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Research Paper

IONIC LIQUID - TETHERED COLLOIDAL SILICA NANOPARTICLES AS A REUSABLE AND EFFECTIVE CATALYST FOR THE SYNTHESIS OF PHENAZINES

THARAGESWARI. K
Research Scholar
M.Phil Chemistry
Bharath Institute Of Higher Education And Research
Mail Id : thara.dhiv@gmail.com

Dr. G. PADMAPRIYA
Associate Professor & Head, Department Of Chemistry
Bharath Institute Of Higher Education And Research

Address for Correspondence:
THARAGESWARI. K
Research Scholar
M.Phil Chemistry
Bharath Institute Of Higher Education And Research
Mail Id : thara.dhiv@gmail.com

Abstract

Heterocycle synthesis has long been a vital and rapidly expanding field of organic chemistry, since heterocycle molecules exhibit a wide variety of biological functions [1-5]. Antitumor [6, antibacterial [7], anti-proliferative [8, antifungal [9], and anti-inflammatory [10] are some of the biological characteristics of phenazines. Phenazines are noteworthy candidates in organic preparation for future consideration because of these characteristics. For the manufacture of phenazines, a variety of methods have been established utilising p-TSA [11], glacial acetic acid [12], 1,4-diazabicyclo[2.2.2]octane (DABCO) [13,14], thiourea-based organocatalysts [15], caffeine [16], theophylline [17], L-proline [18], 1-butyl-3-methylimidazolium Each of these methods may have its own set of benefits, but they all have obvious disadvantages, such as lengthy reaction durations, difficult set-up, non-reusable catalyst, poor yield, or potentially dangerous reaction conditions. To get over these limitations, finding an efficient, readily available catalyst with high catalytic activity for the production of phenazines is still the best option. The production and immobilisation of nanoparticles in ionic liquids (ILs) have been

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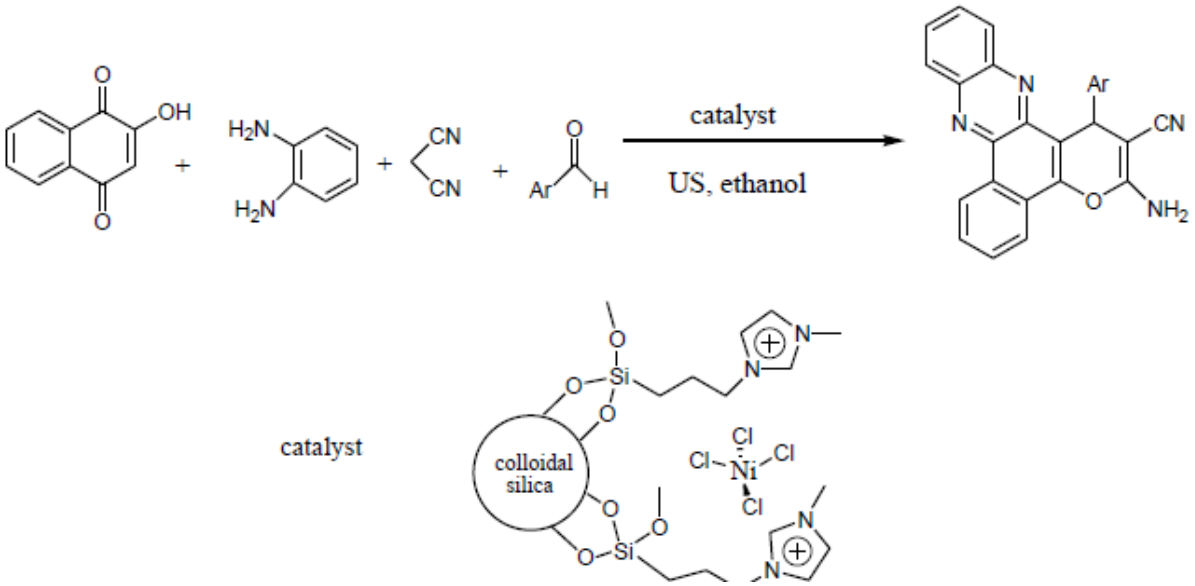
extensively studied in recent years [21,22]. Ionic liquids may be thought of as important catalytic precursor chemicals [23, 24]. The nature of cation-anion interactions in ionic liquids at room temperature is a topic of growing interest [25,26]. [27,28] examined the structures of 1-ethyl-3-methylimidazolium (Emim) and 1-butyl-3-methylimidazolium (Bmim) with transition metal chloride anions such as NiCl42-, CoCl4 2-, and PdCl42-.

INTRODUCTION

In recent years, there has been a lot of focus on developing tidy methods and using eco-friendly and green nanocatalysts that can be easily recycled at the conclusion of reactions. [29-31].



Scheme 1. Synthesis of phenazines under ultrasonic irradiations using nanocatalyst

In this paper, we describe the preparation of bis (1(3-trimethoxysilylpropyl)3-methylimidazolium) nickel tetrachloride tethered to colloidal silica nanoparticles as a resuable catalyst [28] and investigate its catalytic activity for onepot multicomponent phenazines synthesis under ultrasonic irradiations (Scheme 1).

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In both academia and the chemical industry, ionic liquids (ILs) have been recognised as agents of the green chemical revolution. Because of their particular properties, they have the potential to decrease the usage of toxic and polluting organic solvents. These salts in the liquid phase have been referred to as room temperature ionic liquids (RTILs), non-aqueous ionic liquids, molten salt, liquid organic salt, and fused salt. 1 In contrast to water and organic solvents (such as toluene and dichloromethane), ILs are made up entirely of molecules. ILs have a structure comparable to table salt (sodium chloride), which is made up of crystals made up of positive sodium ions and negative chlorine ions rather than molecules. While salts do not melt below 800 degrees Celsius, the majority of ILs are liquid at normal temperature. Sodium chloride and lithium chloride have melting points of 801°C and 614°C, respectively. The use of typical molten salts as solvents is severely restricted due to their high melting temperatures. RTILs, on the other hand, are liquid up to 200°C, while ILs have a broad liquidus range. The accepted highest melting temperature limit for categorization as an ionic liquid is 100 degrees Celsius, and greater melting ion systems are often referred to as molten salts.

In contrast to high-temperature molten salts, ILs are salts that are liquid at room temperature (that melt below 100 degrees). They offer a unique set of physico-chemical characteristics that make them ideal for a variety of applications when traditional organic solvents are ineffective or unavailable.

Although ILs have been known for a long time, their widespread application as solvents in chemical synthesis and catalysis has only lately become apparent. ILs are not new, according to Welton, and some of them, such as ethylammonium nitrate, were originally characterised in 1914. The first IL in the literature was developed for nuclear weapon batteries in the 1970s4. Aluminum chloride-based molten salts were used for electroplating at temperatures of 100°C throughout the 1940s. Early in the 1970s,

Wilkes worked on improved batteries for nuclear weapons and space missions that needed molten salts to function. The molten salts were hot enough to do harm to the materials around them. As a result, the scientists looked for salts that stayed liquid at lower temperatures, ultimately finding one that was liquid at ambient temperature. Wilkes and his colleagues

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proceeded to develop their ILs for use as battery electrolytes, and a small group of researchers started to create and test ILs. ILs were one of the most promising compounds as solvents in the late 1990s. Because they were unstable in air and water, the earliest ILs (such as organo-aluminate ILs) had a restricted range of uses. Additionally, these ILs were not inert to a variety of chemical molecules. The number of air and water stable ILs has been quickly increasing since the initial publications on their synthesis and uses, such as 1-n-butyl-3-methlyimidazolium tetrafluoroborate ([bmim]BF4) and 1-n-butyl-3-methlyimidazolium hexafluorophosphate ([bmim]PF6). Researchers recently discovered that ILs are more than just green solvents, and they've discovered a variety of uses for them, including the replacement of volatile organic solvents, precursors for new materials, effective heat conductors, support for enzyme-catalyzed reactions, host for a variety of catalysts, agents for gas purification, media for homogeneous/ heterogeneous catalysis, and more. Because the study of ILs is still a relatively new area, researchers are currently evaluating some of the fundamental physical characteristics of ILs such as density and viscosity. As a result, it is clear that the quantity of research on ILs and their particular uses is quickly growing. For example, despite the fact that the cation 1-ethyl-3-methylimidazolium was the most extensively researched until 2001, 1-3-dialkyl imidazolium salts have recently become the most studied class of ILs. The goal of ionic liquids research in the future is to commercialise them so that they may be used as solvents, reagents, catalysts, and materials in large-scale chemical processes.

CLASSIFICATION OF IONIC LIQUIDS

In ionic liquids, imidazolium, ammonium, pyridinium, pyrrolidinium, phosphonium, and sulfonium derivatives are common cations. Anions may be inorganic or organic in nature. Halide, tetrachloroaluminate (also tetrachloroferrate and tetrachloroindate), tetrafluoroborate, hexafluorophosphate, and bis(trifluoromethylsulfonyl)imide are typical inorganic anions, whereas trifluoroacetate, lactate, acetate, and dicyanamide are frequent organic anions. On the cation, substituents (the R-group) are typically alkyl chains, although they may also be fluoroalkyl, alkenyl, methoxy, or hydroxyl groups. Functionalized ILs are often created for a specific application, such as specialised reactions, extractions, or separations, and are referred to

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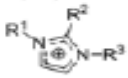
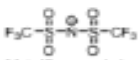
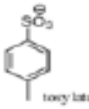
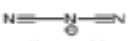
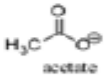
as "task specific ionic liquids" (TSILs). 12 The cations and anions are grouped in Table 2.1 according to their relative acidity and basicity. In terms of discovery and usefulness, the Lewis basic and Lewis acidic families of ionic liquids are constantly growing..

Table 2.1: Structures and nomenclature of the most common cations and anions in ILs, and their acidis/ basic properties.

CATION	ANION	
N,N-dialkyl-imidazolium *Protonated cations, e.g.* methylimidazolium	*Brønsted amphoteric* $H_2PO_4^-$ dihydrogen phosphate; HSO_4^- hydrogen sulfate *Lewis* $AlCl_4^-$, $FeCl_4^-$, $InCl_4^-$ tetrachloroaluminate, -ferrate and -indate	ACIDIC
R ≠ H,  *N,N,N*-trialkyl-imidazolium tetraalkyl-ammonium 1,2-dialkyl-pyrazolium *N*-alkylmethyl-pyrrolidinium *N*-alkyl-thiazolium *N*-alkyl-pyridinium trialkyl-sulfonium tetraalkyl-phosphonium	hexafluoro-phosphate  bis(trifluoromethyl-sulfonyl)imide tetrafluoro-borate  tosylate mesylate sulfonate nitrate Cl^- chloride Br^- bromide	NEUTRAL
1-alkyl-4-aza-1-azoniabicyclo-[2.2.2]octane [$C_n$dabco]	 dicyanamide  acetate lactate	BASIC
R^1, R^2, R^3, R^4 = alkyl, aryl, alkylacid, -ketone, -ester, -ether etc., including chiral.		

The relative acidity and basicity of the component ions imparts variety of physical characteristics to the ionic liquids. A smart distinction can be gives as follows:

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PROPERTIES OF IONIC LIQUIDS, PHYSICAL AND CHEMICAL

Depending upon the application, properties of ionic liquids (whether physical or chemical) can be tailored with the selection of suitable cationic and anionic components. In this section an overview of the properties of ionic liquids ranging from few physical and their common chemical behavior is given.

Melting point and liquidus range; T_m

Molecules or ions are said to melt when they lose their crystal structure and form a chaotic liquid. The melting point (Tm) of an ionic liquid is affected by two constituents: the cation and its matching anion. Charge, size, symmetry, intermolecular interaction, and charge delocalization are some of the major variables that may affect the melting point in general. The melting point of ILs is important because it indicates the lower limit of the liquid's fluidity, and along with thermal stability, it determines the temperature range in which ILs may be used as solvents.

Because their ions do not pack well, ILs stay liquid at ambient temperature, according to researchers. Their chemical makeup is responsible for their low melting behaviour. A regular structure is formed by combining bulky and asymmetrical cations with uniformly shaped anions, reducing the lattice energy and therefore the melting point of the resultant ionic medium. Even the anions may be very big in certain instances, and they can help to decrease the melting point.

Table 2.2 shows the trend in melting point of the imidazolium ionic liquid system as a function of anion size. The coulombic electrostatic interactions with the imidazolium cation in the crystal lattice decrease as the size of the anion increases, and the melting point of the salt lowers. Low solid-liquid phase transition temperatures may be obtained when excellent charge delocalization is combined. In the sequence Cl > NO3 >BF4 >CF3COO, the melting point of a 1-ethyl-3-methyl imidazolium salt decreases from 87 °C to -14 °C (Table 2.2). Except for anion PF6, the melting temperature falls as the radius of the anion increases. Because ILs containing

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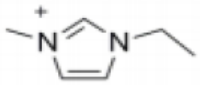
PF6 anions establish strong hydrogen bonds owing to the presence of a fluorine atom, their melting points are greater..

Table 2.2: Effect of anion size on the melting temperature of imidazolium ILs.[43]

Salt		Anion size	mp. [°C]
	Cl^-	small	87
	NO_2^-		55
	NO_3^-		38
	$AlCl_4^-$		7
	BF_4^-		6
	$CF_3SO_2^-$		-9
	CF_3COO^-	large	-14

Purity; Anionic impurity

During synthesis or catalytic applications, impurities such as water, halides, unreacted organic salts, and organics are often retained in ILs. These contaminants may affect the solvent's characteristics and/or interact with the catalyst or biocatalyst.

As a result, determining the purity of the ILs is critical. To measure chloride, either the Vollhard technique or an ion-selective electrode method may be employed, and the latter approach can also be used to detect sodium. Water may be detected in ILs due to poor drying after preparation or absorption from the environment due to the hygroscopic characteristics of the synthesised ILs. Even water immiscible ILs have been found to collect moisture from the

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environment. [C4mim]PF6 can, in fact, absorb up to 0.16 mole fraction of water from the atmosphere (measurement through Karl-Fischer titration).

Water and chloride contaminants may significantly change the physical characteristics of ILs. The presence of chloride contamination may make the ILs viscous, while the presence of water or other co-solvents can make them viscous. Co-solvents decrease viscosity in general, with the impact being greater for co-solvents with a higher dielectric constant. At an equimolar concentration of water and ionic liquid, structural changes impacting the majority of characteristics suggest the development of a hydrogen-bonded complex with water.Solvent properties of ILs

Polarity

Any chemical's polarity behaviour aids in identifying it as a solvent. ILs are extremely polar solvents, as defined by the concept of polar solvent, which is a solvent that can dissolve and stabilise dipolar or charged solutes. However, this cannot be stated with certainty since ILs may be constructed in a wide variety of ways. As a result, ionic liquids may be categorised as dipolar, protic, or aprotic solvents. The values of dielectric constants, dipole moments, and polarizabilities define the solvent polarity for experimental and theoretical investigations. 1 For ionic liquids, however, a direct measurement of the dielectric constant, which requires a non-conducting medium, is not possible.

To explain variations in solvent-mediated reaction routes, reaction yields, synthesis product ratios, chromatographic retention, and extraction coefficients, attempts have been undertaken to establish empirical solvent polarity scales for ILs. Abboud, Kamlet, and Taft assessed several common characteristics, such as dipolarity or polarizability (*), H-bond basicity (), and H-bond acidity (), based on comparisons of the impacts on the UV-visible spectra for sets of closely related dyes. Using solvatochromic dyes, several studies of solvent-solute interactions in ILs have been described. Crowhurst et al. used the Abboud-Kamlet-Taft technique to estimate the solvent parameters *, and of imidazolium ILs using three solvatochromic dyes (Richardt's, N,N-diethyl-4-nitroaniline, and 4-aniline) (Table 2.4). Crowhurst et al. discovered that the

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studied ILs had greater dipolarity or polarizability than alkyl chain alcohols using the * values. Although the variations between the ILs are minor, this parameter has been shown to be affected by both the cation and the anion. The H-bond basicity of the investigated ILs, on the other hand, spans a wide range, from a value comparable to acetonitrile to lower -values. The nature of the anion determines H-bond basicity, whereas the type of the cation determines H-bond acidity (even if a smaller anion effect is there). It has been proposed that the capacity of the cation to serve as a H bond acceptor controls values; a strong anion-cation interaction decreases the cation's ability to hydrogen bond with the substrate. The studied ILs have a lower acidity than water and most short-chain alcohols, but a higher acidity than other organic solvents. 20 Figure 2.1 depicts the polarity scale of numerous organic solvents, including several families of ionic liquids.

Chromatographic methods were also used to examine the ILs' solvent characteristics. Anderson et al. investigated the solvent characteristics of ILs, such as their capacity to function as a hydrogen bond donor or acceptor, by measuring the GC retention periods of a variety of probe solutes on a variety of columns utilising ILs as the stationary phases. High dipolar and dispersion forces were observed to interact with solutes, and the ILs also functioned as strong hydrogen bond bases.

The measurement of keto-enol equilibria is an alternative method to measuring solvent polarity (as this is known to be affected by the polarity of the medium). When used to investigate the polarity of ionic liquids, this technique revealed that [bmim]BF4, [bmim]PF6, and [bmim]NTf2 are more polar than organic solvents like methanol or acetonitrile..

Table 2.4: Kamlet-Taft parameters for few ILs.

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Ionic liquid	E_T [a]	Π*	α	β
[bmim]BF_4	0.670	1.047	0.627	0.376
[bmim]PF_6	0.669	1.032	0.634	0.207
[bmim]OTf	0.656	1.006	0.625	0.464
[bmim]NTf_2	0.644	0.984	0.617	0.243
[omim]PF_6	0.633			
Ethanol	0.650			

[a]E_T = 28592/ (the wavelength maximum of the lowest energy π-π*

absorption band of the zwitter ionic Richardt's dyes).

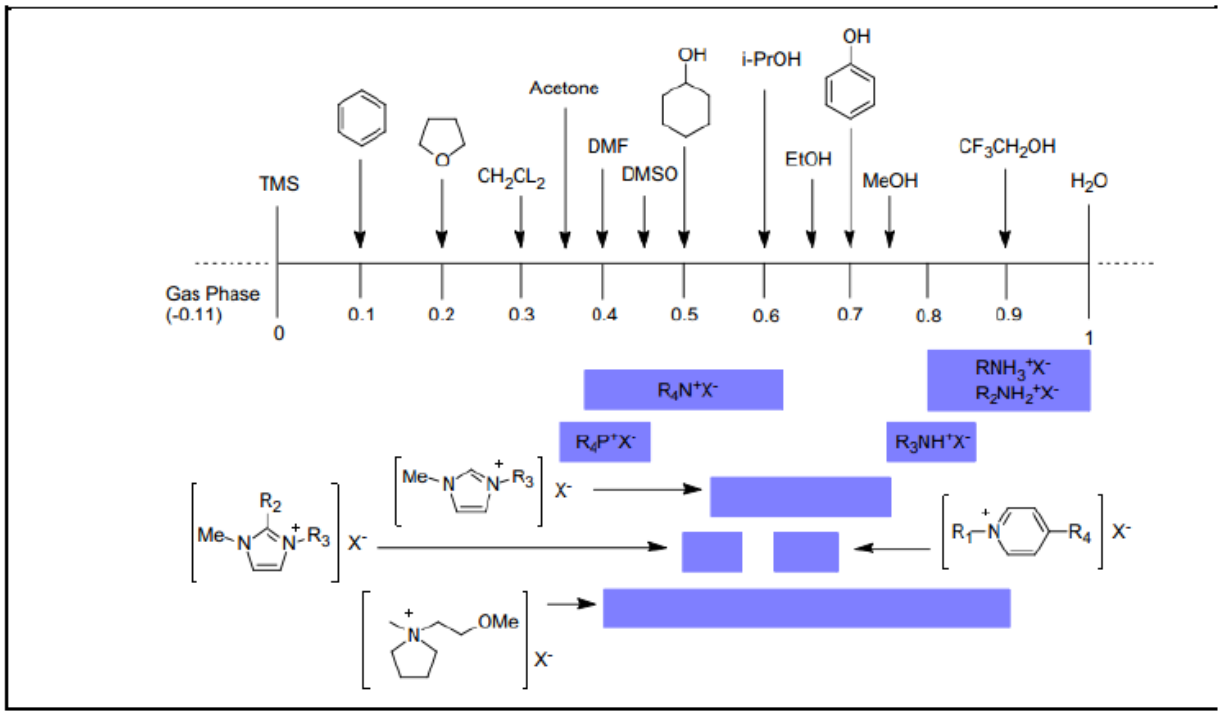

Figure 2.1: Normalized solvent polarity scale for several organic solvents and different groups of ionic liquids.

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In the case of ILs based on 1-alkyl-3-methyl imidazolium cations, the polarity is influenced by the anion, for shorter alkyl chains, whereas for longer alkyl chains the influence of the anion present is less. The polarity typically decreases in the order of NO_2^- >NO_3^- >BF_4^- >Tf_2N^- >PF_6^- and with anion size (more particular with the effective charge density of the anion).

Miscibility behavior of ILs

Because the most commonly used solvents are volatile and harmful, the quest for alternative solvents to satisfy the cleaner technology criteria is ongoing. ILs are excellent solvents for a variety of chemicals, including organic, inorganic, organometallic, biomolecules, and metal ions. They are often made up of weakly coordinating ions, making them highly polar but non-coordinating solvents.

The majority of the chemicals mentioned are sufficiently soluble in ILs to perform well in organic conversions. On the basis of the Abraham free energy connection, it has been determined that ILs resemble polar organic solvents such as acetonitrile, N-methylpyrrolidone, or methanol in terms of their overall solvent characteristics. The use of polar aprotic ILs as a medium for solubilizing biomolecules such as proteins and carbohydrates is one such use (that are sparingly soluble in common organic media). However, it has been shown that even simple sugars, such as [bmim]BF4, do not dissolve to a significant degree in water miscible ionic liquids. [bmim]Cl, on the other hand, may dissolve large quantities of cellulose. Ionic liquids' capacity to serve as solvents or dissolve complex molecules like sugars and proteins is largely determined by the salt's ability to act as a hydrogen bond giver and/or acceptor, as well as the degree of charge localization on the anions. 1,79 The physical characteristics of ILs are influenced by charge distributions across anions, H bonding ability, polarity, and dispersive interactions. Imidazolium-based ILs, for example, are highly ordered, hydrogen-bonded solvents with significant influence on chemical reactions and processes.

The miscibility of ILs with water is likewise unexpectedly variable. Water is miscible for [bmim]BF4 and [bmim]MeSO4, but not for [bmim]PF6 and [bmim]Tf2N. On the Reichardt

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scale, these ionic liquids have similar polarity, and the coordination strengths of the BF4- and PF6- anions are similarly comparable. A study of the H bond accepting characteristics of such ionic liquids found that BF4- and MeSO4- (= 0.61 and 0.75, respectively) are stronger H-bond acceptors than PF6- (= 0.50), which may explain the difference in water miscibility. It is important to remember that aqueous IL mixes may not be homogenous at the molecular level since water does not mix with methanol at this level and is present as strings or clusters of molecules. As previously stated, even water-immiscible ionic liquids may be hygroscopic because they absorb water easily. Water interacts with the anion mostly via the creation of double H bonds, according to IR spectroscopic research, at least when the cation is a weak hydrogen bond donor.

The miscibility of ILs and organic solvents, on the other hand, is poorly understood. Lower alcohols and ketones, dichloromethane, and THF (= 7.58) mix with [bmim]Tf2N, while alkanes and ethers do not, according to one theory. Most ILs are incompatible with most organic solvents, making them a non-aqueous, polar option for two-phase systems.

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Volatility; Low vapor pressure

In contrast to conventional organic solvents like benzene, acetone, and toluene, ILs do not emit vapours due to their very low vapour pressure. The vapour pressure of [bmim]PF6 at 298.15 K, according to Kabo et al.86, is 10Pa11Pa. ILs may be utilised as green solvents because, unlike volatile organic compounds (VOCs), they have very low vapour pressure, are non-explosive, and can be recycled and reused in certain circumstances. Furthermore, these non-evaporating ILs eliminate the dangers of exposure and contamination. ILs, unlike traditional solvents, do not evaporate into the atmosphere, and their low volatility allows them to be used in high vacuum systems. Furthermore, ILs have the potential to be excellent solvents for many

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chemical processes when distillation is not feasible or when water insoluble or thermally sensitive products (e.g. some medicinal compounds) are involved. 2 Although it was previously thought that ILs could not be distilled owing to their poor volatility, Earle et al. demonstrated that many ILs, particularly bistriflamide ILs, can be distilled at 200–300 degrees Celsius and low pressure without breakdown..

Thus, due to their stability, non-volatility, adjustable miscibility and polarity, ILs may be used as ideal substitutes for conventional organic solvents.

SYNTHESIS METHODS OF IONIC LIQUIDS

ILs are 'designer solvents' since their specific properties can be tuned for a particular need. A specific IL can be designed by choosing negatively charged small anions and positively charged large cations and these specific ILs can be utilized to dissolve certain chemicals or to extract them from a solution. The fine-tuning of the structure provides tailor-designed properties so as to satisfy the requirements for a specific application. The physical and chemical properties of ILs can be varied by changing the alkyl chain length on the cation and the anion. As an example, Huddleston et al. concluded that density of ILs increases with a decrease in the alkyl chain length on the cation and an increase in the molecular weight of the anion. It is estimated that by combining various kinds of cation and anion structure, ILs can be designed.

The most widely used cations are imidazolium, pyridinium, phosphonium and ammonium ions. The overall properties of ILs result from the composite properties of the cations and anions, where the anion controls the water miscibility and the cation also has an influence on the hydrophobicity or hydrogen bonding ability of the ionic liquid.

Anion

ILs with varied properties can be obtained by introducing different anions. IL anions can be of two types: fluorous anions such as PF_6^-, BF_4^-, $CF_3SO_3^-$, $(CF_3SO_3)_2N^-$ and non-fluorous anions such as $AlCl_4^-$. Anions most commonly encountered in an IL are; chloride, nitrate, acetate, hexafluorophosphate and tetrafluoroborate. However, in designing ILs, fluorous anions

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are usually opted because of the distinct properties they impart. As an example, as already discussed, IL with 1-n-butyl-3- methylimidazolium cation and $PF6^-$ anion is water-immiscible, whereas IL with same cation and BF_4^- anion is water soluble. This exemplifies the 'designer solvent' property of ILs, i.e. by changing the anion the density, hydrophobicity, viscosity and solvation properties of the IL system can be altered.[8] Although PF_6^- and BF_4^- are the two anion types that are utilized in most of IL applications, they suffer from a serious disadvantage. These anions undergo decomposition when heated in the presence of water and liberate HF. Following the discovery of this phenomenon, fluorous anions containing C-F bond which is inert to hydrolysis were started to be used. Consequently, ILs bearing $CF_3SO_3^-$ and $(CF_3SO_3)_2N^-$ anions in which the fluorine is bonded to carbon have been produced. However, fluorinated anions tend to be expensive and toxic to the environment. Hence, alkylsulfate anions derived from inexpensive bulk chemicals have been found as the most popular non-fluorous anions due to their non-toxic and biodegradable structures.

Cations

The preferable cation for any ionic liquid is one having a bulky structure with low symmetry. Most of the ILs currently in research are based on ammonium, sulfonium, phosphonium, imidazolium, pyridinium, picolinium, pyrrolidinium, thiazolium, oxazolium and pyrazolium cations. Properties of ILs, such as melting temperature, density, viscosity etc. are affected differently with variation in size, symmetry and alkyl chains attached to cation (as already discussed in Section 1.4). Not only this, different ILs can be designed by introducing a suitable functionality into the cation leading to the formation of third generation ILs-Task specific ILs. An essential target to chemists involved in organic transformations and total synthesis is tuning the stereochemistry of the product. In this respect, chiral ILs have been suitably designed to carry out the work of asymmetric synthesis.

Synthesis

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The synthesis of ILs generally proceeds in two steps: formation of the cation followed by anion exchange (metathesis). Typical synthetic pathways for the preparation of ILs are shown in Figure 2.2, where the preparation of imidazolium based ILs is taken as an example.

The cation formation step, most often described as a quaternization reaction, imparts ionic nature to the compound. The starting material, imidazolium (or amine, pyrimidine, etc.), is alkylated with an appropriate alkyl halide (RX) and in halogen based ILs, this is the only step which is required. However, quaternization with alkyl halides sometimes may leave traces of halide ion in the ionic liquid. Not always, but halide ions can also interfere with metal catalysts, can cause corrosion problems in chemical plants and interfere with measurements of physical property of ILs. As an alternative, ILs can be synthesized via a “halogen- free” route, where an alkyl alkylsulfonate, usually alkyl methylsulfonate (mesylate) or alkyl toluenesulfonate (tosylate), is used for the quaternization reaction. The quaternization reaction can also proceed by protonation with a Brønsted acid.

The anion exchange reactions can be brought about in two possible ways: a halide salt can be treated with a Lewis acid to form a Lewis acidic ionic liquid, or an exchange reaction can be carried out by anion metathesis. Typical Lewis acids that can be used in this context are $AlCl_3$, BCl_3, $CuCl_2$, $FeCl_2$, or $SnCl_2$.

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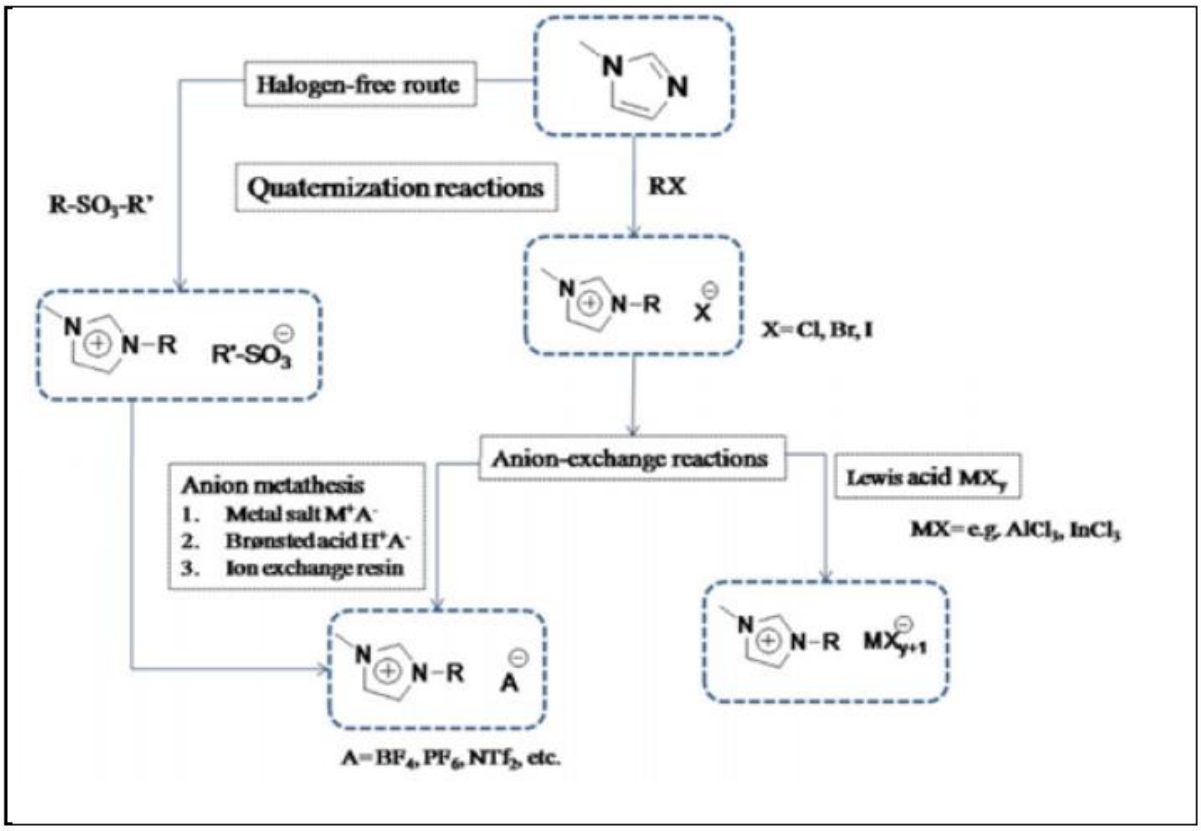

Figure 2.2: Synthesis routes for the preparation of methylimidazolium based ionic liquids.

The beginning of IL preparation dates back to 1914, where ethylammonium nitrate ($[EtNH_3]NO_3$, mp 13°C-14°C) was prepared by neutralization of ethylamine with concentrated nitric acid. The discovery did not attract much scientific interest and these new materials went largely unrecognized till the 1970s when organic chloroaluminates (first-generation ILs, Figure 2.3) were investigated. In the 1990s, Wilkes and Zaworotko reported the preparation of air- and moisture-stable ILs (second- generation ILs, Figure 2.3) using new combinations of cations and anions. Since then, a wide range of ILs have been developed including TSILs (third generation ILs, Figure 2.3), which were introduced by Davis in 2004.

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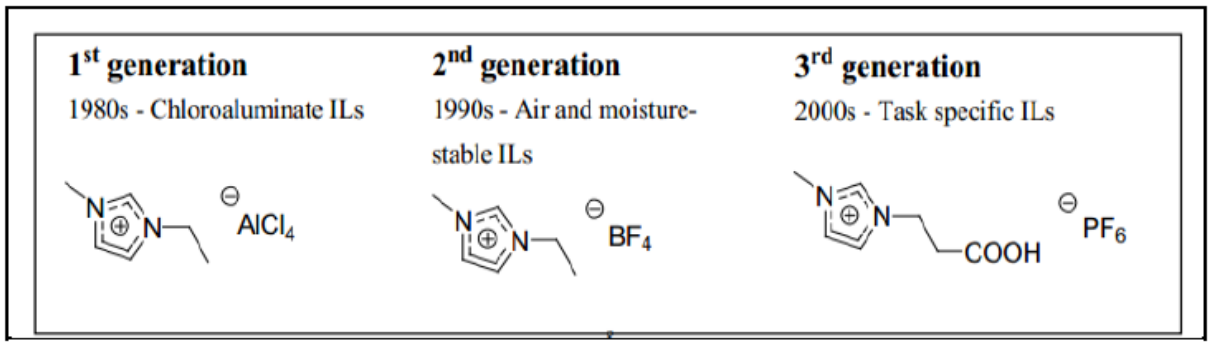

Figure 2.3: The three generations of ionic liquids.

Below is thus summarized, generation vise synthesis of ILs; ranging from ammonium ILs, non- functionalized ILs, functionalized task specific ILs (TSILs) and chiral ILs.

CONCLUSIONS

In conclusion, we have reported an efficient method for the synthesis of benzopyranophenazines using ionic liquid/colloidal nano-silica as a superior catalyst under ultrasonic irradiations. The new catalyst is characterized by 1H NMR, FE-SEM, EDS, DLS and TGA. The current method provides obvious positive points containing environmental friendliness, reusability of the catalyst, low catalyst loading and use of ultrasonic irradiation as a valuable and powerful technology.

Cost is a major challenge to be encountered in synthesizing ILs on an industrial scale. A kilogram of ionic liquid used to cost about 30,000-fold greater than a common organic solvent such as acetone. Renner38 reported that this cost could be reduced to approximately 1000-fold depending on the composition of ionic liquid and the scale of production. anticipated that the price of cation systems based on imidazole will be in the range of € 50 kg−1–100 kg−1, if larger quantities of ILs are produced. The price can be lowered even below € 25 kg−1 if ILs are prepared with cheaper cation sources on a ton scale. Further, another estimation was done by

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Wassersheid and Haumann. They expected that for 'bulk ILs" choosing proper (relatively cheap) cations and anions lead to prices approximately € 30 l−1 for production rates of multi-ton.

Moreover, scientists emphasize that although the price of the ILs may lookdiscouraging but still, the essential factor is the price to performance ratio. If the performance of an IL is extremely high as compared to that of the material (solvent) it aims to replace, less amounts of the IL may be needed for a given specific job, thereby totally or partially overcoming the price disadvantage.

A problem is faced while manufacturing ILs and that needs to be tackled. This is the use of VOCs in the manufacture of ILs. Recently, some advancement has been achieved in the solventless syntheses of ILs. For example, 1-alkyl-3- methylimidazolium halides have been synthesized in open containers in a microwave oven without any VOCs by Varma and Namboodiri at the Environmental Protection Agency of U.S.,2001.38

Recycling of ILs is another important issue that concerns the researchers working with them. Many processes for cleaning up ILs involve washing with water or VOCs which creates another waste stream. This problem has been solved by adopting supercritical extraction technologies to recover the dissolved organic compounds from ILs or using membrane separation processes. A green solvent, which has been discovered and solves all the problems and recovers various kinds of solutes from ILs without cross contamination, are supercritical fluids (SCFs).The advantages of using SCFs as extraction medium include low cost, nontoxic nature, recoverability and ease of separation from the products. SCFs have been adapted for product recovery from ILs and supercritical fluid extraction (SCFE) is shown to be a viable technique with the additional benefits of environmental sustainability and pure product recovery. Among the SCFs, aninexpensive and readily available one, scCO2 has become a partner of IL and two environmentally benign solvents have been utilized together in several applications. The volatile and non-polar scCO2 forms different two-phase systems with non-volatile and polar ILs. The product recovery process with these systems is based on the principle that scCO2 is soluble in ILs, but ILs are not soluble in scCO2. Since most of the organic compounds are soluble in

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scCO2, with the high solubility of scCO2 in ILs, these products are transferred from the ionic liquid to the supercritical phase.

Thus, designing of ILs and their applications in the field of research at every level should deal with toxicity and biodegradability issues wherever possible.

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