recovery and dispersion. The effectiveness of SAILs was measured by their capacity to develop microemulsions. Moreover, it was stated that efficient SAILs could develop a stable microemulsion throughout extended periods at low surfactant concentrations. Similarly, normal ionic liquids (ILs) gained significant attraction as a dispersion medium for colloidal systems as a potential alternative to volatile organic solvents. Colloidal stability is a crucial parameter for evaluating the characteristics and efficacy of colloidal systems. Therefore, the main emphasis is critically discussing the fundamental studies on colloidal stability. Considering the importance and significance of surfactant and colloidal behavior of ILs, this chapter describes these properties by employing recent relevant literature on the topic. The aggregation properties of SAILs alone and the mixed systems of SAILs and conventional surfactants are discussed with their usage in environmental clean-up. Moreover, the colloidal stability of SAILs, as well as the important factors that influence colloidal stability, are discussed in this chapter.

Keywords: Aggregation behavior, Colloidal properties, Colloidal stability, Environmental remediation, Ionic liquid-based surfactants, Poly ionic liquids.

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1. INTRODUCTION

Ionic liquids (ILs) have attracted considerable interest because of their exceptional characteristics, including lower volatile rate, higher thermal stability, and high surface properties [1]. The unique physio-chemical characteristic of ILs at room temperature has attracted the attention of many researchers. Due to the amphiphilic character of the anion or cation of ILs, they have become remarkable surfactants. Prior studies have shown that 1-alkyl-3-methylimidazolium with a minimum of one long alkyl chain attached to the imidazolium cation is an effective surface-active ionic liquid (SAILs) [2]. SAILs have many of the same characteristics as ILs, including low vapor pressure, thermally and chemically stable, high surface properties, and tailor-made molecular structure. Like other surfactants, SAILs form micelles in water systems over the critical micelle concentration (CMC), as depicted in Fig. (**1**) [3, 4].

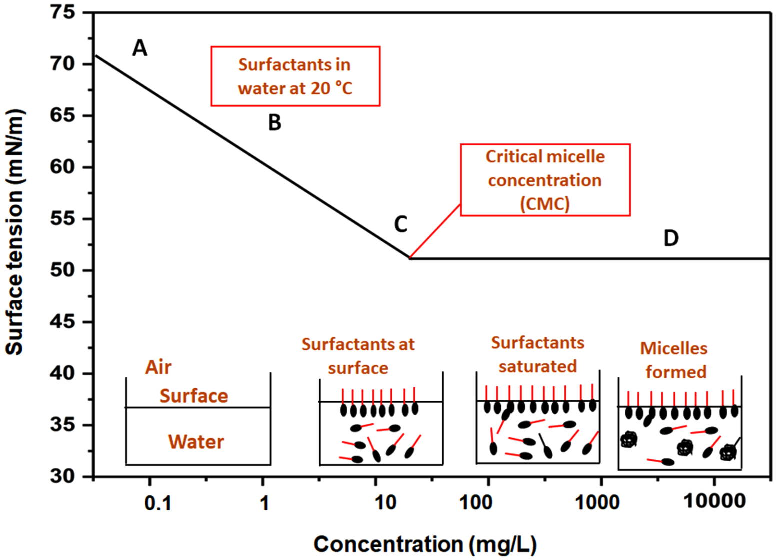

Fig. (1). Micelle formation at CMC by surfactants molecules, (Adapted from ref [3]).

This is commonly recognized that numerous anions and cations could be combined in various ways to form a variety of ILs [5]. As a result, desirable SAILs have been developed by using various anion and cation mixtures or by adding appropriate functional groups in their design [6]. Various studies have examined the aggregation characteristic of SAILs with various head groups, such as pyridinium, imidazolium, pyrrolidinium, and piperidinium cations [7, 8]. The aggregation properties of SAILs can be changed by altering the alkyl chain length and with a head group [9]. As a result, the production of structurally different

SAILs is particularly important for commercial and field usage, as it adds to the area of surfactant technology by finding the structure connections of SAILs.

Colloidal dispersion played a significant part in a wide variety of well-established usage due to its fascinating properties, such as reinforcing, shear-thinning, thickening, and gel production. These distinct rheological characteristics depend highly on the inner microstructures of colloidal dispersions (stable dispersions or aggregates). Several factors affect the stability of colloidal dispersions, including the composition of the dispersed phase and the colloidal surface characteristics [10]. ILs are also potential alternatives for colloidal dispersion medium for nanomaterials owing to their distinct physicochemical features. Several colloidal mixtures with ILs have been currently developed along with the dispersion of metals and semiconductor nanoparticles, such as increment of colloidal stability in ILs [2] and phase transfer of ILs in other dispersion mediums catalytic reaction by the usage of nanoparticles in ILs [11]. Surprisingly, it was observed that certain colloidal particles might be successfully floating in ILs, avoiding aggregating in the ILs without stabilizers like surfactants and polymers often used in aqueous and organic suspension stabilization procedures [12]. It is significant to thoroughly understand colloidal stabilization to apply it to various colloid-IL systems. So, in this chapter, we concentrate on the three various types of repulsions forces among the colloidal particles.

2. SIGNIFICANCE PROPERTIES OF SURFACE-ACTIVE IONIC LIQUID (SAILs)

Surface-active ionic liquids (SAILs) are a subgroup of ionic liquids (ILs) having amphiphilic properties that are significant to the physicochemical characteristics of the basic ILs [13]. SAILs can self-aggregate in solution, inhibiting the behavior like surfactants; certain ILs cations or anions have a charged hydrophilic headgroup and a hydrophobic tail [7]. The alkyl chain length, category of headgroup, and counterion all influence the hydrophobicity of SAILs, which function as surfactants. Thus, it is possible to fine-tune the dynamic and shape of the aggregates developed, such as micelle. Therefore, SAILs-containing formulations have industrial usage in cosmetics, detergents, and biological processes such as surface wetting, solubilization, emulsification, and dispersion [14, 15]. To lower crude oil interfacial tension (IFT) and alter wettability while forming a stable emulsion with high foaming qualities, researchers have improved the knowledge of SAILs, which has led to greater interest in using them in EOR processes [15]. The SAILs examined several benefits over traditional surfactants used in EOR, including (a) task-specificity; they may be tailored to a specific reservoir condition. (b) Without adding a co-surfactant, SAILs may change

CHAPTER 5

Adsorption of Ionic Liquids on The Metal Surface: Co-ordination Chemistry Of Ionic Liquids

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Abstract: Today, Ionic liquids have been very well recognized in the field of corrosion as efficient inhibitors of various metals and alloys, owing to their environmentally friendly nature and strong adsorption properties. The alteration in the cationic part of the ionic liquids increases the electron donation capacity which makes their interaction feasible with the metal surface in the aggressive medium. This attraction leads to the protection of the metal surface from dissolution. The dissociation behavior of ionic liquid indicates the mode of adsorption on the surface of the metal. The adsorption of ionic liquid is also dependent on its chemical structure, the nature of a charge on the metal surface, and many other factors. This chapter gives an overview of factors governing the adsorption of inhibitors on the metal surface, mechanistic details, *etc*., with significant illustrations as documented in the literature.

Keywords: Adsorption, Ionic liquids, Inhibition efficiency, Mild steel.

1. INTRODUCTION

Researchers have recently aimed to design and develop sustainable techniques for improving the environment and attainment of sustainability of the ecosystem. Ionic liquids (ILs) are used in a green context because of their unique properties, such as negligible vapor pressure, which contributes to decreasing their tendency to pollute the environment [1, 2]. Apart from their negligible vapor pressure, several fascinating properties of ILs include low melting point, high polarity, low toxicity, very high thermal and chemical stability, non-flammability, high ionic conductivity, and high range of pH stability, which contribute to less hazardous

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influence on the environment and living being [3 - 6]. Chemically, they are ionic salt in a liquid state with a low melting point lesser than 100°C at room temperature. The organic cationic part of ionic liquids may be a derivative of N, N′-disubstituted imidazolium, N-substituted pyridinium, N-substituted pyridinium, ammonium, phosphonium, *etc* and anionic fragment may be an organic or inorganic anion (CF_3COO^-, HSO_4^-, Cl^-, Br^-, I^-, PF_6^-, SCN^-*etc.*) (Fig. **1**) [7 - 9]. ILs can be considered designer chemicals because their physicochemical properties turned on, changing the nature of cations, anions, and functional groups, since they are used in many applications, such as synthesis and catalysis [10, 11], biology [12], material and medicinal chemistry [13], solar cell [14], waste recycling [15], an electrolyte for battery [16], separation and extraction [17 - 19]. In recent years, they have emerged as promising green corrosion inhibitors for mild steel [20, 21], aluminum [22], copper [23, 24], zinc [25], and a variety of metals and alloys in many electrolytic media.

Ionic liquids are composed of organic cations heteroatoms, such as N, O, P, and S with double or triple bonds), and anions have strong adsorption capacity onto the anodes and cathodes of the metal surface [26]. Ionic liquids contain cations and anions, which are adsorbed onto the anodes and cathodes of metal surfaces, respectively. Metal dissolution significantly decreases as a result. The ionic liquid active site's capacity to donate electrons is the only factor that influences how well the inhibitor can adsorb. By adjusting the ratio of cations to anions, the physiochemical properties, including binding with the metallic surface, can be easily customized [1]. The electrostatic force of attraction, also known as physisorption bonding, chemical bonding, or a combination of the two, also known as physiochemisorption bonding, may be used by ionic liquids to adsorb on the surface of metals in aqueous environments. Adsorption blocks both the cathodic and anodic reactions at the metal solution interface thereby, they inhibit corrosion if they are used as corrosion inhibitors in aqueous electrolytes [1]. Additionally, factors influencing the effectiveness of ionic liquids as inhibitors include their electronic structure, electron density at the donor atoms, functional groups, conjugation, and availability of electrons, type of charge on the metal surface, pH of the solution, inhibitor concentration, temperature, and electrolytic media [27 - 29].

2. MECHANISM OF ADSORPTION OF IONIC LIQUIDS ON THE METAL SURFACE: COORDINATION CHEMISTRY OF IONIC LIQUIDS

The generally accepted theory describes the corrosion inhibition mechanism as the adsorption of ionic liquids onto the metal surface. Ionic Liquids (ILs), like organic inhibitors, tend to substitute the adsorbed water molecules from the metal surface [30, 31].

$$\text{ILs (sol.)} + \text{n}H_2\text{O (adsorbed)} \rightarrow \text{ILs (adsorbed)} + \text{n}H_2\text{O(sol.)}$$

Where, n represents the number of water molecules substituted by Ionic liquids as corrosion inhibitors.

This adsorption on the metal surface may be either physical or chemical, or mixed type [32]. Primarily, there is physisorption due to the physical electrostatic interaction between the electropositive metal surface and the electronegative ions furnished by the ionic liquids or aggressive medium. This interaction is due to strong dipole-dipole intermolecular forces or weak London forces. Following physisorption, chemisorption operates through charge transfer between non-bonding electrons present on heteroatoms of ionic liquids or π electrons of the imidazole, Pyridazine, or another ring generally present in ILs structure and empty d orbitals of the metal [33, 34]. Given the electrochemical theory of corrosion, there is the formation of anodic and cathodic areas (galvanic cells) by different metals or on metallic surfaces. As reported by Likhanova *et al.* [28] in an aqueous acidic solution (corrosive media), two complementary reactions occur simultaneously at the anodic and cathodic sites of the metallic surfaces. These are documented and explained at both sites with and without ILs in an acidic environment.

2.1. Reaction at the Anodic Site (in the Absence of ILs)

$$M + nH_2O \leftrightarrow M(H_2O)n_{ads} \tag{1}$$

Adsorption of water molecules on metal surface

$$M(H_2O)n_{ads} + X^- \leftrightarrow [M(H_2O)_n X^-]_{\text{ads}} \tag{2}$$

Adsorption of X^- on hydrated metal surface

$$[M(H_2O)_n X^-]\text{ads} \leftrightarrow [M(H_2O)_n X]_{ads} + e^- \tag{3}$$

Oxidation of the Metal

$$[M(H_2O)_n X]_{ads} \rightarrow M^+ + OH^- + X^- + H^+ \tag{4}$$

Desorption of anions

CHAPTER 6

Interactions of Ionic Liquids With Metal Surface: Effect of Cations And Anions

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Abstract: The motivation behind recreating this chapter is to give a summary of the bibliographical insights expected to make the segment. In the first part, we examine the adsorption of ionic liquids (ILs) as efficient, effective and eco-friendly corrosion inhibitors for various alloys and metals surface in different corrosive media environments and the restraint and coordination chemistry of ionic liquids. The anti-corrosive activity of different ILs has been examined with electrochemical techniques followed by weight-loss measurement. The impact of the ILs composition (polar and nonpolar substituents in anions & cations, and alkyl tail length), temperature, concentration, and nature of the medium, which influence the metal corrosion protection, was discussed. In the second part, we examine the interfacial structure and adsorption mechanism of different ILs on the Au (111) surface investigated *via* quantum chemical calculations.

Keywords: Adsorption mechanism, Corrosion inhibitor, Coordination chemistry, Ionic liquids.

1. INTRODUCTION

1.1. ILs: Property and Application

ILs are compounds (salt composition) extracted at temperatures below 100 °C. The structures of ILs are shown in Fig. (**1**).

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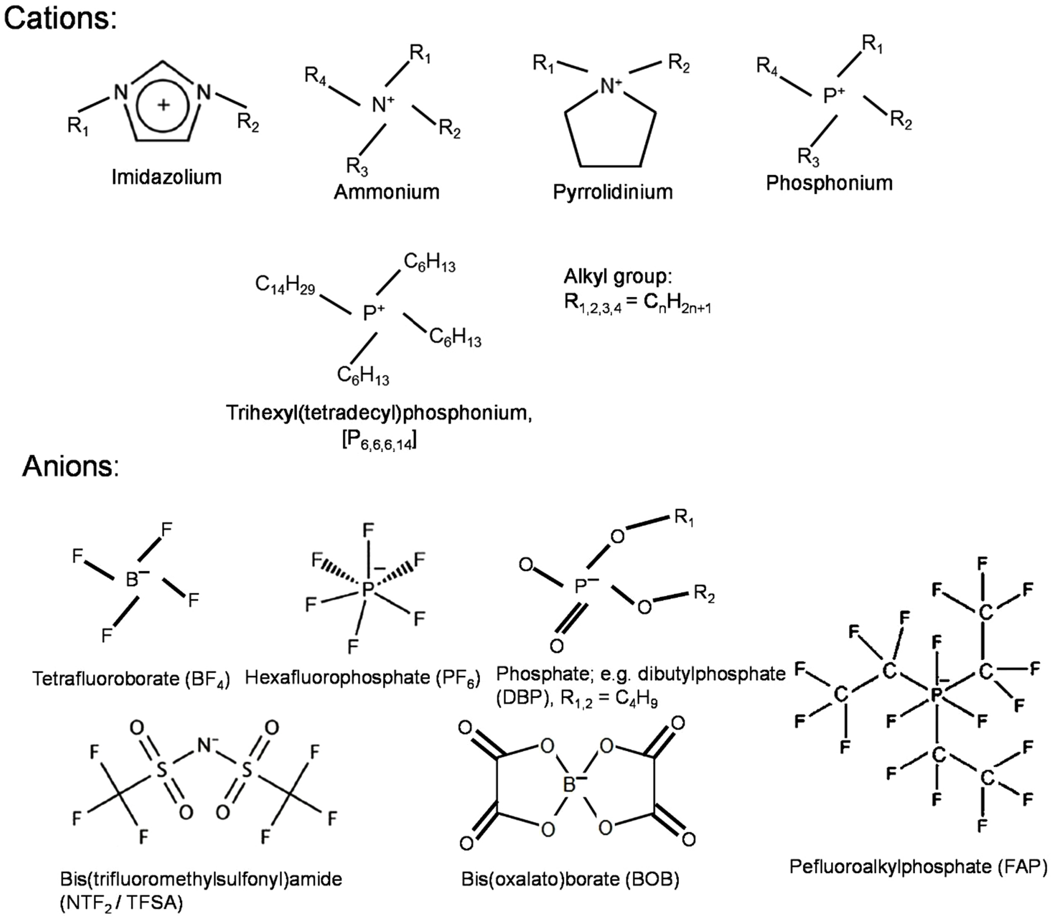

Fig. (1). Typical structures of cations and anions in ILs. Reprinted with permission from [1], © 2017 Elsevier Publications.

ILs are related to some remarkable properties which include high viscosity, low melting point, superior thermal stability and chemical stabilities, low molten temperatures, non-ionizing ability, low vapor pressure, poor conductors of electricity, highly miscible and high combustible temperature with organic compounds [2 - 5].

The common use of ILs in the industry is documented in recent research and shown in Fig. (**2**).

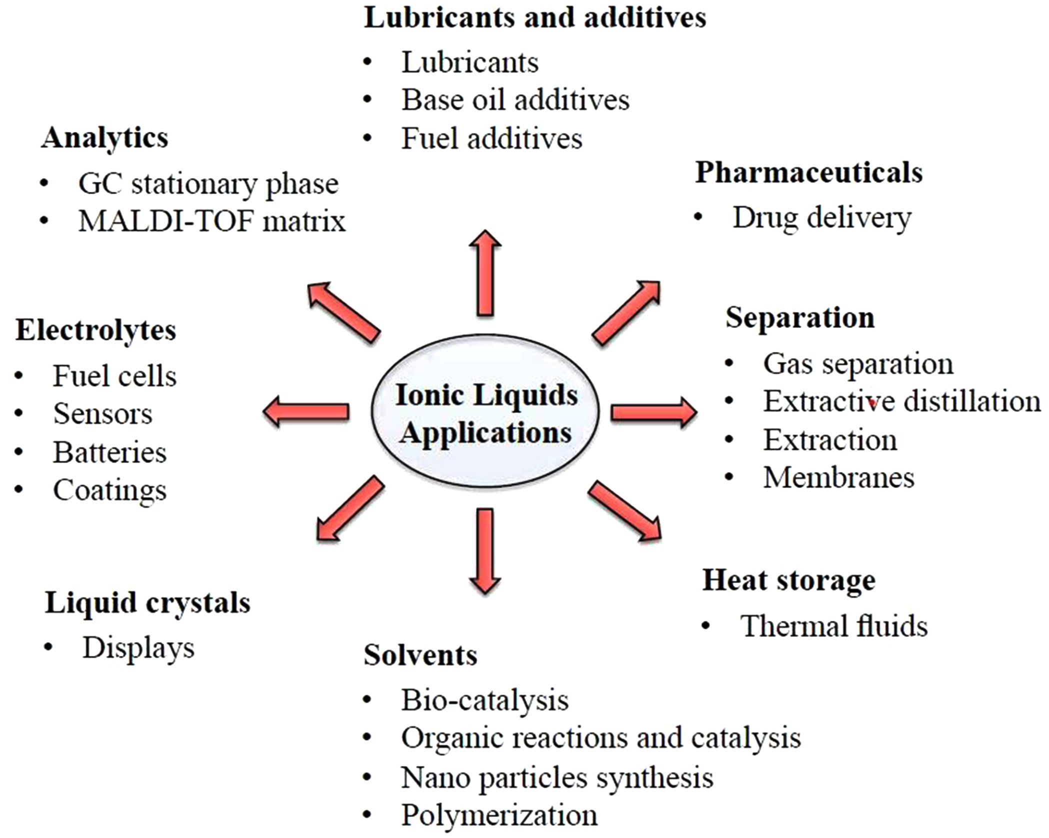

Fig. (2). Engineering applications of ILs in the industry [6].

ILs are widely used in industries such as separation, processing, electrochemistry, nanotechnology, biotechnology, mechanical engineering, solvents, catalysts, and substrates for the production of a variety of materials and their choice and activities depending on the nature of the anions and cations [7 - 11].

1.2. Mechanism of Corrosion Inhibition Using ILs

The establishment of a protective film as a result of the ionic liquids' adsorption on the metal substrate shields the metals (alloys) from the corrosive environment and prevents corrosion. Ionic liquids based on imidazoles have been used the most frequently of all the ionic liquids that are currently available. To develop and design functional materials for a variety of applications, including supercapacitors, fuel cells, corrosion protection, and catalysis, it is crucial to understand the interfacial phenomena. This can be done by studying the

CHAPTER 7

Self-Assembled Nanostructures within Ionic Liquids-based Media

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Abstract: Ionic liquids (ILs) have shown immense potential as suitable alternatives to environmentally damaging volatile organic solvents (VOS). These unique materials possess very unusual physicochemical properties, such as low melting point, high boiling point, excellent thermal and chemical stability, large electrochemical window, very low volatility and high conductivity. One of the most important features associated with ILs is that their physicochemical properties, like viscosity, density, hydrophobicity, solubility, polarity, *etc*., can be effectively tuned for desired applications just by tuning the structures of cations and/or anions. Further, these designer solvents show dual behavior, *i.e*., electrolytes and solvents. In the last two decades, these unique materials have shown tremendous application potential in various interdisciplinary research areas, such as synthesis, catalysis, separation, extraction, nanoscience, and pharmaceutics, among many others. Further, the formation of surfactant self-assembled nanostructures (micelles and microemulsions (ME)) within ionic liquid-based systems of immense importance due to the vast utility of these nanostructures well as ILs in various fields of science and technology. These micro-heterogeneous systems can be effectively used as greener alternatives to those environmentally harmful volatile organic solvents which are largely used for academic and industrial research purposes.

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The IL-based self-assembled nanostructures show major advantages due to their affinity to solubilize many chemical and biochemical solutes (both hydrophilic as well as hydrophobic), thereby expanding their potential application as solubilizing media, media for synthesis, catalysis and biocatalysis, separation and extraction, drug delivery vehicles, and media for biochemical stability (*e.g*., protein and enzyme stability). This book chapter will highlight the formation and utility of various types of self-assembled nanostructures formed by surfactants, polymers, *etc*., within Ils-based media.

Keywords: Aggregation, Critical micelle concentration, Ionic liquid, Micelles, Microemulsions, Surfactant.

1. INTRODUCTION

New approaches for more environmentally friendly chemical processes are needed, driven by rising regulatory pressure as well as growing awareness of safe, sustainable, and environmentally friendly chemistry. Given that organic solvents typically make up more than 50% of the materials used to produce drugs or other fine chemicals, their use is one of the key factors influencing the risk and environmental impact of a chemical process. In the past few decades, the idea of replacing hazardous VOS used in various industrial processes has sparked considerable interest. Researchers across the world are searching for different types of green solvent systems that can replace or reduce the use of these VOS and hence reduce the environmental impact. So far, a variety of green solvent systems, such as deep eutectic solvents, ILs and supercritical fluids, have shown tremendous potential as replacements for those VOS. Over the last two decades, ILs have emerged as one of such environmentally benign solvents attracting researchers from interdisciplinary research areas including green chemistry. ILs are electrolytes consisting of cationic and anionic parts and are liquids (below 100 °C) [1 - 5]. The cations of ILs are generally bulky and asymmetric organic cations, *e.g*., N-alkyl pyrrolidinium, imidazolium, alkylammonium, alkylpiperidinium, alkylpyridinium, alkylsulfonium, phosphonium ions, *etc*. The anions can be organic or any inorganic anions, such as halides (F^-, Cl^-, Br^-, I^-), $[BF_4]^-$ $[PF_6]^-$, acetate (CH_3COO^-), $[CF_3SO_3]^-$, $[(CF_3SO_2)_2N]^-$, *etc* (Fig. **1**). To adjust the physicochemical characteristics of the ionic liquids, one can take advantage of the symmetry of the cation, which offers a different structural organization. Ionic liquid geometry on metallic surfaces is significantly impacted by the cations symmetry. In addition to symmetry, it is discovered that the length of the alkyl group attached to the cation plays a critical role in determining the ion structure close to the solid surface. The shorter alkyl group cations (less than four carbon atoms) have ring planes that are either parallel to the surface or perpendicular to it in the first adsorbed layer. In general, asymmetric cations with intermediate-length alkyl groups have higher levels of structure at the interface than their asymmetric counterparts. These unique materials (behaving as both electrolytes and solvents) have shown unusual physicochemical properties high boiling point, low melting point, negligible volatility, high thermal stability, greater chemical stability, larger electrochemical window, *etc*. The more important aspect is that their properties can be effectively altered for specific applications just by modifying the structures of the ions (cations and/or anions). Hence these are often regarded as designer solvents; we can design numerous numbers of ILs just by changing cation-anion combinations.

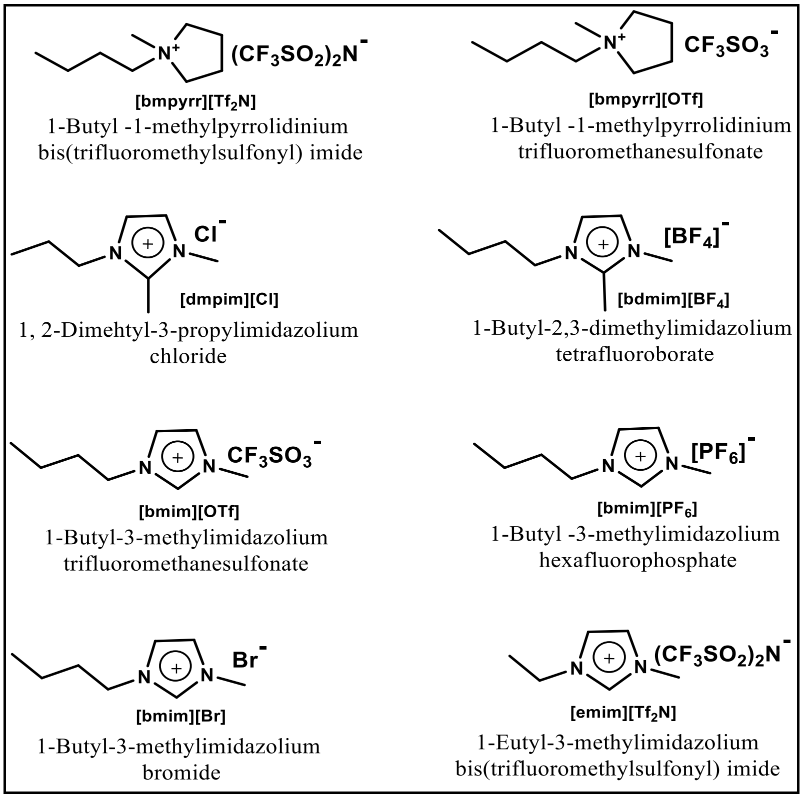

Fig. (1). Names and structures of some commonly used ILs.

Ionic liquid-based surfactants are ILs that hold hydrophobic “tails,” causing them to aggregate into colloidal particles in water, such as micelles and vesicles. Ionic liquid (IL)-based surfactants have proven to be excellent alternatives for a variety of industrial, biological, and environmental uses due to their exceptional properties, which include high surface/interfacial activity, low critical micelle concentration and better solubilization. These novel ionic materials have been used as solvents for a variety of chemical and biochemical reactions due to their distinctive properties, showing different reactivity and selectivity compared to conventional organic solvents. ILs have shown immense application potential in

CHAPTER 8

Ionic Liquids: Eco-Friendly Substitutes for Surface and Interface Applications

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Abstract: The use of ionic liquids as solvents or catalysts has a notable impact. As a result, there is increasing interest in developing applications for them in a variety of synthetic reactions. The purpose of this chapter was not to be entirely complete, but rather to summarise some of the most recent advances in the use of ionic liquids in organic synthesis as a catalyst. The present chapter focuses on a general introduction to green and sustainable chemistry, as well as how it relates to homogeneous catalysis. A brief history of ILs as homogeneous catalysts is presented, various along with preparative routes and applications. Starting with their application, ILs have been used as catalysts in a variety of organic reactions. This focuses on the synthesis, significance, and applications of ILs. Although they are not particularly useful as solvents, they are now being used as catalysts in organic chemistry catalytic reactions.

Keywords: Catalysis, Ionic liquids, Organic synthesis, Phase Transfer Catalyst (PTC).

1. INTRODUCTION

PTC is particularly effective for catalysing reactions between anions (including some neutral molecules such as H_2O_2 and transition metal complexes such as $RhCl_3$) and organic substrates. Catalysts for phase transfer speed up reactions between two immiscible reactants. Many anions (in the form of their salts, such as NaCN) and neutral chemicals are soluble in water but not in organic solvents, whereas organic reactants are often insoluble in water. The catalyst functions as a shuttling agent, removing the anion or neutral chemical from the aqueous or solid phase and transporting it into the organic reaction phase (or interfacial area), where it may easily react with the organic reactant already present in the organic phase [1]. The PTC concept is based on the capacity of specific "phase-transfer

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agents" (PT catalysts) to aid the movement of one reagent from one phase into another (immiscible) phase containing the other reagent. Thus, the reaction is made feasible by combining chemicals that were previously in distinct stages. However, for good PT catalytic activity, the transferred species must be in an active state and regenerate during the organic process [2].

Finding novel catalysts capable of performing high-activity, high-selectivity condensation processes for the production of pharmaceuticals and fine chemicals is a constant issue. Room-temperature ionic liquids (ILs) have attracted a lot of attention in recent years as environmentally benign or "green" alternatives to traditional molecular solvents. They are distinguished from molecular solvents by their distinct ionic nature as well as their "structure and organization", which might result in specialized effects [3].

Ionic liquids (ILs) are increasingly being employed as solvents and catalysts in "green" chemistry because of their unique features. The simplest basic definition of an IL, a salt that melts below 100 degrees Celsius, spans a wide range of compounds. While ILs are often regarded as a novel and interesting class of molecules, numerous substances utilized in chemistry during the twentieth century, notably certain ammonium, phosphonium, and sulfonium salts, may be classified as ionic liquids [4]. Ionic liquids have lately come to be recognized as potentially ecologically friendly alternative chemical process solvents. Ionic species, unlike most organic solvents, do not contribute to VOC emissions due to their extremely low vapor pressures. It has been established that they may be used in both reactions and separations. Although many other types of reactions have been studied in ionic liquids, there are no instances of nucleophilic substitution reactions in the literature. Since onic liquids are made up of bulky organic cations, they appear to be well suited for the sorts of reactions that PTC is successful for. There is even a chance that the solvent will function as a catalyst, activating the anion for reaction. Although the ionic liquid cation may not be as good a catalyst as other PTCs, its high concentration as a solvent should overcome this restriction, resulting in a high reaction rate [5]. Ionic liquids can also be used as catalysts for phase transitions. The introduction of phase transfer catalysts has resulted in 10^7 rate increases for the Halex reaction. Several phase transfer catalysts have been described, including tetra-alkylammonium, phosphonium, guanidinium, carbophosphazenium, and bis(phosphoranylidene) ammonium salts. As a result, the development of highly efficient and thermally stable ionic liquids remains critical. Phosphonium salts have a substantially higher thermal stability than ammonium salts. Furthermore, unlike the imidazolium cation, the phosphonium cation lacks acidic protons, allowing carbene production to be avoided [6]. ILs may be manufactured in a variety of methods, with the majority including heterocyclic organic compounds, such as imidazole, pyrrolidine, piperidine, pyridine, and so on. Furthermore, imidazolium-based ILs act as a phase transfer catalyst (PTC) in SN^2 processes (including fluorination). Unfortunately, the majority of these catalysts continue to be difficult to remove from the reaction mixture. If the product and IL are somewhat soluble in one other, the separation becomes much more complex, with just a few examples yielding good results. Catalytic activity, selectivity, and catalyst separation techniques are also critical for large-scale synthesis. As a result, the development of active and characteristic separable catalysts for SN^2 fluorination under moderate circumstances is highly desirable and a hot topic in green chemistry as well as contemporary chemical synthesis [7].

2. WHAT ARE PHASE TRANSFER CATALYSTS (PTC)?

A phase-transfer catalyst, or PTC, is a catalyst in chemistry that enables the migration of a reactant from one phase into another where the reaction happens. A subset of heterogeneous catalysis is phase-transfer catalysis. In the absence of a phase-transfer catalyst, ionic reactants are frequently soluble in an aqueous phase but insoluble in an organic phase. The catalyst acts as a detergent, allowing the salts to be dissolved into the organic phase. The inclusion of a phase-transfer catalyst accelerates the process, which is referred to as phase-transfer catalysis. Using a PTC method, one can accomplish quicker reactions, greater conversions or yields, produce fewer byproducts, reduce the requirement for expensive or hazardous solvents that dissolve all the reactants in one phase, eliminate the need for expensive raw materials, and/or limit waste concerns.

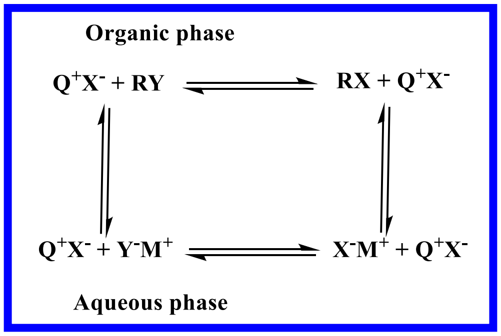

Fig. (1). Extraction mechanism of PTC [8, 9].

Fig. (**1**) depicts the PTC cycle when the PTC is partitioned between organic and aqueous phases.

The extraction mechanism of Starks for a nucleophilic substitution reaction implies that the quaternary salt must dissolve in the water phase to extract the

CHAPTER 9

Ionic Liquids in Wastewater Treatments

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Abstract: The scarcity of water has motivated diverse research efforts toward developing efficient techniques for the treatment of wastewater for its reuse. The applications of conventional wastewater treatment technologies, such as chemical precipitation, ion exchange, flotation, flocculation and coagulation, membrane filtration, *etc*., have been identified with diverse limitations. The commonest of them include high investment and operational costs, the formation of toxic by-products and sludge generation. Ionic liquids (ILs) have been used in numerous analytical and industrial extraction processes; however, their potential in the treatment of wastewater is yet to be fully exploited. This chapter, therefore, explores the applications of various ILs in wastewater treatment and proposes their versatility in the deployment of effective, selective, and rapid extraction processes for the removal of diverse water pollutants. However, the application of technologies based on the use of ILs possesses various challenges, which include a choice of an appropriate ionic liquid, high testing requirement for private applications, disposal, the regeneration process of ILs, scaling-up of the whole removal of pollutants, and technological applications.

Keywords: Adsorption, Green adsorbents, Ionic liquids, Pollution control, Wastewater treatment.

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1. INTRODUCTION

In recent times, the rise in population growth and the high rate of industrialization have presented severe adverse impacts on society, especially as the scarcity of water is becoming an ever-increasing challenge [1]. Nearly 2 billion of the global population is affected by water stress, and this situation is projected to exacerbate further with increasing urbanization. In addition, the resultant degradation and pollution of the ecosystem threaten the already decreasing water supply with the emergence of diseases as well as the concomitant huge economic costs, stimulation of migration and even sparking of freshwater. Although many regions still depend only on natural resources for fresh water supplies, the opportunities to generate potable water from wastewater sources remain potential resources yet to be explored. Currently, the benefits offered to human health, sustainability of the environment and economics are far less than the cost associated with the management of wastewater [2]. A good number of wastewater pollutants (dyes, radioactive, HMs, pharmaceutical compounds, organics, *etc.*) have been reported to be chemically unreactive and stable [3], and recent strategies exploited in wastewater treatment do not often result in the complete mineralization of these pollutants, which leads to bioaccumulation and possibilities of biotransformation into extremely harmful compounds [4]. The generation of harmful by-products is commonly reported in the use of some traditional strategies during the process of wastewater treatment (*e.g.*, ozonation) [5]. Consequently, there is lower in consumption of solvents a significant need to employ requires lower volume of sample used and tools that are more eco-friendly, lower consumption of solvents, rapid, lower volume of sample used, and cost-effective, to realize exceptional high enrichment factors for the removal of contaminants from wastewater.

Room temperature ionic liquids (RTILs) have demonstrated promising environmentally friendly and cost-effective applicability in wastewater treatment [6, 7]. Sequel to their low toxicity, versatility, thermal stability, lower corrosivity, low vapor pressure, handling, safe preparation, and mineral acids, the RTILs solvent group has attracted much attention in the extraction of inorganic, organometallic, and organic compounds dissolved in the wastewater. As a result of their extremely low vapor pressure, the risks associated with inhalation of ILs are minimal compared to the case associated with handling conventional volatile organic solvents. With additional progress in comprehending the charge transfer mechanism and dissolved ions solvation state, ILs can be realistically formulated with state properties that are well-defined and engineered for the efficient removal of contaminants from wastewater. Hence, ILs for task-specific applications can be produced, presenting an almost inexhaustible structural possibility in contrast to narrow structural alternatives obtainable with orthodox organic solvents. Such dynamic properties make ILs designer solvents adaptable for wastewater treatment [8].

Recently, Poly(ionic liquids) (PILs) have been used in place of traditional ionic liquids. Poly(ionic liquids), also known as polymerized ionic liquids, are a subcategory of polyelectrolytes that contain an ionic liquid (IL) species in each monomer repeating unit. These units are connected by a polymeric backbone to create a macromolecular architecture [9]. The poly(ionic liquids, or PILs) have several benefits, such as high thermal conductivity, high chemical and thermal stability, high heat capacity, high storage capacity, high wastewater treatment capability, more adsorption sites, and high density. However, they come with a few drawbacks, such as cost and polymerization issues, such as the need for pricy and toxic solvents. The PILs may also suffer solubility problem, which greatly lies in the length of hydrocarbon moiety.

Several studies, therefore, have investigated the ability of ILs to effectively eliminate various pollutants, such as heavy metals, surfactants, pesticides, dyes, and pharmaceuticals from industrial, agricultural, and municipal sources [4, 8, 10 - 13]. These studies have successfully reported the treatment of wastewater. This chapter provides recent insight into reported ILs that have been utilized in wastewater treatment. The effectiveness, possible mechanisms of reaction, and limitations of these reported ILs, such as Tricaprylylmethylammonium methylthiosalicylate, Tricaprylmethylammonium thiocyanate, Tricaprylylmethylammonium thiosalicylate, Methyltrioctylammonium chloride, 1-ethyl-3-methylimidazolium bis(fluorosulfonyl) imide, *etc.* are comprehensively discussed. Furthermore, future perspectives of ILs in wastewater treatment are presented.

2. WATER POLLUTION AND WASTEWATER TREATMENT TECHNIQUES

2.1. Water Pollution

There are several ways of defining water pollution. But in general, any addition of one or more substances that could negatively modify the quality of potable water results in water pollution [14, 15]. These substances are generally chemicals that could be harmful to humans, the environment, animals, and their habitats [16]. The pollution of water by these toxic chemical substances has emerged as a key concern and priority for researchers, environmentalists, and the whole world of industry. Water pollution could be classified under two broad categorizations, based on sources, namely point and non-point [17, 18]. The point sources refer to single-source pollutants, (*e.g.*, industrial effluents discharged into the water),

CHAPTER 10

Ionic Liquids in Decontamination of Toxic Metals Impurities

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Abstract: The wide use of noxious and non-degradable metals due to industrialization has become a major factor in rising health concerns. Diseases associated may involve cardiovascular disorders, brain damage, cancer, *etc*., and this leads to the development of certain methods for the sole purpose of cleaning water, soil, air, *etc*., to remove metals categorized as toxic ones. Ionic liquids with remarkable thermal stability, association ability, exhibiting low vapour emission, *etc*., are considered eco-friendly for the decontamination of toxic metal impurities. These ionic liquids involve certain modes of interactions like an electrostatic, dipole, van der Waals, *etc*., for the effective separation and extraction of metals. Also, the property of reusability associated with ionic liquids makes them be used on a wide scale.

Keywords: Alkylation, Decontamination, Ionic liquids, Metal impurities.

1. INTRODUCTION

Metals having a relatively high density in the range of 3.5-7g cm^{-3} are categorized in the class of heavy metals, and the toxicity and non-biodegradability of these have been seen to affect the environment severely [1,2].

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These metals exhibit properties to induce harmful chronic diseases like cancer. Numerous sources of such heavy metals are responsible for their increasing concentrations in nearby surroundings like geogenic industries, agriculture, pharmaceuticals, *etc*. [3,4]. In general, these have been seen to be present in trace quantities. Further, their presence in water sources is attributed to certain states like colloidal and solubilised states. Chromium (Cr), Iron (Fe), Manganese (Mn), Nickel (Ni), Copper (Cu), Cobalt (Co), *etc*., which are considered to be heavy metals, have been seen playing a prime role in applications like chlorophyll synthesis, electroplating, industries, *etc*. [5, 6]. There comes a critical point when their concentrations exceed a certain limit (as permitted safe for the environment), making them turn into heavy metals. The high solubility of such heavy metals is responsible for their accumulation in living organisms, involving aquatic organisms that lead to a phenomenon called 'bioaccumulation' [5]. Due to high toxicity, these heavy metals induce various acute disorders that are a detriment to the reproductive system and nervous systems. In addition, these incite the uncontrollable growth of cells and can also lead to cancer [7]. Various initiatives have been proposed to bring heavy metals to their permissible levels for a safer environment [8].

Numerous works have been carried out to inspect a cost-effective, efficient and biodegradable method for decontaminating such metal impurities. Some certain specifications are required to be followed while selecting the extracting solvent for heavy metals, *i.e*., it should possess excellent thermal stability with a good range of solubility and high polarity with incombustible properties [9]. Certain works have been reported involving volatile compounds as an extracting agent for toxic metals but resulted in health issues [10]. So, it became a major concern to search for alternatives that overcome this drawback associated with volatile organic compounds [11]. Green chemistry considers the approach of utilising non-toxic solvents, and as per the principles of green chemistry, ionic liquids have the potential to act as an excellent extracting solvent for the decontamination of toxic metals.

2. IONIC LIQUIDS

Ionic liquids (IL) are organic salts comprising substantial inorganic groups in the form of cations like ammonium, sulfonium, imidazolium, *etc*., being coordinated to anions of inorganic or organic origin (halides, tetrafluoroborate, triflate, *etc*.) [12]. Ionic liquids have been seen to exist in numerous forms, like salts in fused form and ionic and molten forms. Additionally, they have been seen to apprehend hydrophilic as well as hydrophobic behaviour depending upon the nature of anions and cations associated.

Various characteristics and features associated with ionic liquids are high dissolution along with thermal stability, non-inflammability, and non-volatile nature which make them a green approach to the elimination of toxic metal impurities illustrated in Fig. (**1**). Further, in this regard, it has been observed that ionic liquids involve a range of interactions with molecules like van der Waals, ionic, dipole, hydrogen bonding, *etc*. Such kinds of interactions can be modified by altering anionic and cationic moieties associated with these ionic liquids, and this further helps in the speculation of ionic liquids with specific characteristics of physicochemical origin like solubility, polarity, viscosity, *etc*., required for various separation processes [13]. This is attributed to the wide use of ionic liquids as an extracting or separating solvent in diversified fields like pharmaceuticals, electrochemical batteries, lubricants and preservation of tissues, *etc*. Simultaneously it has been reported that the high conductivity of ions brought an increment in rates of certain reactions like polymerization, *etc*. [14]. The most considerable feature that makes ionic liquids a predominant approach in the industrial field these days is their reusable nature.

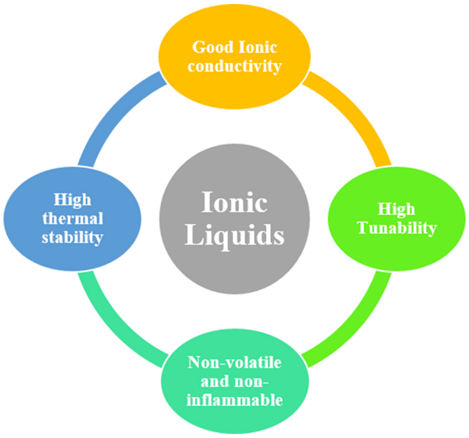

Fig. (1). Characteristic features of Ionic Liquids.

3. STRUCTURE OF IONIC LIQUIDS

Ionic liquids comprise a variety of anions and cations where cations are large organic compounds accompanied by smaller anionic compounds of inorganic origin. The difference in sizes of respective anions and cations leads to the formation of weak ionic bonds, and these compounds seem to exist in liquid form below a certain temperature of 100°C. It has been evidenced that the structural aspects of ionic liquids have been observed to be similar to salts, but strong interactions there between respective anions and cations provide them with the crystalline structure which melts at the comparatively higher range of

CHAPTER 11

Ionic Liquids In Corrosion Protection

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Abstract: The utilization of metals and alloys has been on the increase due to rapid technological advancement and industrialization. Nevertheless, these widely used metallic materials are subject to degradation due to exposure to the environment. Several methods have been applied by scientists to address the problem of corrosion. One of the most successful methods to control metallic degradation remains the application of chemical inhibitors. Ionic liquids are renowned organic compounds with high adsorption abilities and exceptional properties which have drawn attention to their use as corrosion inhibitors. In contemporary years, different types of ionic liquids have been reported to showcase their effectiveness in protecting metallic surfaces from corrosive ions. This chapter discusses recent advancements in the utilization of high-performance ionic liquids as eco-friendly inhibitors in different corrosive environments, as documented in literature over the last three years.

Keywords: Corrosion protection, Green corrosion inhibitors, Ionic liquids, Langmuir adsorption isotherm, Mixed-type inhibitors.

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1. INTRODUCTION

Corrosion is an irreversible and undesirable phenomenon that occurs when metals and alloys come in contact with the surroundings, such as alkalis, salt, acid, and air. Common identified forms of corrosion include uniform, filiform, galvanic, pitting, fretting, intergranular, stress corrosion cracking and so on. The degradation of materials as a result of environmental exposure leads to several undesirable consequences, such as economic losses, material wastage, environmental pollution, fatal accidents and death [1, 2]. Economic losses due to material degradation are aggravated during industrial operations often performed in numerous metal-based industries. The assessment conducted by the National Association of Corrosion Engineers (NACE) estimates that the losses due to corrosion could be as high as US $2.5 trillion (3.5% of the global GDP) annually [3]. In a study conducted by Goni and Mazumder [4], the cost of corrosion was classified as shown in Fig. (**1**). Studies have revealed that the cost of corrosion can be reasonably lessened using reliable control strategies. Over the years, industry-based experts and academic researchers have worked tirelessly to develop novel and reliable methods to mitigate the corrosion process. These methods include but are not limited to alloying and dealloying, protective coatings, galvanization, cathodic protection and inhibitor application [5 - 7].

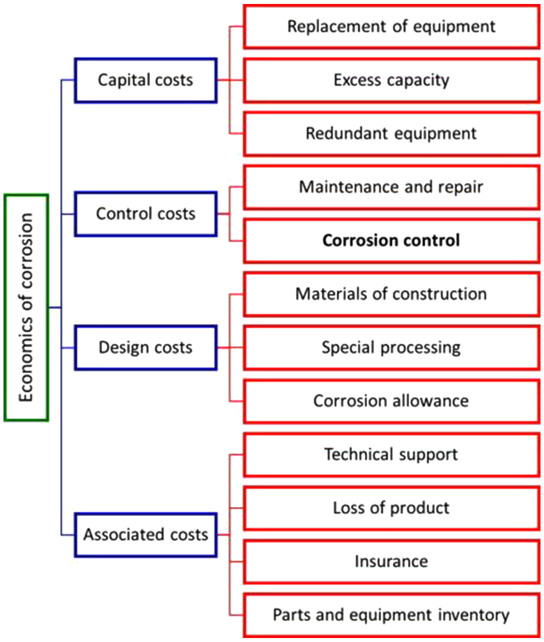

Fig. (1). Classification of corrosion cost [4].

The development of inhibitors to control corrosion has become widespread because of their low cost, high performance and reliability [8 - 10]. Generally, chemical inhibitors (additives) used to control corrosion could be classified as organic or inorganic inhibitors. Inorganic inhibitors such as nitrites, phosphates and chromates are very popular in industrial use but are environmentally harmful. Hence, legislations have been established to restrict their use in favour of environmental safety. As a result, current trends in the field of inhibitor formulators are focused on the designing and development of eco-friendly organic chemical inhibitors.

In the past few decades, the search for eco-friendly and sustainable inhibitors of corrosion has propelled research interest in the direction of natural and synthetic substances that are “green”. Among these are substances obtained from natural sources such as plant parts and synthetic organic substances prepared following the principles of green chemistry. Literature outcomes posit that these synthetic and natural inhibiting substances become effective by adhering to the metal/electrolyte boundary [8, 11, 12]. After adsorption, inhibiting substances form a protective cover that restrains the contact of the metal substrate with the corrosive surrounding. The formed inhibitive layer also acts as a shield by disallowing the percolation or diffusion of corrosive species to the metal surface. Generally, inhibiting substances often adhere to the metal substrate *via* physical and/or chemical adsorption. Physical adhesion occurs by the electrostatic attraction between the charged metal specimen under consideration and the charged inhibitor molecule, while chemical adsorption, otherwise known as dative bonding, occurs through charge sharing or transfer. Moreover, different adsorption isotherms, such as Langmuir, Freundlich and Temkin isotherm models, are widely used to delineate the adhesion process of these additives on the metallic substrates.

2. UTILIZATION OF IONIC LIQUIDS AS HIGHLY EFFECTIVE AND ECO-FRIENDLY CORROSION INHIBITORS

Ionic liquids (ILs) are popularly known by several names, including molten salts, ionic fluids, fused salts, ionic melts and so on. They are organic salts with melting point temperatures below 100 °C. They are known to comprise a pair of ions; an anion of an inorganic or organic origin and a cation of an organic origin. Common cations used in the designing of ILs are imidazolium, pyridinium, phosphonium, and ammonium, while commonly reported anions include halides, acetates, sulfonates, phosphates and so on [13 - 16].

In recent years, ILs have become one of the most promising and sustainable inhibiting materials as compared to their counterparts, owing to their numerous

CHAPTER 12

Tribological Properties and Applications of Ionic Liquids

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Abstract: The main focal point of this chapter is to divulge the tribological properties and best application of ionic liquids (ILs). Specifically in the petroleum-based lubrication industry and energy transfiguration process, oil add-ons have been reporting the best applicability of ionic liquids (ILs). The much-influenced counterparts of ILs have been extremely reported to design efficient lubricating oil with the use of ILs. The specific type of ILs which are halogenated and non-halogenated synthesized was ethyl ammonium nitra is also revealing themselves as the best corrosion inhibitors for studying the tribology on different metal surfaces. In addition, the performance of ILs as oil-additive has been giving good results in terms of tribological performance. The main feature which has to mold the performance of the tribological property, is the modification of anion in ILs. This all enhances the effectiveness of lubricant and oil-additive properties. The main reason behind the corrosion and formation of thin films over metal surfaces is also discussed in detail using different types of ILs and metal surfaces.

Keywords: Corrosion, Halogenated and nonhalogenated ILs, Ionic liquids (ILs), Lubricant, Tribological properties.

1. INTRODUCTION

The best-defined way for Ionic liquids (ILs) is that they are those compounds that are comprised of ions having a melting point of less than 100°C [1, 2]. The first ever IL synthesized was ethyl ammonium nitrate reported in 1914 by Paul Walden 1914. At that time, he would never think of such importance of these liquids, and now they have become the most important research area in almost one century. Nowadays ILs have emerged as innovative fluids that have gained wide attention in almost the last two decades. From the sustainable or green chemistry principle, the most important point is the usage of that kind of substance or solvents, or in-

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termediate agents must be eco-friendly [3]. Some toxic or hazardous solvents generally make a harsh impact, particularly on the environment, from mainly chlorinated hydrocarbons by emissions and sweeping in underground and surface water. This factor leads to the opening of a new door for non-conventional solvents as another route to an eco-friendly environment [4]. So, the ILs have gained much importance and are generally called by multiple names, such as designer solvents, molten salts, ionic fluids, and neoteric solvents. Most of the ILs are made up of cationic (organic) and anionic (inorganic) parts, which remain in liquid form at room temperature. The polar nature and the hydrophilicity/hydrophobicity ratio of ILs can easily be adjusted by combining different kinds of cations and anions. So due to this specific quality, they can be designated as "Designer Solvents" and so can participate in several reactions [5 - 15]. Three researchers, Dupont, Souza, and Saurez have excelled in the use of ILs in the catalytic phase for different organometallic reactions [16]. Furthermore, the applications of ILs as a catalyst in the synthesis of metal nanoparticles have been predicted by Migowski and Dupont [17, 18]. As per the design of ILs, can be classified as follows:

a. Room-Temperature ILs (RTILs) [19 - 23],
b. Task-Specific ILs (TSILs) [24, 25],
c. Polyionic Liquids (PILs) [26, 27], and
d. Supported IL Membranes (SILMs) [28 - 31].

Technically, the task-specific ionic liquids are also called functionalized ionic liquids, as they seem to attempt the potential to "design" the capacity of ionic liquids, which makes them good working systems rather than reacting media. In the tribological studies of the ILs, where the uses mainly relate to lubricants, several papers were published [32 - 57]. As a lubricant, ILs especially have very low vapour pressure, high ion conductivity, and high thermal stability. Depending upon these characteristics, ILs can best exploit various applications of lubricants in extreme surroundings, vacuums, and at high temperatures [58 - 69]. Some uses of ILs have been summarised in Fig (**1**).

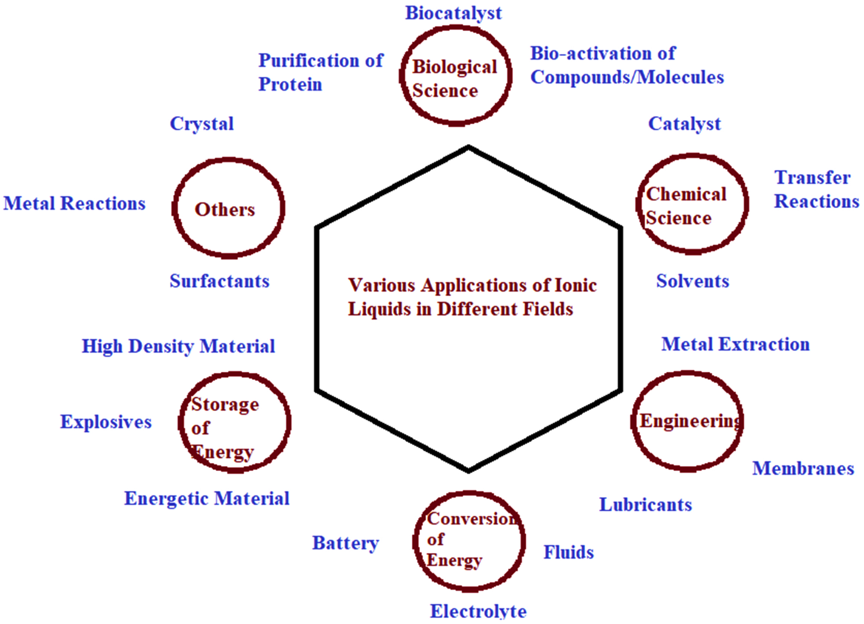

Fig. (1). Various applications of ILs in different fields.

2. PREPARATION OF IONIC LIQUIDS

After the successful preparation of ILs at room temperature, binary ILs were synthesized from the mixtures of aluminium (III) chloride and N-alkyl pyridinium or 1,3-dialkyl imidazolium chloride [70, 71]. The ILs are having two main divisions based on their compositions:

a. Simple Salts (comprises of single anion and cation), *e.g.*, $[EtNH_3][NO_3]$and
b. Binary Ionic Liquids (salts where equilibrium is involved), *e.g.*, Mixtures of aluminium (III) chloride and 1,3-dialkyl imidazolium chlorides.

The general synthesis of ILs can be especially described in two steps [72]:

a. The Formation of the Expected Cation:

$NR_3 + R'X \rightarrow [R'R_3N]^+ X^-$

Here, the expected cation can be synthesized *via* two routes, (i) Protonation of the amine by an acid, (ii) Quaternization reactions of amine with a haloalkane and allowing the mixture to heat.

CHAPTER 13

Ionic Liquid in Phase Transfer Catalysis

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Abstract: Ionic liquids (ILs) are environmentally friendly solvents and catalysts that are made up of ions that melt at temperatures below 100 degrees Celsius. Due to their favorable features, they were used in a broad range of reactions. A phase-transfer catalyst (PTC) is a type of heterogeneous catalysis that involves chemical reactions that occur when a reactant migrates from one phase to another where a reaction can proceed. High reaction specificity and transformations can be made easier with PTC reactions. PTC has been used in oxidations, alkylation, nucleophilic replacements, polymerizations, reductions, and other processes. In recent years, scientists have become more interested in employing ILs instead of traditional PTCs in biphasic reactions. Their cation architecture and chain length changes have been shown to have a substantial impact on their performance as PTCs. This chapter aims to discuss the role of ILs as phase transfer catalysis in organic synthesis.

Keywords: Biphasic, Catalysts, Designer solvents, Ionic liquids, Organic synthesis, Phase transfer.

1. INTRODUCTION

The expansion of catalytic asymmetric carbon-carbon bond developing reactions is considered a difficult attribute of organic synthesis [1]. As a result, developing environmentally friendly organic chemistry catalysts and solvents is critical. Several molecular catalysts have been designed so far, out of which phase transfer catalysts (PTC) bearing various advantages like mild reaction environments, security, and easy operation have been extensively recognized as the best reagents in the industrial sector. A phase-transfer catalysis is a practical approach for producing a wide range of non-chiral and chiral chemicals. The phase-transfer catalyst, usually quaternary ammonium salt or crown ether, works as a carrier for

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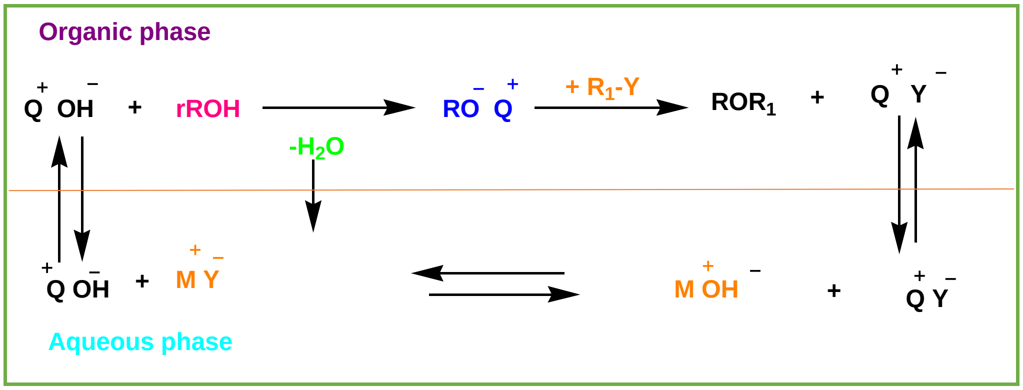
the reactant anion among the polar and non-polar phases that contain the salt and organic reactants, respectively. Various efforts have been made to achieve asymmetric conjugate incorporation of malonates into chalcones *via* chiral catalysts. Out of various principles of green chemistry, the most important is the consumption of auxiliary materials like solvents as well as separation moiety, which should be created preventable and if utilized, should be harmless [2]. The poisonous and menacing characteristics of numerous solvents, predominantly chlorinated hydrocarbons, are responsible for causing several critical environmental apprehensions like atmospheric emissions as well as an impurity of H_2O effluents.

It is acknowledged that retaining the utilization of non-conventional solvents as substitutes for biologically unfavorable conventional solvents can lessen surplus solvent fabrication and therefore decrease the harmful effect on surroundings [3]. The maximum predominant of these modern solvent systems consist of H_2O, supercritical liquids, ionic liquids, *etc*., out of which ionic liquids have appeared as a favorable substitute [4]. Ionic liquids are materials, which comprise of only ions bearing a melting point lower than 100°C. Presently, a chief effort is proceeding in the industry as well as academia to form eco-friendly technologies to replace traditional ones. Ionic liquids are known as ecologically friendly replacements for volatile organic solvents owing to their low vapor pressure as well as their capability to work as catalysts. Besides, ionic liquids hold various other striking characteristics like extraordinary conductivity and high stability towards heat and chemicals. Ionic liquids are also called neoteric solvents, designer solvents, and ionic fluids, besides molten salts. An ionic liquid mainly consists of organic cations as well as inorganic anions. Their polarity, as well as hydrophilicity/hydrophobicity, can be changed through an appropriate assortment of cations as well as anions. Due to this unique characteristic, ionic liquids are also known as designer solvents. Moreover, ionic liquids are utilized in various reactions as solvents [5 - 10]. Dupont and his co-workers comprehensively appraised the solicitation of ionic liquids as a catalytic phase in numerous organometallic reactions [11].

Migowski and Dupont have explored catalytic implementations of metal nanoparticles in an ionic liquid environment. Ionic liquids are normally regarded as a new and awesome category of compounds, and in the present century, many compounds in chemistry can be called ionic liquids, which includes a large number of ammonium, sulphonium as well phosphonium salts [12, 13]. Ionic liquids, which are made up of bulky organic cations, appear to be best suited to the categories of reactions to which phase transfer catalyst (PTC) is effective. It has been proven that ILs can be used as PTCs in oxidation, electrophilic as well as alkylation reactions. The alkylation of diethyl malonate employing a solid-liquid

PTC condition has also been demonstrated [14]. Some important examples of ionic liquids used in phase transfer catalysis include imidazolium-based ionic liquids, pyridinium salts, as well as ammonium salts which are generally utilized as phase transfer catalysts in the presence of KF or CsF for non-enantioselective fluorination reactions [15 - 17]. Furthermore, Tetra alkyl ammonium ILs have been employed as phase transfer catalysts to support the passage of anionic moieties from one liquid phase to another liquid phase where a particular reaction occurs. The phase transfer catalysis procedure for an etherification reaction of water-immiscible alcohol employing a tetra alkyl ammonium (quat) catalyst, Q^+, to deliver the base throughout the phase borderline is illustrated in Scheme **1**. The extraction procedure accomplishes the catalytic cycle by exchanging OH^- for Y^- in the quat, culminating in the Q^+OH^- ion pair, which is prepared to be retrieved entirely into the organic phase and then interact with R^-Y [18].



Scheme (1). Schematic representation of phase-transfer catalysis esterification.

Therefore, the opportunity for phase transfer catalytic reactions has developed intensely in the past decade. Thus, has been employed in a large number of reactions, as mentioned above. In this regard, the chapter mainly emphasizes how diverse types of ILs are utilized as catalysts in various organic syntheses.

2. IONIC LIQUIDS AS CATALYSTS

The growing percentage of studies published in this sector, which has climbed by over 400 publications each year for the last five years Fig. (**1**), indicates that ILs in catalysis exploration are regarded as a promising topic of catalysis research [19, 20].

CHAPTER 14

Ionic Liquid-Based Electrolyte for Application in Photoelectrochemical cells: A Future Insight

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Abstract: In this chapter, a series of asymmetric and symmetric ionic liquids (ILs) and IL-modified materials were considered for their versatile application as electrolytes and redox mediators in Photoelectrochemical (PEC) cells. Dye-sensitized solar cells (DSSCs) are PEC cells and third-generation photovoltaic (PV) cells that convert solar PV energy into electrical energy. They have piqued the interest of researchers worldwide due to their simple cell fabrication methods under ambient conditions, as well as their enormous commercialization potential due to their low cost; additionally, the benefits of colorfulness, probable plasticity and high power conversion efficiency (PCE) under indoor irradiation make PEC cells appealing. To attain a high PCE of cells, an organic solvent has to be included with the formulation of the redox mediator in the electrolyte. However, organic solvents are prone to evaporation and leakage. Consequently, PEC cells' durability is reduced because of the chemical and thermal instability of the redox mediator in the electrolyte.

The purpose of including ionic liquids into the redox mediator in the electrolyte was to solve the above-mentioned issue and to allow the PEC cells to act as sustainable energy cells. The chapter describes the integration of ionic liquids into the redox mediator in the electrolyte formulation and evaluates the impact of ionic liquids on the PCE of the cell in various electrolyte conditions.

Keywords: Dye-sensitized solar cells, Electrolyte, Ionic liquid, Open circuit photovoltage, Organic solvent, Photoelectrochemical cells, Power conversion efficiency (PCE), Redox mediator, Solar cell, Short-circuit photocurrent density.

1. INTRODUCTION

The first French scientist, Alexandre-Edmond Becquerel [1], invented the theory of the photoelectric effect in 1839, and since then, researchers and technologists

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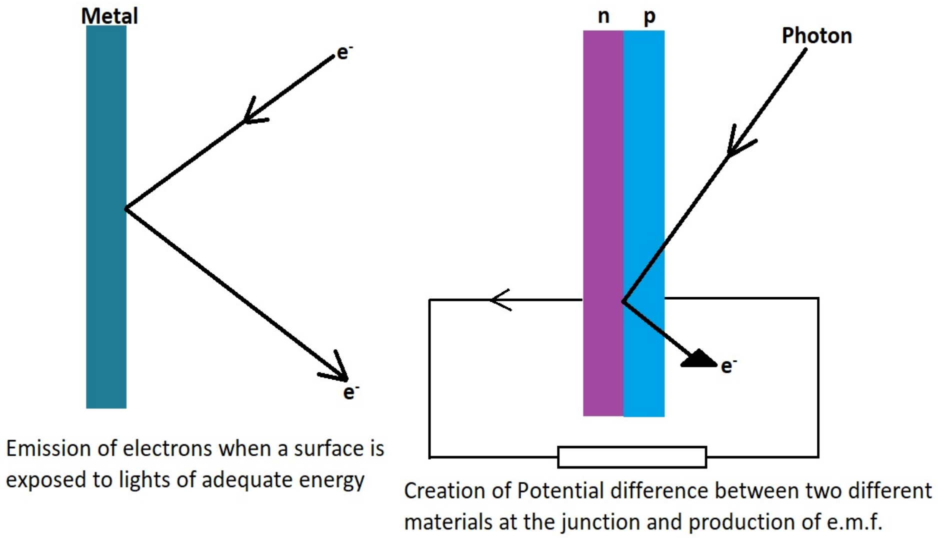
have been drawn to the concept of converting photons into electrical energy or chemical fuels. Their primary goal is to convert the easily accessible energy from solar light into a beneficial and strategically influential asset, namely electrical energy, or to use it to generate fuels, such as hydrogen. A photon, also known as a light quantum, is a tiny packet of energy emitted by electromagnetic radiation, the energy of which is determined by the wavelength, frequency, or color of the light. The concept arose as a result of Albert Einstein's photoelectric effect postulates in 1905, which demonstrated the existence of discrete energy packets *via* photon transmission. The energy of visible light is sufficient to excite electrons from lower energy states to higher energy states, where they have more freedom to move within the material, but the excited electrons quickly relax back to their lower energy state. Photovoltaic (PV) takes advantage of the fact that solar light striking the surface of semiconductors can generate electron-hole pairs. This effect can create an electrical potential difference through the interface between the two different types of materials at a PN junction, as shown in Fig. (**1**).



Emission of electrons when a surface is exposed to lights of adequate energy

Creation of Potential difference between two different materials at the junction and production of e.m.f.

Fig. (1). Shows the photoelectric effect and the photovoltaic effect in a PV device.

Until now, photovoltaic cell science has been reliant on devices made of inorganic semiconductor materials, typically doped with crystalline or amorphous silicon, and benefiting from the knowledge and material accessibility provided by the semiconductor manufacturing industry. We have now seen more applications of photovoltaic cells made from semiconductor III/V group compounds for high power conversion efficiency (PCE) aerospace components and cells made from $CuInS_2$/selenide compositions materials for thin-film technology and low-cost terrestrial cells. But the supremacy of the area by inorganic PV cells faces many more challenges in the forthcoming years because the fabrication is energy-intensive, extreme-temperature, high cost, and high vacuum required. Progressively, organic-based solar cells are relatively inexpensive to fabricate, can be employed on flexible films, and can be designed or decorated to suit decorative applications. It is now even likely to switch entirely from the conventional inorganic-based cells, by substituting the segment in contact with the semiconductor with an ionic liquid-based electrolyte, thus stated as a PCE device. Well-known active research groups have been founded around the world that are currently working in photovoltaic cells, including in Europe, Japan, Korea, China, India, and Australia. The best-recorded cell efficiency of inorganic & organic solar cells [2] is depicted in Fig. (**2**).

2. HISTORICAL BACKGROUND OF PEC CELLS

In 1839, Becquerel discovered the first photovoltaic effect while experimenting with irradiation on a silver chloride-coated film immersed in an ionic liquid electrolytic solution and combined with a counter electrode to form an electric field. The device created by Becquerel is now known as a photoelectrochemical (PEC) cell [3]. After 40 years of research, researchers who discovered selenium's photoconductivity created the first solid-state solar cells. In 1877, William Grylls Adams and Richard Day investigated the electrical performance of selenium material, particularly its photon sensitivity [4, 5]. Vogel's first sensitized to the dye on silver halide emulsions in 1883, which extended the photosensitivity to higher wavelengths [6]. Moser developed the concept of photosensitization using erythrosine dye on silver halide electrodes to form PEC cells in 1887 [7]. Namba and Hishiki 1964 successfully used the same dyes for processes recognized in photosensitization history [8]. Nelson proposed in 1965 that the dye be adsorbed on the semiconductor photoanode in a tightly packed monolayer for high PCE [9]. Tributsch and Gerischer [10] demonstrated that electron transfer was the dominant method for both photographic and photoelectrochemical sensitization methods. In 1970, Hauffe published a series of papers on the sensitization of ZnO using PEC cell processes [11].

CHAPTER 15

Ionic Liquids for the Surface Modification of Polymers and Medical Devices

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Abstract: Ionic liquids (ILs) attracted global attention owing to their superior functional properties, making them useful for many applications. Low volatility, wide liquidity range, better miscibility with organic and inorganic materials, better electrochemical stability, and negligible toxicity earn them a green solvent status. ILs are suitable alternatives to many volatile and flammable organic solvents that chokes our environment. The presence of asymmetric organic/inorganic ions gave them unique characteristics similar to biomolecules. They could interact with the cell membranes and penetrate the lipid bilayers to destroy bacterial cell membranes. They can self-assemble at the interfaces of polar and non-polar media. The nature of substrates, concentration, counter-ions, and polarity of the medium influence the extent and stability of the self-assembly. The self-assembled monolayers (SAMs) and multilayers of ILs impart intriguing properties to the surfaces. Surface modification with ILs is preferred over other methods considering their eco-friendly nature. The IL-mediated surface modification would help to improve the surface properties of polymers, metals, nanoparticles, ceramics, stones, medical devices, *etc*. The modified surfaces would have improved wettability, biocompatibility, and antimicrobial or antiviral properties. IL-modified surfaces could anchor enzymes to generate sustainable biocatalysts for a wide range of reactions. The inherent affinity of ILs towards gases like CO_2 makes them suitable for generating gas-adsorbing surfaces. Assembled charge carriers in ILs are helpful in energy storage and electrochemical sensing applications. Poly(ionic liquids) (PILs) are also receiving much attention recently since they display synergistic properties of polymers and ILs to be employed in divergent fields. PILs are also suitable for the surface modification of different substrates. This chapter reviews the surface modification of materials using ILs and PILs and their biomedical applications.

Keywords: Antimicrobial, Ionic liquids, Polymeric medical devices, Surface modification, Wettability.

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1. INTRODUCTION

Ionic liquids (ILs) are composed of asymmetric organic/inorganic ions and have melting points lower than 100 °C. They have been known by the scientific community for at least a century. The history of ILs began with the synthesis of ethyl ammonium nitrate by Paul Walden in 1914 [1]. Even though this curious compound has a lower boiling point (~12 °C), no further studies were reported, and it slipped into oblivion. After nearly 40 years of dormancy, the ILs emerged in the limelight through the works of Hurley and Wier. They employed low-melting mixtures containing alkyl pyridinium halides and metal halides for electroplating applications [2]. Thirty years that followed witnessed the usage of different kinds of quaternary salts containing halometallate anions, particularly for electroplating applications.

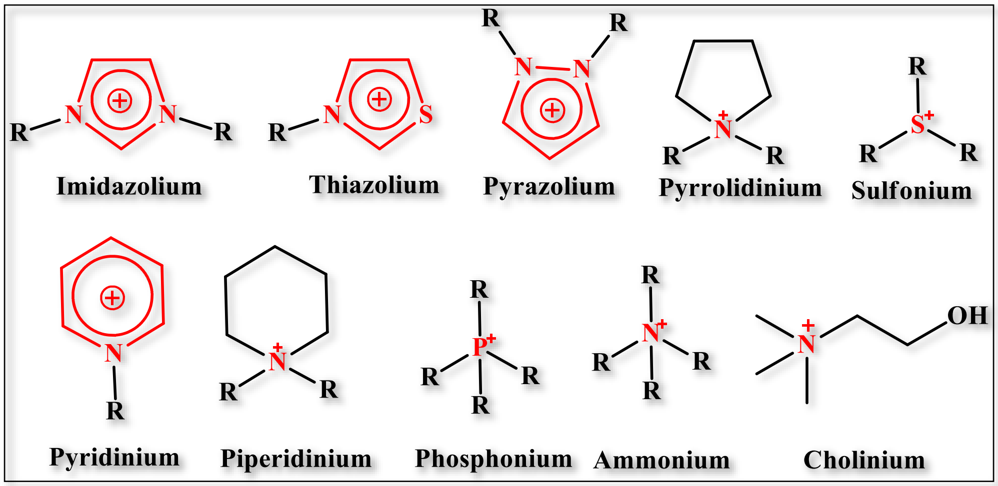

Fig. (1). Major cations explored for IL synthesis.

In the early 1980s, Wilke's group introduced dialkyl imidazolium cations to the ILs arena, and since then, it has been considered one of the most efficient cations for producing low-temperature ILs [3]. IL research gained momentum in the 1990s, and many cations and anions have been explored for a wide range of applications Fig.**(1)** displays the chemical structures of the major cations investigated to prepare ILs. Halides (Cl^-, Br^- and I^-) were the counteranions in most of the initially reported ILs. Later other anions like hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), acetate, hydrogen sulphate, methyl sulphate, dimethyl phosphate, bis (trifluoromethyl sulfonyl) imide (TFSI), and dicyanamide were also explored. ILs found to have multiple applications, namely, as designer solvents, reaction media, phase transfer agents, lubricants, electrolytes for energy storage systems, *etc* [4]. Hydrophobic side chains in the ionic appendages of ILs enable them to self-assemble in response to the external environment. Self-assembly of ILs with side chains bearing four or more carbon atoms forms supramolecular structures such as liquid crystalline phases, micelles, gels, *etc*. The molecular assortment of ILs at the interfaces would be an appropriate strategy to modify the surface characteristics of materials.

The biomedical applications of ILs were reported in the late 1990s [5]. Initially, they were used for stabilizing and solubilizing enzymes and other biomolecules. Within a decade, ILs discovered to have antimicrobial activity and were found suitable for anticancer drug development. Many drug ingredients were converted into ILs to overcome their poor solubility and thermal stability and are known as Active Pharmaceutical Ingredient-ionic liquids (API-ILs). Charged centres and lipophilic side chains enable them to be better antimicrobial agents. They were found to be useful in biosensing, protein stabilization, and also in developing controlled drug delivery systems and formulation excipients for insoluble drugs.

The term, ‘surface’, is generally used to represent an interface between a condensed phase and gas/air. The surface properties are quite intriguing compared to that of the bulk. Healthy surfaces are inevitable for the longevity of any materials or device as the surface is the first entry point to the bulk. Corrosion, pathogenic attack, colony formation, tissue attachment, *etc*., all start at the surface. Surface modification implies the engineering of surfaces to enable them to withstand any external threats. Many physical, chemical and biological approaches are reported for the surface modification of materials and devices. This chapter discusses the use of ILs in modifying the surfaces of polymers and other materials used in medical applications.

2. SURFACES AND INTERFACES

The terms surface and interface are used synonymously these days. The interface is defined as the boundary between two physically distinct phases [6]. So, a variety of interfaces could be seen, like solid-solid interface, solid-liquid interface, gas-liquid interface, liquid-liquid interface, and so on. Interfaces are the boundaries where molecules belonging to two or more distinct phases meet and interact. The molecular gradient around these phase boundaries is the driving force for many processes, such as diffusion, dissolution, adsorption, absorption, *etc*. The rate, direction, and completion of these processes are governed by the nature of the phases that form the interfaces. The physicochemical properties of the interfaces are quite different from that of individual phases in bulk and may have synergistic variations also. When one of the phases forming the interface is

CHAPTER 16

Sensing Applications of Ionic Liquids

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Abstract: The Molten salts having melting points near to or less than room temperature is termed ionic liquids (ILs). A full IL unit generally comprises two oppositely charged ions with a remarkable size difference, *i.e.*, bulky cation and comparatively small anion. The ILs are also labelled as future solvents due to their design flexibility and greener approach. Owing to their large number of favourable characteristics, such as less toxicity, good solvating capacity, high conductivity, non-volatility, super sensitivity, selectivity and electrochemical stability, these ILs have provided a broader range of applicability in the field of sensing. ILs are proven to be of good use in the area of sensors as well as biosensors, *i.e.*, optical sensing, thermometric sensing, electrochemical sensing and fluorescent sensing, *etc*. The ILs can be tailored by changing cations and anions as per the demand of the applications. In the present chapter, various aspects of ILs, including the use of these ILs in various sensing applications, have been explored and summed up to present an organized view for the researcher community as well as general readers.

Keywords: Biosensors, Electrochemical sensors, Gas sensors, Ionic liquids, Optical sensors, Sensors.

1. INTRODUCTION

Chemical Industry is revolutionizing these days and is shifting towards green chemistry. Due to the volatile nature of organic solvents, they lead to the production of hazardous organic waste. In this dilemma, ionic liquids are proving themselves as an eminent choice due to their greener approach because of negligible vapour pressure. Ionic Liquids are characterized as salts made up of ions, which remain in a liquid state below 100ºC. However, that's a random definition, which is generally given to differentiate them from molten salts [1]. The differentiating line between the two seems more strong when we look into the broad applicability of IL's in various fields. The size difference in the cation, *i.e.*,

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bulkier and an anion which is comparatively much smaller, does not permit the lattice packing of ions and leads to disorganization of ions, which results in the fact that these IL's are liquid at room temperature. Walden [1a], in 1914, reported the first IL, *i.e*., ethyl ammonium nitrate, whose melting point is 12 ºC, and the journey continued. The IL's exceptional properties, like trivial vapour pressure, broad potential window, good solubility and conductance properties, are highly stable to thermal changes [1b]. The mix of several types of cations with suitable anions can change these characteristics [2, 3]. The miscibility behaviour of ILs with other solvents can also be tailored as per requirement by changing their ions. Their low flammability, high thermal resistance, high ionic conductance and non-volatility have made these ionic liquids be used in various fields, such as chemical sciences, biochemistry and material sciences [4 - 7]. Moreover, some ionic liquid limitations, such as moisture sensitivity and acidity/basicity, may limit their usage in specific applications. Ionic liquids' toxicity, degradation, and ecotoxicity have also lately been investigated [8]. Therefore, it is necessary to investigate the consequences on people's health, the environment, the economy, and society to achieve long-term development in ionic liquid usage for various applications (Fig. **1**). ILs are more environmentally friendly than conventional organic solvents because they provide a number of benefits. ILs have the ability to dissolve compounds that are inorganic, organic, or organometallic. High solubility gases are desirable solvent supplies for catalytic hydrogenations, carbonylations, hydroformylations, and aerobic oxidations. Examples of such gases are O2, benzene, nitrous oxide, ethylene, ethane, and carbon monoxide. IL's are especially well suited as a reaction medium for electrochemical (and also chemically driven) polymerization methods that result in conducting polymers because of their wide electrochemical window. The majority of ILs are volatile. They may be employed in high vacuum environments thanks to this feature, which also makes them easy to contain, use, and transfer. This crucial characteristic lowers long-term solvent vapour exposure. ILs are recyclable. With the ILs, the recovery and recycling of catalysts and reduction of waste production and the loss of valuable catalysts are also feasible. Due to their non-flammability, high ionic conductivity, and electrochemical and thermal stability, ILs are excellent electrolytes for application in electrochemical devices such batteries [9 - 12], capacitors [13 - 15], fuel cells [16], photovoltaics [17 - 22], actuators [23], and electrochemical sensors. Experts have recently developed an interest in ILs and want to employ them in a variety of analytical uses. When used as stationary phase or as additives in gas-liquid chromatography [24 - 27], liquid chromatography [26], and capillary electrophoresis [28], ILs can enhance the separation of complicated mixtures of polar and non-polar substances. Additionally, they are utilised in optical sensors [29, 30] and to enhance MALDI-(matrix-assisted MS's laser desorption ionisation mass spectrometry) analytical performance [31].

The employment of ILs in various applications is governed by their intrinsic features [32]. One definite feature that shows deviation from the general definition is that not all the ionic liquids are in liquid form below the defined temperature for them, *i.e*., 100 ºC; some of these ILs have a low value of glass transition temperature and thus possess slow crystallization kinetics. Out of the entire range of ILs that have the same ions (cations and anions), some analogues having a lengthy chain of carbon atoms but are in a solid state are also labelled as ILs [33, 34].

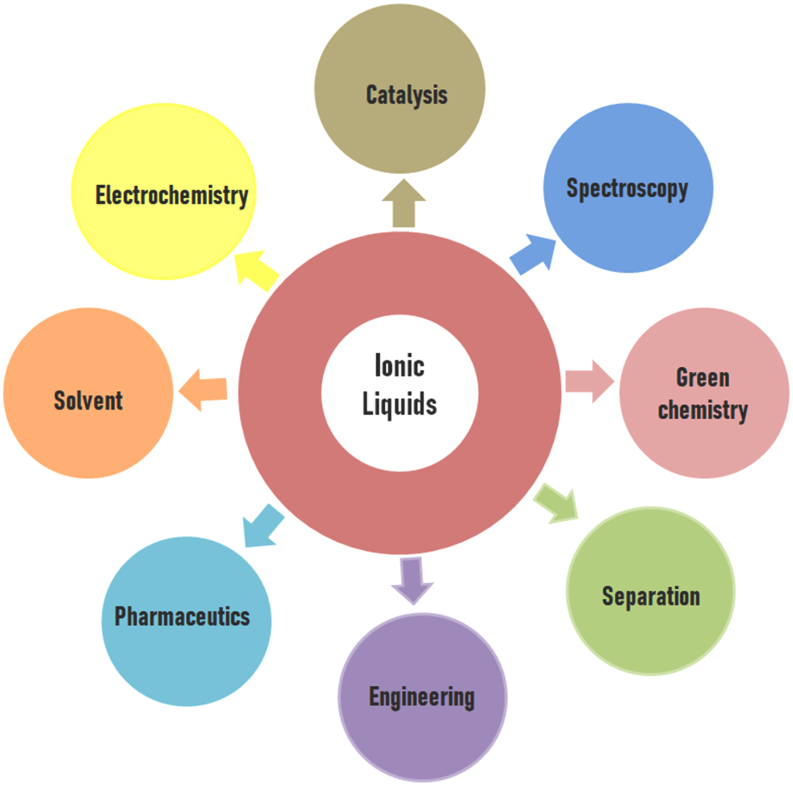

Fig. (1). Schematic representation of the applicability of IL's in various fields.

In this chapter, we will be exploring the various sensing activities of these ILs.

2. APPLICATIONS OF ILS AS SENSORS

A sensor is a device that measures physical quantities and transforms the same into an output signal, which can be identified and measured by an observer or the device [35]. A sensor gets some input signal from the physical environment and

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