CRITICAL STUDY ON NOVEL IONIC LIQUIDS (ILS)

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Abstract

The term "green chemistry" or "sustainable technology" is often used to characterize the trend toward ecologically friendly chemical processes and products. Green chemistry encompasses all aspects of the chemical supply chain, including teaching, research, and commercial application. The world's climate is changing as a result of ever-increasing air pollution. The chemical industry's move toward clean technology, which places a greater emphasis on waste reduction at the source, will necessitate a high degree of innovation and new technologies. The concept of "green" solvents expresses the desire to reduce the environmental impact of solvent consumption in chemical synthesis. The world's climate is changing as a result of ever-increasing air pollution. The chemical industry's move toward clean technology, which places a greater emphasis on waste reduction at the source, will necessitate a high degree of innovation and new technologies.

The concept of "green" solvents expresses the desire to reduce the environmental impact of solvent consumption in chemical synthesis. The use of ionic liquids instead of traditional solvents would prevent the release of volatile organic compounds (VOCs), a major source of pollution. Ionic liquids can be made to be environmentally friendly, with significant benefits for long-term chemistry. This paper reflects critical study of Novel Ionic Liquids.

Keywords: *Technology, liquids, solvents, ionic, synthesis.*

1.1: INTRODUCTION

The term "green chemistry" or "sustainable technology" is often used to characterise the trend toward ecologically friendly chemical processes and products. Green chemistry encompasses all aspects of the chemical supply chain, including teaching, research, and commercial application. Green chemistry can be achieved through the employment of ecologically friendly technologies or processes, such as the usage of ionic liquids, which are both ancient and new.[1]

Chemistry is certainly crucial in our everyday lives. All because of chemistry: food and drink have been made safe to ingest; medications have permitted the creation and synthesis of novel remedies for illnesses and diseases; cosmetics have allowed us to beautify and admire our appearances. Hundreds of tonnes of hazardous waste are dumped into the air, water, and land every hour of every day in the chemical sector. Solvents are utilized in considerable amounts in the fine-chemical and pharmaceutical industries, in particular. As a result, solvents play a significant influence in a process's environmental performance, as well as safety and health concerns. The world's climate is changing as a result of ever-increasing air pollution. The chemical industry's move toward clean technology, which places a greater emphasis on waste reduction at the source, will necessitate a

high degree of innovation and new technologies. The concept of "green" solvents expresses the desire to reduce the environmental impact of solvent consumption in chemical synthesis. Four new directions in the direction of green solvents have recently been developed: (1) replacement of hazardous solvents with those that have better EHS (environmental, health, and safety) properties, such as increased biodegradability or lower ozone depletion potential;[2-4] (ii) use of "bio-solvents," i.e. solvents made from renewable resources, such as ethanol made from sugar-containing feeds, starchy feed materials, or lignocellulose materials.[5] (this substitution of petrochemically fabricated solvents avoids the use of fossil resources and CO_2 emissions to the environment); (iii) substitution of organic solvents with environmentally friendly supercritical fluids (e.g., the use of supercritical CO_2 in polymer processing[6-9] avoids the use of chlorofluorocarbons and thus reduces ozone depletion); (iv) substitution of organic solvents with environmentally friendly supercritical fluids (e.g., the use of (VOCs). The use of ionic liquids instead of traditional solvents would prevent the release of volatile organic compounds (VOCs), a major source of pollution. Ionic liquids can be made to be environmentally friendly, with significant benefits for long-term chemistry.

The ideal solvent will have a low vapor pressure, a high boiling point, and will not be poisonous. They should be able to dissolve a variety of organic, inorganic, and organometallic substances. It should be chemically and physically stable, recyclable, reusable, affordable, and simple to work with. Solvents that allow for more selective and faster transformations will also have a big impact.

1.2 BRIEF HISTORY OF IONIC LIQUIDS

In 1914, Walden published the first report on the production of molten salt at room temperature (i.e., ethylammonium nitrate salt).[10] He described ethylammonium nitrate's physicochemical characteristics., [EtNH$_3$]NO$_3$, The reaction of ethylamine with concentrated nitric acid produces a substance having a melting point of 8°C. At room temperature, this salt is liquid, though it normally contains a little amount of water (200-600 ppm).

At the Rice Institute in 1948, Hurley and Weir[11] created the first ionic liquid using chloroaluminate ions, such as ethyl pyridinium bromide/AICI, for use in electroplating aluminium. It was made by combining 1-ethylpyridinium bromide with aluminium chloride and warming it (AICI$_3$). Both fundamental and applied studies have been interested in the use of chloroaluminate ionic liquids as electrolytes. Swain et al. published a paper in 1967 describing the use of tetra-n-hexylammonium benzoate as a kinetic and electrochemical solvent.[12] With the resumption of progress in this area by the groups of Osteryoung et al.[13] and Hussey et al.[14] in the 1970s and 1980s, respectively, room temperature ionic liquids (RTILs) became more popular among the general public. They conducted substantial study on organic chloride-aluminum chloride room temperature ionic liquids, with Hussey writing the first substantial review on the subject.[15] The A1C1$_3$-based ionic liquids can be considered the first generation of ionic liquids.

In 1986, the first report on ionic liquids as a new reaction medium and catalyst for the Friedel-Crafts process was published.

[16]Chauvin et al. described the dimerization of propene by nickel complexes dissolved in acidic chloroaluminate melts[17] and Osteryoung et al. described the polymerization of ethylene using Ziegler—Natta catalysts for the first time in 1990.

Because they must be manufactured and handled in an inert gas atmosphere, the hygroscopic character of A1C1$_3$-based ionic liquids has slowed development in their usage in organic processes. As a result, the development of air and moisture stable ionic liquids, which are called the second generation of ionic liquids, piqued interest in their application in a variety of disciplines. Wilkes and Zaworotko reported the first air and moisture stable ionic liquids in 1992, using the 1-ethyl-3-methylimidazolium cation with tetrafluoroborate or hexafluorophosphate as anions. These ionic liquids, unlike chloroaluminate ionic liquids, could be manufactured and safely kept outside of an inert atmosphere. The physical and chemical properties of these ionic liquids are generally unaffected by moisture; however, prolonged contact to moisture can cause some alterations in their physical and chemical properties. This is due to the creation of HF as a result of the ionic liquid decomposing in the presence of water. Therefore, ionic liquids based on more hydrophobic anions such as_ trifluoromethanesulfonate (CF$_3$SO$_3$), bis- (trifluoromethanesulfonyl)imide [(CF$_3$SO$_2$)$_2$N] and tris-(trifluoromethanesulfonyl) methide [(CF$_3$SO$_2$)$_3$C] have been developed. Not just because of their minimal reactivity with water, but also because of their huge electrochemical windows, these ionic liquids have gotten a lot of interest. These ionic liquids may usually be well dried under vacuum at temperatures between 100 and 150°C, with water content below 1 ppm.

Aside from the pioneers in the field of ionic liquids, such as Osteryoung, Wilkes, Hussey, and Seddon, there have been several researchers, such as Rogers, Welton, Wasserscheid, MacFarlane, Ohno, Endres, Davis, Jr. Abbott, and others, who have had a significant impact in introducing ionic liquids in a variety of applications.

1.3 SYNTHESIS METHODS OF IONIC LIQUIDS

In general, there are two primary processes in the synthesis of ionic liquids. The necessary cation must first be created, which is commonly done by direct alkylation/quaternization of a nitrogen or phosphorus atom. The anion produced by the alkylation process can be swapped for a different one in the second stage via a metathesis reaction or a direct combination with Lewis acid, strong acid, or ion-exchange resin. Because of the weak interaction between anions and cations, pyridinium-based ILs have become something of a standard in the IL community. In comparison to other ammonium salts, it has a high thermal stability.

The quaternization reaction produces pyridinium salts with various anions, depending on the alkylating reagent (Step I). If the pyridinium salt with the necessary anion cannot be obtained, then Steps IIa and Ib (Figure 1) must be performed. There are two ways to replace the anion generated during the initial quaternization stage. The first is the direct treatment of pyridinium salts with Lewis acids, which results in the creation of the first generation of ionic liquids of the kind. [RR'py][MX$_{y+1}$] . Alternatively, it is possible to exchange anion with desired anion by addition of metal salt M+[A]$^-$ (with precipitation of M$^+$X$^-$), by displacement of anion by a strong acid H$^+$[A]$^-$ (with evaporation of HX) or by passing over ion-exchange resin.

CATIONS

Innovations in the field of ILs are being reported continuously in the form of novel cation and anion combinations. The cations are generally bulky, unsymmetrical ammonium or phosphonium salts, or heteroaromatics, with low symmetry, weak intermolecular interactions and lower charge

densities. Those described in the literature are based on tetraalkylammonium (**5**),[18]trialkkylsulphonium (**6**),[19]tetraalkylphosphonium (**7**),[20]1,3-dialkylimidazolium (**8**),[21] N-alkylpyridinium (**9**),[22]N,N-dialkylpyrazolium (**10**),[23] N-alkylthiazolium (**11**),[24] N,N-dialkyloxazonium (**12**),[25] N,N-dialkyltriazolium (**13**),[26]S-alkylthiolanium (**14**),[27] organic polycations such as (**15**)[28] and (**27**),[29]Warner's chiral cation (**16**),[30] highly fluorinated phosphonium (**17**),[31] cyclic hexaalkylguanidinium (**18**),[32]Wasserscheid's chiral cations (**19, 20** and **21**),[33]cholinium (**22**),[34]isoquinolinium (**23**)[35] dimeric imidazolium (**24**),[36]N,N-dialkylpyrrolidinium (**25**),[37] sulfonium (**26**)[38] and pyrrolidonium (**28**)[39](**Figure 2**).

Lithium salts, in addition to organic cations-based ionic liquids, are increasingly being produced, notably for secondary batteries and energy storage. They often have lower lattice energy and, as a result, lower melting points than their periodic table neighbours. For example, at temperatures below 0°C, a mixture of LiCl and $EtCl_2$ produces a liquid with a wide range of composition.[40]

ANIONS

The characteristics of IL are heavily influenced by anion chemistry. Polyatomic inorganic substances are the most often used IL anions. As a growing number of alternatives are identified, the introduction of different anions has become more common. The list of cations and anions will be expanded to an almost infinite number in the future. Ionic liquids with various combinations of cations and anions have been carefully engineered for various uses. Lists the various anions that have been documented in the literature.

1.4 PURITY OF IONIC LIQUIDS

The presence of contaminants resulting from their preparation can alter the physico-chemical properties of ionic liquids. When employing ILs as reaction media, especially for transition metal catalysis, the purity of the ILs is a crucial consideration. Although there are only a few reports on "distillable ionic liquid," in the majority of these procedures, the ILs were neither distilled nor recrystallized. In addition, purifying ILs via column chromatography is difficult. As a result, when the ILs have produced during the synthesis, purification can become a hassle. Halide anions, organic bases formed from unreacted starting material, and water are the most common contaminants in ILs. The level of unreacted alkyl imidazole (0.2 mol percent) in the ionic liquid was recently determined using a colorimetric technique. Impurities such as halides can sabotage transition metal catalysed processes. Washing ILs with water can remove halide impurities, as can titration with $AgBF_4$, which is, of course, rather expensive and can result in silver impurities in ILs. Alternatively, strategies for avoiding the usage of halide-containing starting materials have been proposed.

Gallo et al. investigated the effect of halide contaminants on catalytic Michael addition processes in great detail. They discovered that the amount of halides present in the ILs had a major effect on the system, reducing the transition metal catalyst's activity. Furthermore, even when the same synthetic technique is followed, the overall amount of halide contaminants in different IL batches varies. Klingshirn et al. got to the same result for a palladium-catalyzed copolymerization of styrene and carbon monoxide. This is because to the relatively weak contacts between the halide anion and the imidazolium cation, which causes the dissociation of the halide from a transition

metal complex to become thermodynamically disfavored in ILs, according to Daguenet and Dyson.

Color is the second significant purity issue. In their purest state, most ILs are colourless, but in actuality, they are more likely to be pale yellow to dark orange in hue. Because these (often trace) contaminants are not identifiable by NMR or IR spectroscopy, the source of this is still unknown. The colour is most likely due to degradation of the initial material. Colourless ILs can be obtained by (1) using freshly distilled starting material for the synthesis; (2) performing the alkylation step under a protective atmosphere at the lowest temperatures possible (i.e., avoiding overheating); and (3) cleaning the final IL product with activated charcoal stirring.

The amount of water contained in the ILs is the third factor concerning purity. This is a concern not just for performing reactions with water-sensitive chemicals, but the amount of water in an IL can drastically alter its physical properties. As a result, it is always a good idea to dry ILs overnight at a high temperature in a high vacuum with vigorous stirring before utilising them. Because of the high viscosities and the fact that water desorption occurs only at the liquid phase's surface, stirring is essential. In extreme circumstances, IR spectroscopy or, of course, standard Karl Fischer titration can be used to determine the amount of water present. In some circumstances, such as PF6-based salts, residues of water might cause the anion to decompose, resulting in the creation of HF. Organic solvents are normally cleansed by distillation before use, but due to their non-volatile nature, this process is ineffective for cleaning ionic liquids. For these reasons, the maximum feasible purity must be achieved during the synthesis process.

1.5 PHYSICO-CHEMICAL PROPERTIES OF ILS

Before incorporating a new solvent into an industrial application, a basic understanding of its chemical and physical properties must be established. Low viscosity to allow mixing and a big density differential in contrast to other process fluids to speed phase separation would be ideal physical features. The solvent would have a large capacity for the solute chemically. To encourage widespread usage of the solvent, it should be economical to manufacture, recyclable, and durable enough to withstand a variety of processing settings.

Melting point, boiling point, density, surface tension, and viscosity are all physical parameters that are relevant to the mechanics and engineering components of a process. For example, density, viscosity and surface tension will determine important parameters including rates of liquid-liquid phase separation, mass transfer, power requirements of mixing and pumping. Despite offering a bulk property description, some physical qualities like as refractive index are related to specific chemical properties. Structuredness, polarity, relative hydrogen bonding, and donating and accepting ability are all chemical qualities that are more directly tied to the molecular chemistry of their application. Due to intermolecular interactions, these parameters measure, these chemical properties are believed to play a major role in determining solubilities, partition constants, and reaction rates.

The choice of appropriate cations and anions can change the physico-chemical properties of ILs. As a result, their properties can be tailored to meet the needs of a certain process. The ILs have been dubbed "designer" solvents as a result of this.

As a result, it's critical to comprehend how ionic liquids' physico-chemical properties influence organic reactivity, as well as how these qualities are influenced by structural factors. This will be demonstrated using a few specific examples, which are as follows:

Melting point

The melting point of the IL is its most critical feature. The melting point of IL is below 100 degrees Celsius. The choice of anion has a significant impact on the melting point of a given cation. Halides have high melting points because they are coordinating and hydrophilic, whereas weakly coordinating and hydrophobic anions have low melting temperatures. A decrease in melting points is also caused by an increase in the size of the anion with the same charge.

The low melting points of ILs are due to both cations and anions. The melting points of ILs are influenced by cation size and symmetry. Symmetrically substituted cations are easy to crystallise, resulting in ionic solids with a high melting point. Low substitution symmetry can make crystallisation difficult, resulting in low melting points.

The melting point can be fine-tuned by varying the length of the alkyl chain in the cation. The melting point of pyridinium cations decreases as the alkyl chain lengthens, but only to a limit (rule of thumb for pyridinium cations: C8 offers the lowest melting points) (Table 3, entry 3). In addition, extending the alkyl chain raises the melting point once further. Furthermore, the melting temperatures of ILs are lowered due to a favourable charge distribution in the cation and weak intermolecular interactions such as weak hydrogen bonding. The melting points of ILs are affected by cation size, symmetry, charge distribution, and alkyl chain length, as shown by a comparison of melting points of different salts.

Viscosity

The viscosity of ionic liquids is an important feature. Ionic liquids have higher viscosities than traditional solvents, however the value varies greatly depending on chemical structure, content, temperature, and the presence of impurity solutes. At room temperature, viscosities range from 10 mPa-s to around 500 mPa-s. A high viscosity can slow down numerous organic reactions and slow down the migration of redox species. The necessity for low viscosity materials is driving current development towards new and more versatile IL. Van der Waals forces and hydrogen bonding determine the viscosity of ILs. In n- butylmethylimidazolium IL, when triflate anion was displaced with (n-$C_4F_9SO_3$) ion and from the trifluoroacetate ion to (n-C_3H_7COO) ions. Comparison of the viscosities of [BMIm] $CF_3;SO_3$ with [BMIm]($CF_3SO_2)_2N$, reveals a lower viscosity despite stronger van der Waals interactions for ILs with ($CF;SO_2)_2N^-$ ion**.** The total suppression of hydrogen bonding compensates for the anticipated rise in viscosity in this scenario. Electrostatic forces may also have a significant impact. Increased viscosity is caused by alkyl chain lengthening in the cation and fluorination in the cation/anion. This is owing to increased energy requirements for molecule mobility due to higher van der Waals interactions between cations. In addition, anions' ability to form hydrogen bonds has a significant impact on viscosity.

Density

Density is one of the basic and important physical properties of ILs. In general, IL is denser than water with values ranging from 1 to 1.6 g cm^{-3}.

The density of an ionic liquid is determined by the length and type of substituents in the cation, as well as the type of anion. The total density of ILs is influenced by the anion's molar mass, alkyl chain length 101, and bulkiness in the cation. The density of ionic liquid is also affected by temperature. The density of [BMIm] [BF$_4$] falls linearly as temperature rises from 293 to 313 K..

Vapor pressure and thermal stability

Ionic liquids have these special features. Their vapour pressure is quite low. From a process engineering standpoint, this is a significant benefit, as distillation of a reaction mixture becomes a more effective technique of product isolation. There is no azeotrope development between the solvent and the products, which is a well-known issue.

The strength of ionic liquids' heteroatom-carbon and heteroatom-hydrogen bonds, respectively, limits their thermal stability. Direct protonation of an amine or phosphane produces ionic liquids. Most ILs have high thermal stability; breakdown temperatures recorded in the literature are typically over 400°C, with minimal vapour pressure below that temperature.

Polarity

A liquid's polarity is an important characteristic. This is often recorded as the 'polarity' of the pure liquid for molecular solvents, and is often denoted by its dielectric constant. In fact, this scale is incapable of providing appropriate correlations with a wide range of experimental data and quantitative characterizations of 'solvent polarity.'

The effect of the solvent on solvent-dependent processes, such as the rate of chemical reactions, the absorption of light by solvatochromic dyes, and partition methods, was used to develop empirical polarity parameter scales.

ILs-solvatochromic probe interactions: Solvatochromic probes are generally simple to use, and if the interpretation is properly considered, they may be useful. In general, each probe is sensitive to a specific type of interaction (hydrogen bonding, dipolarity/polarizability, and so on); nevertheless, solvent polarity is determined by the total of all potential intermolecular interactions, thus different probes might provide different polarity scales..

Neutral probes: Nile red and aminophthalimides. Carmichael and Seddon[104] performed the first experiment with a solvatochromic dye, specifically Nile red (Fig. 3), on a series of 1-alkyl-3-methylimidazolium ILs. Nile red's visible absorption band has one of the biggest solvatochromic changes ever recorded. Changes in solvent dipolarity/polarizability are most likely sensitive to this probe, while it's unclear which factors influence the shift in its absorption maximum. The polarity of a number of 1-alkyl-3-methylimidazolium ILs is comparable to that of short-chain alcohols, according to the results.

The polarity data acquired with different neutral solvatochromic dyes reveals some variation. When two fluorescent neutral probes, 4-aminophthalimide (AP) 30a and N, N'-dimethyl-4-aminophthalimide (DAP) 30b (Fig. 3) were utilised with a series of ILs, a distinctive polarity trend was seen. 106 Pyridium salts are more polar than acetonitrile and less polar than methanol, according to these probes. Imidazolium salts are more polar than pyridinium salts.

$Et_{(30)}$ values: The most widely used empirical scale of polarity is the Et $_{(30)}$scale, where $E_{T (30)}$ (in keal mol^{-1}; 1 kcal = 4.184 kJ) = 28 592/λmax (in nm) and λmax is the wavelength maximum of

the lowest energy π-π* absorption band of the zwitterionic Reichardt's dye. Often a normalized scale of Et(30) polarity, E_N^T obtained by assigning water the value of 1.0 and tetramethylsilane zero, is used.The solvatochromic shift of this probe is greatly influenced by the solvent's hydrogen-bond donor capacity (Fig. 4), which stabilises the ground state more than the excited state. The Et (30) scale is thus primarily, but not exclusively, a measure of the solvent system's hydrogen-bonding acidity.

Solubility in water

The solvation properties of IL are influenced by its hydrophilic/hydrophobic activity. It is necessary to dissolve reactants, but it is also important for the solvent extraction recovery of products. In addition, the water concentration of ILs can impact response speeds and selectivity. The solubility of ILs in water is a crucial consideration for their industrial application. On the miscibility of pyridinium ILs with water, there is a wealth of information. The solubility of these ILs in water is determined by the anion's type, temperature, and the length of the pyridinium cation's alkyl chain. The ILs that are not water soluble have a tendency to absorb water from the air. Water molecules received from the air are predominantly present in the free state, according to IR studies.[89] It has been bonded via H-bonding with $[PF_6]$,- $[BF_4]$, $[SbF_6]$,-$[HSO_4]$,- $[ClO_4]$,- $[CF_3SO_3]$- and $[NTf_2]$- with a concentration of the dissolved water in the range 0.2-1.0 mol dm.$^{-3}$ Most of the water molecules should exist in symmetrical 1:2 type H-bonded complexes: anion...HOH...anion. The strength of H-bonding between anion and water increases in the order $[PF_6]$-< $[SbF_6]$- < $[BF_4]$- <$[NTf_2]$- < $[ClO_4]$- <$[NO_3]$- < $[CF_3CO_2]$-.

Surface tension

Surface tension is a characteristic that may be essential in multiphase processes. ILs are commonly utilised in transition metal catalysed processes that take place in a multiphase environment. The reactions take place at the interface between the IL and the organic phase above it. These reactions should be based on the catalyst's access to the surface and the material's transport across the interface, i.e. the speeds of these processes should be based on surface tension.The liquid/air surface tension of ILs is generally higher than that of conventional solvents [(3.3-5.7) x10^{-4} N cm^{-1}]. Surface tension varies with temperature and is influenced by the length of the alkyl chain.

Conductivity

When compared to traditional solvents/electrolyte systems, ILs have high ionic conductivities (up to 10 mS cm^{-1}). Some systems can achieve a conductivity of 0.1-1 cm-1 at higher temperatures, such as 200°C. Their conductivities are usually lower at room temperature than those of concentrated aqueous electrolytes. Ionic liquids are expected to have high conductivities because they are made entirely of ions. Any solution's conductivity is determined not only by the amount of charge carriers, but also by their mobility. Ionic liquids' large constituent ions diminish ion mobility, which results in poorer conductivities. Ion pair formation and/or ion aggregation also result in lower conductivity. Ionic liquids' conductivity is inversely proportional to their viscosity. As a result, higher viscosity ionic liquids have lesser conductivity. Temperature improves conductivity while decreasing viscosity.

Electrochemical window

The electrochemical window is a critical characteristic in the electro-deposition of metals and semiconductors utilising ionic liquids. The electrochemical window is the range of electrochemical potentials in which the electrolyte is not reduced or oxidised at an electrode. The electrochemical stability of solvents is determined by this number. The electrochemical window of water, which is only around 1.2 V, limits the electro-deposition of elements and compounds. Ionic liquids, on the other hand, have far bigger electrochemical windows. In general, the wide electrochemical windows of ionic liquids have opened the door to room-temperature electro-deposit metals and semiconductors that were previously only available from high-temperature molten salts.

1.6 SALIENT FEATURES OF ILS

Some of the salient features of ILs are as follows:

1. They have a low or non-existent vapour pressure and are not combustible.

2. They are extremely thermally stable.

3. They're a good way to solubilize gases like H2, CO, O_2, and CO_2, and ionic liquids and supercritical CO_2 are currently used in a lot of reactions.

4. Their ionic nature boosts reaction speeds significantly in a variety of processes, including microwave-assisted and ultrasound-assisted chemical synthesis.

5. Their capacity to dissolve a variety of inorganic, organic, organometallic, and polymeric substances.

6. Solvents that are highly polar but non-coordinated.

7. Most ionic liquids may be stored for an extended amount of time without breakdown.

8. They have superacidity, as well as Bronsted, Lewis, and Franklin acidity.

9. They are immiscible with a variety of organic solvents and provide a non-aqueous, polar two-phase system alternative. Ionic liquids that are hydrophobic can also be employed as immiscible polar phases with water.

10. Products could be easily isolated by vacuum distillation because to their non-volatile nature, leaving the IL clean enough for recycling after the reaction.

1.7 APPLICATIONS OF IONIC LIQUIDS

In current synthetic organic chemistry, tonic liquid is a broad term. Due to their distinctive features, as well as their tunability, ILs have recently sparked a lot of attention in organic synthesis. ILs are used in two ways: to replace organic solvents with ionic liquids because of their unique solvent qualities, and to replace liquid acid with ionic liquids because of their changeable acidity. Diel-Alder reactions, Heck reactions, and Morita— Baylis—Hillman reactions are examples of the former, while coupling reactions and Friedel-Crafts reactions are examples of the latter. ILs are commonly utilised as reaction media, reagents, or catalysts in organic synthesis, particularly in transition metal catalysed reactions. In most circumstances, ILs outperform standard organic solvents in terms of reaction rate, yield, and selectivity.

➢ **Task Specific Ionic Liquids [TSILS]**

Ionic liquids with a functional group covalently tethered to the cation or anion (or both) of the ILs are known as task-specific ionic liquids (TSILs). In organic processes, these ILs can be used as reagents or catalysts. Many attempts have recently been made to investigate functional ionic

liquids by adding extra functional groups to the cation and/or anion. Various forms of "task-specific ionic liquids" (TSILs) have recently been devised and manufactured for specialised tasks such as catalysis, organic synthesis, material separation, and the production of nanostructure materials and ion conductive materials, among others. Many of them, particularly the pyridinium cation, were focused on incorporating functionality into a branch appended to the cation.

TSILs are pyridinium salts that possess the following characteristics: i) ionic liquids in which a functional group is covalently tethered to the pyridinium salts' cation or anion (or both), acting as a reaction medium as well as a reagent or catalyst; (ii) A standard ionic liquid solution of a functionalized pyridinium salt that is not liquid at room temperature. Because the functionalized pyridinium salts become integral constituents of the total ionic liquid solution and can introduce a functional group into the liquid, it might potentially be classified as a TSIL.

➢ **Chiral Ionic Liquids [CILS]**

Chiral ionic liquids are the most complicated ionic liquid application. With simple molecular solvents, chirality is difficult to produce, but it is a problem with complicated liquids. There are only a few review publications that discuss chirality in ionic liquid cations and anions. [152] Furthermore, only a few review articles discussed the use of chiral ionic liquids in organic processes. When compared to typical solvent systems, a high molecular order may have a favourable influence on asymmetric induction in ILs. There is no real evidence that chirality in the solvent causes asymmetry in reactions.It is possible to lock the reactant in a certain conformation around the IL if the ionic liquid contains a free hydroxy group. The chiral catalyst, which is integrated into the solvent, would be the free hydroxy.

The anion in the first report is chiral ionic liquid lactate. This is still one of the few cases where an anion's chirality is induced.In chiral ILs, chiral pyridinium and imidazolium cations have also been employed as a cation .The alkyl-chain linked to nitrogen in pyridinium salts shows asymmetry (Menthyl group). Chiral pyridinium derivatives could be built to include pyridinium as a component of a larger ring system.

These new chiral solvents should play a vital role in enantioselective chemical synthesis and, hopefully, broaden the scope of chiral solvents due to their simplicity of synthesis and distinctive features. The majority of papers focus on the synthesis and characteristics of the novel chiral ILs, with only a handful addressing their use in organic processes.

➢ **Supported ionic liquids(SILs)**

Ionic liquid catalysis with heterogeneous support materials (SILC) is a concept that combines the benefits of ionic liquids with those of heterogeneous support materials. An eutectic mixture of palladium chloride and copper chloride was supported on a porous silica gel and explored for the partial oxidation of olefins in a very early example of supported ionic liquid catalysis (Wacker catalysis). The melting point of this supported molten salt (423K) was slightly greater than that of ionic liquids at ambient temperature. The promise of such supported ionic systems was recognised, paving the way for further research. At the same time, the related field of supported aqueous phase catalysis was researched, which contributed to the advancement of supported catalysis.

The first supported Lewis acidic ionic liquid solutions for catalysis were created and investigated.

A pre-formed ionic liquid, which was also the catalytically active species, was infused into a solid support material. These ionic liquids were mostly aluminium chloride derivatives, and they were mostly used to evaluate Friedel-Crafts processes.Although the majority of the research focused on the alkylation reaction, some work was done to assess the acylation of arene complexes.

When a large amount of an ionic liquid is immobilised on a porous solid support material, several layers of free ionic liquid on the carrier can operate as an inert reaction phase, allowing various homogeneous catalysts to dissolve. Despite the fact that such supported ionic liquid-phase (SILP) catalysts appear to be solids, the active species dispersed in the ionic liquid phase on the support retain the desirable characteristics of ionic liquid homogenous catalysts, such as high specificity and molecular entity dispersion. Figure 7 shows a schematic design of the SILP hydroformylation catalyst.

➢ **Biodegradability Of Ionic Liquids**

Since its discovery, ionic liquids' physicochemical properties have been extensively researched. Ionic liquids with various cation and anion modifications have offered desired qualities for a variety of technical applications.[159] However, designing an ionic liquid with the right qualities for a given application isn't enough; ionic liquids' overall life-cycle implications must be considered as well. Only lately have studies begun on the biodegradation of ionic liquids and their possible buildup in the environment.[160] Organic molecules can be degraded aerobically or anaerobically. Microorganisms need a source of nitrogen and other important nutrients to degrade an organic substrate into carbon dioxide and water in both processes. An aerobic treatment necessitates the presence of oxygen, whereas an anaerobic therapy necessitates the presence of an electron acceptor such as $Fe^{3+.3c}$.

➢ **Recycling Of Ionic Liquids**

Ionic liquids must be recovered after usage due to environmental concerns. Because ionic liquids are relatively expensive, recycling them is also required for economic reasons. According to a review by Olivier-Bourbigou and Magna, ILs have been successfully recycled in a variety of processes. Several strategies for recycling ionic liquids have been documented, with recovery efficiency ranging from low to excellent.

After repeated reactions, rates and yields must be maintained at a reasonable level for recyclability. Reactions with a transition metal catalyst immobilised in the ionic liquid of a biphasic reaction system, in particular, have been shown to be recyclable. The non-volatile nature of ionic liquids, as well as the solubility differences between ionic liquids, organic molecules, and water, are used to support recycling. Non-polar solvents can be used to extract products from ionic liquids, or distillation can be used to separate them. Water can be used to wash a water immiscible ionic liquid to extract a water soluble product or side product from the reaction mixture.

➢ **Benign ionic liquids**

Ionic liquid research has previously focused on imidazolium and pyridinium-based ionic liquids because they have good, tunable characteristics for a wide range of applications and are simple to make. Concerns about environmental hazards have prompted a shift in ionic liquid design to include additional eco-toxicology considerations. On the basis of the first toxicological and

ecotoxicological research, new anion possibilities have been proposed. Ionic liquids made up of these anions are non-toxic, biodegradable, and water-soluble. Combining these anions with non-toxic, biodegradable cations, such as butyryl choline, could yield novel ionic liquids with beneficial qualities. There is still a demand for weakly coordinating, hydrophobic anions that could replace routinely used fluorous anions like $[PF_6]$ and $[NTf_2]$, but no viable candidates have been identified to yet.

1.8 LITERATURE SURVEY

The use of ionic liquids (ILs) in organic syntheses has received a lot of interest in the recent two decades. Initially, they were used as solvents, and they were frequently used as catalysts as well. The use of ILs as cosolvents, additives, or catalysts in organic processes is becoming increasingly popular. The widespread use of ILs necessitated multiple studies of reactions in the presence of various ILs. However, there is no clear distinction between when IL is employed as a solvent and when it is just utilised as a catalyst. This review will highlight the usual IL-catalyzed reactions and summarise the examples of organic syntheses facilitated by a catalytic quantity of an IL[41]

Ionic liquids have undeniably become an important topic of research in modern chemistry. We've grown accustomed to seeing an increasing number of papers published in the area each year, but there's some evidence that this is beginning to level off at around 3500 papers each year. Several large reviews and books have been written about them, focusing on various applications and features of their behaviour. I'll show you how interest in ionic liquids grew and developed in this essay.[42]

Ionic liquids (ILs) have developed as a better-for-the-environment substitute for volatile organic solvents. It is possible to design ILs made up of cationic and anionic components to have a specific set of features. The phrase "designer solvents" has been used in this context to describe the potential of these environmentally friendly ILs in chemical processes. Because they are designer solvents, they may be tailored to the reaction circumstances, gaining the moniker "job specific ILs." Because these liquids may dissolve a variety of transition metal complexes, they've recently been used in a number of catalytic organic reactions to improve reaction speeds and selectivity. The purpose of this review is to look into the structural properties, production, and applications of ILs in catalytic organic transformations.[43]

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The combination of water, a green reaction medium, and ionic liquid, a green catalyst, has opened up new possibilities in organic transformation. The developed technology has proven to be a promising combination for producing benzothiazole-2(3H)-one in an environmentally friendly, simple, and efficient manner. This unique method can also be used to synthesise additional related

heterocycles for the development of a significant medication, such as a library. At room temperature, the reaction went off without a hitch.[45]

Ionic liquids have evolved as a better-for-the-environment substitute for volatile organic solvents. They're called "task specific ionic liquids" since they can be modified to suit the reaction circumstances because they're designer solvents. Though they were originally developed as solvents, they are currently being employed in a variety of sectors, including catalysis, electrochemistry, spectroscopy, and material science, to name a few. The goal of this review is to look into the uses of ionic liquids in catalysis as acid, base, and organocatalysts, as well as as soluble catalyst supports.[46]

Ionic liquids have been used in the development of a number of unique and environmentally friendly methodologies in recent years (ILs). IL has served as a catalyst, a solvent, and a catalytic support in various processes. In some circumstances, IL was shown to be more efficient than typical molecular solvents at catalysing processes. In addition, some pressing problems about the fundamental characteristics of ILs, such as toxicity and greener preparation techniques, must be answered. ILs are also discussed in terms of their industrial applications.

A new type of aliphatic quarternary ammonium based chiral ionic liquid was used to perform asymmetric reductive amination of carbonyl compounds. In the presence of sodium borohydride, the chiral ionic liquid S-(+)-2,3-dihydroxy-N,N,N-tributylpropanaminum bromide has been produced, described, and exploited for asymmetric reductive amination of carbonyl compounds. These preliminary findings are encouraging and support the use of a novel ionic liquid as both a medium and a reducing agent in the conversion of ketones to amines. However, a reductive amination process for other substituents must be devised.

Ionic liquids (ILs) have been increasingly popular in the field of green chemical synthesis in recent years due to their unique features. This article gives an overview of ionic liquids and focuses on three types of contemporary IL applications in organic synthesis: single-step chemical reactions in ILs, multistep reactions involving IL-phase synthesis, and multistep processes in which ILs were utilised as reaction media for organic syntheses. The importance of greener ILs will also be emphasised, including their ease of preparation via simple extraction, high yield isolation and purification, amazing reaction selectivity, and efficient reusability.

For the enrichment of aromatic chemicals such as nitrobenzene, 4-nitrophenol, phenol, and aniline from aqueous solutions, both hydrophibic [C8mim][PF_6] and [C_4mim]Cl/(K_2CO_3, K_2HPO_4 or K_3PO_4) aqueous biphasic systems (ABS) were used. The distribution ratio (D) of nitrobenzene and aniline increases with rising pH values of the aqueous phase from 2 to 8, but there is no discernible change for 4-nitrophenol and phenol in the [C8mim][PF6] enrichment system. And as the phase ratio changes from 1/5 to 1/30 (IL phase volume/aqueous phase volume), the D values of aromatic compounds drop. The distribution ratio of [C_4mim]Cl/(K_2CO_3, K_2HPO_4, or K_3PO_4) increases as the salt concentrations rise. Nitrobenzene > phenol > aniline > 4-nitrophenol is the distribution ratio order in [C_8mim][PF_6] and [C_4mim]Cl/kosmotropic salt ABS. These findings are likely to be promising in terms of removing aromatic chemicals from water, particularly for sample enrichment in analytical research.

The use of specific ionic liquids (ILs) as aprotic green solvents for lignin was investigated in this work. The lignin extracted from pine kraft pulp was used in the dissolution studies. In [hmim][CF$_3$SO$_3$], [mmim][MeSO$_4$], and [bmim][MeSO$_4$], up to 20% lignin may be dissolved. The order of lignin solubility for various anions in [bmim]+containing ionic liquids was [MeSO$_4$]>ClBr[PF$_6$], demonstrating that lignin solubility was primarily controlled by the type of the anions. Ionic liquids with large, noncoordinating anions [PF$_4$] and [PF$_6$] were shown to be ineffective as lignin solvents. In compared to 13C NMR data recorded using dimethyl sulfoxide (DMSO), 13C signals utilising ionic liquid as a solvent were displaced upfield by 0.1 to 1.9 ppm in 13C nuclear magnetic resonance (NMR) investigations of lignin and model compounds.

One of the most popular and researched classes of room temperature ionic liquids is 1,3-dialkyl imidazolium salts. Although the physical-chemical properties and/or outcomes of activities carried out in these liquids differ dramatically from those carried out in "traditional" dipolar organic solvents in some situations, they are nevertheless recognised as homogeneous solvents. The hypothesis that pure 1,3-dialkylimidazolium ionic liquids are better represented as hydrogen-bonded polymeric supramolecules of the kind [(DAI)x(X)x-n)] n+ [(DAI)x-n(X)x)] n-n is developed in this brief overview. This structural pattern is a general trend in the solid phase, and it is preserved to a large extent in the liquid and even gas phases. The disruption of the hydrogen bond network caused by the introduction of additional molecules and macromolecules can result in nano-structures with polar and non-polar regions where inclusion-type compounds can form.

1.9 CONCLUSION

The unique physico-chemical features of ILs could speed up the development of clean technology in organic synthesis, medicines, biocatalysis, and biotransformation, particularly in industrial catalytic processes. One of their significant advantages is the ability to tailor the properties of ILs such as hydrophobicity, viscosity, density, thermal stability, polarity, and solubility to the specific process, making them true "designer solvents." Their non-volatility provides major technical benefits for distilative product separation, as well as preventing uncontrolled evaporation and azeotrope formation between products and solvents. ILs are a new class of reaction media for transition metal catalysis that is unlike any other. In the vast majority of cases, catalyst-containing ILs may be easily recycled. They provide a medium in which a clean reaction can be carried out with minimal waste formation and excellent yields and selectivities. As a result, the use of ILs as transition metal catalysis solvents opens up a large arena for future research. ILs can be used as reagents or catalysts (task-specific ILs) and as media for immobilising catalyst or inducing chirality, in addition to being easy alternatives for organic solvents as reaction media for organic processes. It is important to note that reactions in ILs are not difficult to carry out and usually do not necessitate the use of specific equipment or procedures. In comparison to traditional solvents, the reactions are frequently faster and easier to carry out.In addition to the benefits indicated above, ILs have certain drawbacks, such as the fact that most of the time, separating the products from the ILs necessitates extraction with non-polar volatile organic solvents. Because of their high viscosity relative to typical solvents, stirring and homogeneity of the reaction medium is difficult,

resulting in sluggish dissolving of solid reactants and a reduction in reaction rate. Other disadvantages include their higher cost when compared to most regularly used organic solvents, and the fact that most ionic liquids are poisonous in nature, as evidenced by many toxicological data collections aiming at a wide range of organisms. As a result, it is necessary to devise a strategy for synthesising non-toxic and ecologically acceptable ionic liquids.

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