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Review Paper

Emerging Trends in Ionic Liquid Formulations: A Critical Review

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ABSTRACT

Ionic liquids (ILs) have transformed industrial processes and chemical research by providing versatile, environmentally friendly solvents for a broad range of uses, from materials science to catalysis. Despite obstacles such as enzyme denaturation, recent developments have increased the usefulness of ILs in homogeneous systems and biocatalysis. Their uses in gas purification and catalysis have expanded due to task-specific ILs and continuous study into their physical and chemical properties. However, issues like labour-intensive enzyme preparation and batch variation continue to exist, in addition to aspects like cost and suitability for catalysts that are sensitive. Unlocking the full potential of ILs in a variety of scientific and industrial contexts—including biodiesel production, where waste reduction and catalytic activity optimization are critical—requires addressing these issues through creative synthesis methods and optimization strategies. Current research endeavours to surmount these obstacles and optimize the advantages of ILs throughout diverse domains of chemistry and industry.


INTRODUCTION

Only a small number of specialist research organizations were aware of the concept of "ionic liquids" (ILs) twenty years ago. Even those groups either tried ILs or thought they might be the most appropriate response solvents for a wide range of reactions, such as carbonization, esterification, depolymerization, Beckmann restructuring, acidic breakdown, polymerization, alkylation, and pre-extractions (Singh & Savoy, 2020). Chemicals termed ionic liquids have recently transformed

chemical industries and research facilities. Reducing the usage of poisonous, hazardous, and environmentally detrimental substances requires certain elements, which are found in environmentally favourable compounds like solvents. Liquids with ions These are liquid-at-100 degrees organic materials made of ions. The fact that scientists are trying to find a practical substitute for volatile solvents in the industry is one of the factors driving the current surge in ionic fluid research (Ehsan Kianfar & Sajjad Mafi, 2020)

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While salts that melt below 373 K are connected with this description, higher melting point salts are not excluded by the phrase "ionic liquid." Actually, the terms "ionic liquid" and "molten salt," which are commonly used interchangeably to refer to high temperature liquids, are practically interchangeable.(Rooney et al., 2009)." There are two straightforward reasons why solvents rank highly among harmful chemicals: (i) They are widely utilised; (ii) These are typically flammable liquids that are difficult to confine; and the key to the ongoing success of IL research will be our capacity to revise definitions, reclassify, and develop new design strategies(Jordan & Gathergood, 2015). ILs are considered superior molecular and/or environmentally friendly solvent replacement for the widely used volatile organic solvent. A small number of ILs, such as Olah's reagent, are protic ILs and are only considered ionic when described as deep eutectic solvents. Furthermore, at ambient conditions, ILs exhibit low vapor pressure, low viscosity, and non-volatility. In comparison to mineral acids and bases, they have a wide range of temperature stability, tuneable solubility, acidity, basicity, and extremely low corrosivity, among other characteristics. ILs have no adverse effects on air photochemistry and do not exhibit the explorer risk associated with volatile organic because of their incredibly low vapor pressure, solvents. Additionally, the non-volatility of the majority of ILs results in their non-flammability at ambient circumstances, as demonstrated by a number of low-boiling solvents, including acetone, dichloromethane, pet ether, and many more (Singh & Savoy, 2020) Recently, it has been demonstrated that certain ILs can dissolve a wide range of substrates that are typically insoluble in organic solvents, including ascorbic acid, amino acids, fatty acids, triglycerides, and up to 10–20 percent (wt.) cellulose. β -D-glucose, sucrose, lactose, and β -cyclodextrin are among the other

carbohydrates that can dissolve, as well as >100 g L⁻¹. These natural products' ability to undergo chemical changes in homogenous systems has been made possible by the solubility of carbohydrates in ILs. These ionic liquids (ILs) have anions, usually strong hydrogen bonds with carbohydrates to dissolve them, such as chloride (Cl⁻), dicyanamide (dca⁻), formate (HCOO⁻), and acetate (OAc⁻). These ILs also have the potential to denature enzymes, preventing enzymatic reactions from transforming dissolved substrates. Complicated ligand clusters have the potential to enhance the catalytic activity of their reaction processes(Olivier-Bourbigou et al., 2010). Consequently, it is necessary to raise the stability as well activity of enzymatic processes in ILs, especially those ILs that inactivate enzymes. For these reasons, a number of common non-aqueous enzymology techniques for stabilising and activating enzymes have been adapted for use in ionic media, along with the development of certain novel techniques. This review's objective is to provide an overview of these techniques and offer guidance to researchers looking to advance them in order to expand the field of biocatalytic applications in ionic liquids(Zhao, 2010). Besides from being utilized as replacement solvents, ionic liquids have recently been used made progress in the development of functional ionic liquids or "task-specific ionic liquids"(TSIL). The phrase "task specific ionic liquids" or "functionalized ionic liquids" refers to an effort to turn ionic liquids from mere reaction media into actual working systems by utilising its potential "design" capacity(Ratti, 2014). Interaction of ILs with metal ions or other cocatalysts. As a result, compared to other catalysts, ILs have many advantages (like zeolites, enzymes, metallic salts, solid acid catalysts, etc.) For example, techno-economic and environmental factors are crucial components of IL catalytic system adoption and readily managed because they are applicable to an ongoing



procedure with a small effluent output (Tiong et al., 2017). A good catalyst should be highly reactive and selective, with ease of separation and reusability being highly desirable from an industrial perspective. Using ILs increases the process's economic viability while lowering the quantity of reactions and purification steps (Ong et al., 2021). Since air- and moisture-stable ILs are easily handled and utilised in a wide range of conditions, we concentrate on their current analytical applications in this study. t. Nevertheless, only a small number of studies on other facets of IL research—such as synthesis/catalysis and the clarification of ILs' structures and properties—were chosen for this study (Qureshi et al., 2014). Compared to molten salts at high temperatures, at room temperature, ILs are known to be liquid salts. Their distinct range of physio-chemical characteristics renders them appropriate for a multitude of uses where traditional organic solvents prove to be insufficiently efficacious or inappropriate. Short noted that while there were few patent applications for intellectual labours (ILs) in 1980, there were 100 in 2000, and by 2004 there were over 800. This demonstrates unequivocally how highly academics and business associate themselves with the ILs (Keskin et al., 2007). According to Wilkes and colleagues: Finding a new ionic liquid is not too difficult, but finding out its physical and chemical properties is a much more significant investment if you want to use it as a solvent. The best trick would be a technique to predict the composition of an ionic liquid with a given set of

attributes. Ionic fluids obtained more focus in recent years because of their diverse range of applications. New generations and families of ionic liquids having wider specialized as well as desired attributes have been added to the range of ionic liquids now available. This growing interest has prompted several reviews of the physicochemical characteristics of ionic liquids, the creation of new groups of ionic liquids, chemical engineering, and a variety of configurations (liquid phase, multiphase, immobilized on supports, etc.) in which they have ILs. have been used, as well as pilot or industrial development. Because the early ILs, like organo-aluminate ILs, were unstable in the presence of water and air, their range of uses was restricted. Moreover, these ILs weren't inert to different chemical substances. After preliminary research on the synthesis and application of air-stable ILs, such as 1-n-butyl-3-methylimidazolium tetrafluoroborate [BF₄] and 1-n-butyl-3-methylimidazolium hexafluorophosphate [PF₆], the number of air- and water-stable ILs started to rise quickly. More benefits have been discovered recently for ionic liquids (ILs) than for green solvents alone. Their numerous uses have been discovered, such as the substitution of volatile organic IL solvents, the development of new materials, effective thermal conductivity, the encouragement of enzyme-catalysed reactions, the hosting of different catalysts, the purification of gas, homogeneous and heterogeneous catalysis, biological reaction media, and the removal of metal ions. (Keskin et al., 2007)

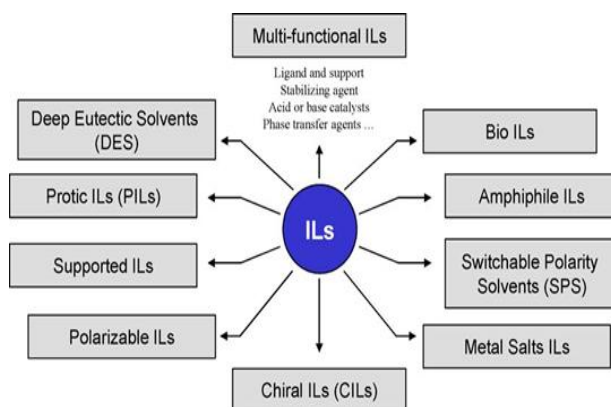


Fig: Evolutions Of Ionic Liquids Generations(Olivier-Bourbigou Et Al., 2010)

History:

According to Welton, ILs are not brand-new; in fact, several ILs, including $[\text{EtNH}_3][\text{NO}_3]$, were originally documented in 1914. The first deliberate IL in the literature dates back to the 1970s and was developed for nuclear weapon batteries. Molten salts based on aluminium chloride were used for electroplating in the 1940s at temperatures as high as hundreds of degrees Celsius(Keskin et al., 2007). However, as the activities of the latter time period unfold, unfavourable long-term environmental implications can and have become a significant legacy. The earlier years of the last century seem to contain entirely helpful achievements in science and technology toward humans(Park & Kazlauskas, 2003). Armstrong and colleagues synthesised 39 imidazolium- and pyrrolidinium-based di-cationic ILs in 2005 to investigate the relationship between structure and characteristics. The head groups reacted with four distinct conventional anions because they were connected by an alkyl chain that ranged in length from three to twelve carbons (Br, NTf₂, BF₄, and PF₆)(Nusaibah Masri et al., 2016). 17 ammonium-based symmetrical di-cationic ILs by combining 3 equivalent moles of 1-alkylbromide with tetramethyl ethylenediamine, tetramethylpropylenediamine, or tetramethylhexylenediamine in a cold bath using acetone as the solvent for 24 hours (Nusaibah Masri et al., 2016)Although ILs have long been

recognised, their widespread usage as solvents in catalysis and synthesis reactions has just lately gained attention(Keskin et al., 2007). The chemists eventually found one salt that is liquid at normal temperature after searching for salts that stay liquid at lower temperatures. A small team of researchers started creating ILs and assessing their characteristics after Wilkes and his associates carried out more refinement of their ILs for use as battery electrolytes. ILs emerged as one of the most promising materials for use as solvents in the late 1990s. The early ILs' range of applications was limited because they were unstable in the presence of water and air, such as organo-aluminate ILs. Moreover, these ILs weren't sensitive to other chemical molecule. (Keskin et al., 2007)Ethyl ammonium nitrate $[\text{EtNH}_3][\text{NO}_3]$ (m.p. 12°C), which was originally documented in the literature in 1914, is the first IL(Singh & Savoy, 2020). Since IL research is still in its early stages, scientists are currently analysing some of the fundamental physical features of ILs, such as density and viscosity.[8]. The literature is seeing a sharp rise in the number of studies on ILs and their particular uses. As an illustration, the most extensively researched cation until 2001 was 1-n-ethyl-3-methylimidazolium. But as of right now, Imidazolium salts with 1-3 dialkyl are the most widely employed and studied group of ILs. The goal of research on ILs going forward is to commercialise them so that they can be used as

materials, reagents, solvents, and catalysts in extensive chemical applications (Keskin et al., 2007). In the first of these, Paul Walden searched for liquid salts that were melted at temperatures that allowed him to utilize his equipment without needing to make any additional adjustments (Welton, 2018). He found that the melting point of $[\text{EtNH}_3][\text{NO}_3]$ is 12°C . Additionally, this was the first time a protic ionic liquid (PIL) was used. Hiroyuki Ohno later made a new discovery of PILs (Hirao et al. 2000), and they went on to become an important subclass of ionic liquids (Welton, 2018). Walden was curious in the connection between the conductivity and these liquid salts' molecular size. Sadly, this discovery's potential was disregarded for a very long time, with the exception of a passing mention in a 1927 study on a number of fused salts (Sugden and Wilkins 1929) (Welton, 2018) (Hagiwara et al., n.d.). The report by Cooper and O'Sullivan is thorough and must have to be read by everyone, even though it is not surprising that the Wilkes group is most frequently credited with discovering this novel and practically significant class of solvent liquids—they were previously well-known for their study of molten salts at ambient temperatures. The possibilities that awaited in the domains of materials science and synthetic chemistry, these novel low vapour pressure solutions were quickly recognized by groups like Gratzel in Switzerland and MacFarlane in Australia. If not for the vision of Seddon and other synthetic organic chemists, it is unlikely that either group's innovations would have gotten any attention for the chloroaluminates (Welton, 2018). If viscosity had a higher Arrhenius activation energy than conductivity performed, the fractional Walden rule likely explained the larger halide ions' quasilattice being broken by the smaller silver ion. When it came to Specifically, silver iodide was an excellent conductive even in its crystallized state condition at certain temperatures around, the

moment at which melting occurs this picture was particularly clear (Austen Angell et al., 2012)

These Walden rule aberrations are currently referred to as "superionic" behaviour within the domain of glass-forming solid electrolytes are found in ionic liquids, which are valued, particularly protonated Ionic liquids (which could act as electrolytes in fuel cells) (Cooper & Angell, 1983) (Poole et al., 1989) Later research revealed that the purported stability of these—both hydrolytic and thermal—was a little exaggerated.

Aim: Emerging Trends in Ionic Liquid Formulations: A Critical Review

Objective:

1. **Tailored Properties:** Customize the chemical structure and composition of ionic liquids to achieve desired physical and chemical properties, such as low volatility, high thermal stability, or specific solvation capabilities.

Thermophysical Properties: Understanding and optimizing the thermophysical properties of ionic liquids, such as viscosity, density, and thermal conductivity, to tailor them for specific applications.

Ionic Liquid Classes:

Anti-Aprotic Ionic Fluids: Most ionic liquids include organic molecule ions as their cation, which is perhaps why the number of papers in this field has increased dramatically since the mid-1990s. Resonant stabilised cations of dialkylimidazolium and alkyl pyridinium which date returning to Weir and Hurley in the midst of the 20th century, are two examples. They combined different metal chlorides and nitrates with N-substituted alkyl and aryl pyridinium halides to create low-liquids, which they then used to carry out electro-chemical extractions (though they seem to be best known for their efforts on aluminium deposition on which they took the first patents). The cyclic and non-cyclic tetraalkylammonium salts, such as those containing cations of alkylpyrrolidinium and



especially those with ether oxygenated sidechains, have been developed much more recently (Cooper & Angell, 1983). Anions with an oxidic character, such as nitrate perchlorate, or a more common fluorinated-oxidic character, such as triflate, typically compensate for the charge of such cations. Triflate (trifluoromethane sulfonate, CF_3SO_3) and bis-trifluoromethanesulfonyl-imide ($(\text{CF}_3\text{SO}_2)_2\text{N}$, or NTf_2) ions have been identified in PF_6 , BF_4 , and NTf_3 are some of the most prevalent of the latter. Due to van der Waals interactions' reduction in viscosity (caused by the fluorine electrons' tightly bound, therefore unpolarizable, nature), the fluorinated anions are more noticeable. Henderson mentioned that the NTf_2 anion is particularly successful because it has two isoenergetic forms, which allows it to provide an additional (and hence liquid-stabilizing) mode to the configurational entropy. This anion is rather massive., (Austen Angell et al., 2012)

1. **Protic Ionic Liquids:** A proton is simply transferred from pure Brønsted acid to pure Brønsted base to generate these. As previously mentioned, the Ohno laboratory in Japan was the driving force behind the invention of the first artificial intelligence (IL) in the contemporary age. This procedure creates a proton potential in the liquid result, which gives this class of ionic liquids a unique tunability due to its nature and reversibility. The NTf_2 anion that was discussed in the preceding section works just as effectively to reduce these liquids' cohesiveness and, consequently, their fluidity. Protic ionic liquids, however, have the potential to become more conductive than aprotic ones through the manipulation of cohesion through adjustments to the proton transfer energy. In fact, some of the most conductive liquids ever discovered have been produced by utilising these properties. (Austen Angell et al., 2012)

2. **Inorganic Ionic Liquids:** These can be created by exploiting the same packing issues that result in low-melting ILs of the organic cation type, in both aprotic and protic forms. Aprotic examples include lithium chlorate (melting point 115 C) and its glass-forming eutectic with lithium perchlorate; protic examples include hydrazinium nitrate, T_m $\frac{1}{4}$ 80 C; low-melting mixtures of ammonium salts; and lastly, the largely unexplored cases of salts with inorganic molecular cations, like PBr_3Cl^+ , SCl_3^+ , $\text{ClSO}_2\text{NH}_3^+$, etc., with the appropriate weak base anions. These examples may be few in number, but they do exist. (Austen Angell et al., 2012)

3. **Solvate (Chilate) Ionic Liquids:** Recognizing this as a mostly unexplored class of ILs is essential since the class contains cases of multivalent cation salts that would not normally be able to satisfy the condition of $T_m < 100$ C. Melted salt hydrates, such as $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, were the first members of this class to be identified. It was discovered that their mixtures of alkali metal salts were almost ideal, with the majority having liquidus temperatures much below ambient. Despite doubts about the water molecules' lifetime in the cation coordination shell, these were hailed as a "new class of molten salt mixtures." This must be long in respect to the diffusion time scale in order to properly categorize "ionic liquids." More instances of molecules with a long lifetime guaranteed by the fact that all of the ligating groups are a part of the same molecule have been published recently by the Watanabe team. Therefore, Tamura et al. substitute four alkoxy groups linked together, such as tetraglyme chelating the Li^+ cation, for four water molecules and find that the imide type anion-containing salts are liquids at room temperature (therefore possessing numerous

advantageous cell electrolyte properties).(Austen Angell et al., 2012)

ADVANTAGES:

The following are the primary benefits of ionic liquids:

- They have extreme polarity.
- They have a low vapour pressure and are non-volatile.
- They are typically stable and heat resistant to 300 degrees Celsius.
- They are liquid at temperatures as high as 200 °C.(Keskin et al., 2007)
- These substances have extremely high electrical conductivity.
- Numerous typical organic solvents are incompatible with these substances.
- ILs are polar nonaqueous substitutes for phase transfer procedures.(Keskin et al., 2007)
- Numerous different organic, inorganic, and organometallic compounds can be dissolved by ILs.(Keskin et al., 2007)
- The ability to modify the cation or anion to affect qualities like viscosity, melting temperature, water miscibility, and density is

one benefit of RTILs' chemical structures.(Park & Kazlauskas, 2003)

- Ionic liquids with synergistic benefits including enhanced yields, safer delivery of reactive species, or more selectivity. (Chowdhury et al., 2007)
- For certain base-catalysed procedures, the combination of an ionic liquid and an inorganic base has lower catalytic efficiency and is less convenient for recycling.(Ratti, 2014)
- Although this has a lot of benefits, it also prevents the employment of catalysts or reagents that are sensitive to water, which is frequently more significant. Furthermore, it might be extremely challenging to eliminate trace levels of organic compounds from water.(Welton, 1999)

DISADVANTAGES:

Nevertheless, there are certain drawbacks to PEG modification as well. For instance, there may be a lot of work involved in the preparation, and various immobilisation batches may have varied enzyme catalytic characteristics.(Park & Kazlauskas, 2003)

Methos Of Purification and Recovery	Identitive Feature	Advantages	Disadvantages
The process of distillation	When volatile substances are distilled, ILs are left behind as a residue.	Simple to carry out	High energy demand
Crystal formation	IL was recovered as a crystal through solution, melt, and pressure-induced crystallization.	Elevated purity	High energy demand
Membrane Dissociation	Ion exchange membranes allow cations or anions to pass through while cations or volatile compounds are separated, eliminated, or separated using pressure-driven membrane	Selective separation with little energy consumption	Membrane Depletion



	techniques and electrolysis.		
Extracting	Extraction: recovery of hydrophilic, hydrophobic, or both hydrophilic and hydrophobic interleukin (ILs) using organic solvents, water, and supercritical carbon dioxide	Simple to carry out, affordable	Need for specialized equipment and cross-contamination
Field of Force	Using centrifugation, gravity, or magnetic separation, ILs can be separated as immiscible liquids, emulsion, or magnetic fields.	Simple to use, low energy consumption	Low separation rate and restricted application
Separation in Two Phases	Based on temperature-based biphasic separations and chemical addition to water or vice versa: adding salts, carbon dioxide, or polysaccharides to separate biphasic	Quick, affordable, and scalable	High concentration of salts or demand for organics
Combination Approach			
Distillation and centrifugation	Emulsion or immiscible ILs are separated as a residue using centrifugation and distillation.	Elevated purity	Elevated energy needs
Distinction and distillation using membranes	Distillation and pressure-driven membrane techniques: removing organic molecules or water, and separating or eliminating ILs	Elevated purity	Cost-effective method, membrane fouling

FIG: Different techniques for the recovery and purification of ILs, as well as their attributes, benefits, and drawbacks(Singh & Savoy, 2020)

Variations In Ionic Liquid Generations:

1. **Initial generation:** These Ionic liquids are compounds that are commonly used as

solvents. By changing the cations or anions in these compounds, one can improve their unique physical properties. Ionic liquids are presented as the first generation in figure (Ehsan Kianfar & Sajjad Mafi, 2020)

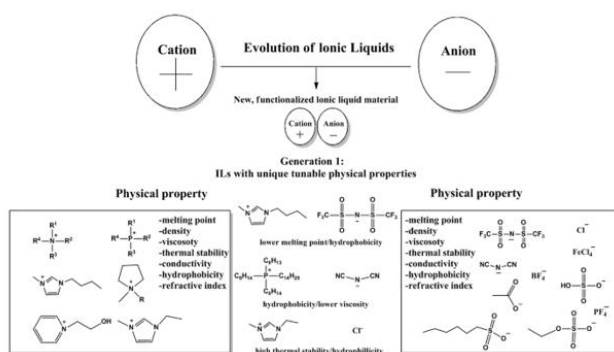


FIG: Physically, chemically, and biologically, the first generation of ionic liquids

Generation two: Ionic liquids with specialised chemical uses are a class of ionic liquids that were created in response to the growing popularity of these chemicals. A cation in these compounds has one or more unique functioning teams that are able to engage in play different chemical roles. For example, they are used as sophisticated ligands

and lubricants. These materials, sometimes known as the second-generation ionic liquids, combine the physical properties already discussed with chemical efficiency. These ionic liquids are presented as the second generation in Figure (Ehsan Kianfar & Sajjad Mafi, 2020)

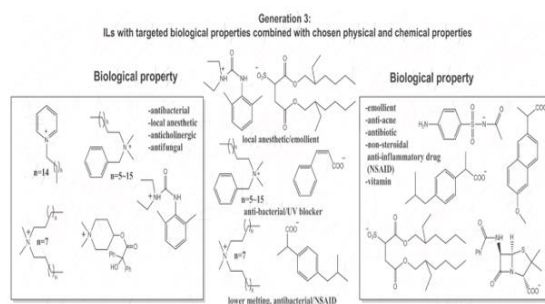


FIG: Physically, chemically, and biologically, the third generation of ionic liquids

Applications:

- Applications for ILs are being investigated in the fields of analytical chemistry, electrochemistry, separation chemistry, cellulose processing, polymers, energy, and organic synthesis and catalysis.(Qureshi et al., 2014)
- Exceptional task specificity with a broad range of uses in extraction and separation, solvent and catalysts, electrochemistry, and lowest environmental release
- Chemistry in engineering, analytical, physical, synthetic, biological, and more(Singh & Savoy, 2020)
- Among the applications of ILs are as liquid crystals, solvents for organic and organometallic synthesis and catalysis, electrolytes in electrochemistry, fuel and solar cells, lubricants, stationary phase for chromatography matrices for mass spectroscopy, supports for enzyme immobilizations, separation technologies, templates for synthesis nanomaterials and materials for tissue preservation, preparation of polymer-gel catalytic membranes and production of high conductivity materials.(Keskin et al., 2007)
- Anions and cations of ILs can independently modify the physicochemical characteristics of the IL (melting point, viscosity, density, conductivity, refractive index, and so forth) and present characteristics for a specific

application (regulating the hydrophobicity and solute solubility as opposed to chirality, hydrophilicity, and the addition of functional groups for catalysis. objectives of responsiveness, etc.)(Ong et al., 2021)

- Key places where ionic liquid is used:

Replacement of solvent Gas purification Both heterogeneous and homogeneous catalysts Media for biological reactions

- These solvents are economically feasible for use in several applications, including polymer impregnation and dry cleaning.(Keskin et al., 2007)

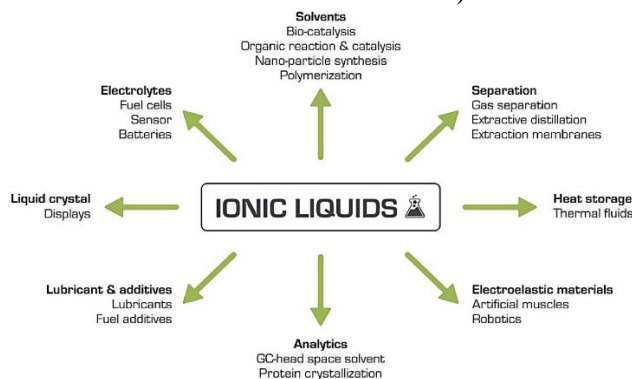


FIG: The use of ILs in many contexts.(Ong et al., 2021)

Formulation Of Ionic Liquids:

Ionic liquids' basic characteristics include their environmental effects and their green elements.(Singh & Savoy, 2020) There are two main methods for making ionic liquids: the first is metathesis of a halide salt with an anion of choice (e.g., silver, group 1 metal, ammonium salt); the other technique is neutralization processes between acids and bases.(Welton, 1999) The first room temperature ionic liquids [EtNH₃] [NO₃] (m.p12 degree c) was discovered in 1914. But it wasn't until the discovery of binary ionic liquids – comprising of mixtures of N-alkyl pyridinium or 1,3-dialkylimidazolium chloride and aluminium (III)chloride-that interest began to rise.(Ratti, 2014) These ionic liquids are always mixtures of organic salts or at least one organic component. N-alkyl pyridinium, N, N'-dialkylimidazolium, alkylammonium, and alkyl phosphonium cations are the most commonly utilized salts. (Welton, 1999) Maintaining the chirality of the original biological applications, over 100 ILs were synthesised directly from either natural AAs or AA ester salts. (Jadhav et al., 2021) Remarkably, the first polysaccharide-based RTIL was produced

in 2007 by synthesizing a polysaccharide. The RTILs were made by combining 1-ethyl-3- 5 methylimidazolium hydroxide with carboxymethylated chitosan.(Jadhav et al., 2021) The one-step synthesis of 1-methylimidazolium halides produced a stoichiometric amount of waste but also maximum atom economy or efficiency. (Singh & Savoy, 2020) In comparison to the conventional conductive heating process, the microwave irradiation approach uses less energy, accelerates reaction rates, increases the desired product's selectivity, and requires less reagent quantities. In some circumstances, the synthesis of ILs without the use of solvents is carried out, resulting in less hazardous waste that is simpler to dispose of. (Singh & Savoy, 2020)Halides and organic substrates containing water are the most significant ionic liquid pollutants. Usually, these substrates come from unreacted materials, which are the starting points of ionic liquid synthesis that don't alter throughout. The primary attributes of ionic liquids are their green components and their influence on the environment.

- **Procedures for making ionic liquids:**

1. Alkylation

2. **Solvent-free synthesis**
3. **Creation of chiral**
4. **Ionic liquid synthesis with a unique performance**
5. **Ion exchange synthesis** (Ehsan Kianfar & Sajjad Mafi, 2020)

1. Alkylation:

A nucleophile, or suitable precursor, and an alkylating agent such as d-alkyl sulfide or haloalkane can be used to form an alkyl cation in a variety of ionic liquids based on ammonium, imidazole, pyridinium and phosphonium. For example, imidazole's alkylation easily yields alkyl imidazole, the main ingredient in ionic liquids based on imidazole. The same is true for halogens of alkanes, which are employed to create alkyl salts of pyrimidine. Halides Phosphorus tetrachloride asymmetric compounds, for example, are often created by raising the halo alkanes and the third type of phosphine's nucleus friendship

2. Solvent- Free Synthesis:

The production of non-alcoholic ionic liquids involves two fundamental steps:

The production of unwanted halide salts following the use of a haloalkane as an alkylating agent during the double anion exchange process. Keep in mind that haloalkanes can be difficult to work with, especially if they have high boiling temperatures that cause them to separate from the reaction product at the end. Furthermore, halide salts- which are produced by double substitution- have a major influence on the physicochemical properties of ionic liquids. Impurities in halide salts or the deactivation of catalysts using an intermediary to allow the ionic liquid, the reaction's solvent, to accelerate metals can both cause poisoning. A wide variety of ionic liquids can be used to make ionic liquids with specific uses or enhanced physical- chemical properties (adjusting physicochemical parameters). Ionic liquids consist of various anions and cations. Anions like BF₄⁻,

BF₆⁻, Br⁻, Cl⁻, and so on are frequently seen. (Ehsan Kianfar & Sajjad Mafi, 2020)

3. Creation of chiral:

For asymmetric synthesis, the use of crystal ionic fluids as a catalyst and solvent is essential material. These molecules come from a variety of chiral sources, including naturally occurring chiral compounds obtained from plants and animals, including amino acids, sugars and terpenes, as well as pre-crystal precursors such as synthetic enantiomers produced industrially. These ionic liquids are often created by an anionic exchange following the alkylation of a pre-crystal precursor. (Ehsan Kianfar & Sajjad Mafi, 2020)

4. Ionic liquid synthesis with a unique performance:

Ionic liquids can be used with large-scale cations or anions. Functional ionic liquids or ionic liquids with special properties like medications, lubricants, and rocket propulsion, are useful solvents in chemical synthesis, catalysts and material applications. Consequently, there is a growing trend in the analysis of the manufacturing process for these materials. There are numerous reported methods for producing ionic liquids with special qualities. Ionic fluids are composed of typically active halo alkanes, and the causative agents in them are imidazolium, phosphonium and pyridinium. One of the initial reports of the emergence of ionic immunosuppressive beverage intended to remove metal ions from water-based solutions. Because anionic exchange occurs between commercial acids and alkaline salts, it is possible to make various ionic liquids using an ionised agent. Other methods exist for sterilising anion, like interested fiction. This approach has been suggested for the creation of ionic liquids containing an anion functionalized from alkyl sulphates. (Ehsan Kianfar & Sajjad Mafi, 2020)

5. Ion exchange synthesis:

Imidazole diacetyl cations are utilized in two processes to prepare hexafluorophosphate and



tetrafluoroborate ionic liquids, two common ionic liquids used in conventional research. The halide salt is initially produced by reacting the necessary cation with the alkyl. The necessary anion is then introduced to the anion halide twice. In this

procedure, an anion of a mineral—such as a metal salt group or silver salts- replaces an anion of an elemental salt.(Ehsan Kianfar & Sajjad Mafi, 2020)

Table: To create ILs linked to 1, 3 di-alkyl imidazolium cations, anionic metathesis is used

Anion	Anion Sources	Chemical compound
[CN(N)2]	NeN(CN)2	Dicyanamide sodium
[SCN]	NaSCN	Thiocyanate of sodium
[BF4]	NaBF4, NH4BF4, and HBF4	Trifluoroboric acid, Trifluoroborate of ammonium, and Trifluoroborate of sodium
[PF6]	HPF6	Acid hexafluorophosphoric
[(CF3SO2)2N]	Li (CF3SO2)2N	Bistrifluoromethylsulfonyl imide of lithium
[CF3SO3]	NH4CF3SO3, CF3SO3CH3.	Sulfonyl imide, or methyl trifluoromethane
[CH3CO2]	AgCH3CO2	Acetate of Silver
[CF3CO2]	AgCF3CO2	Acetate of Silver
[CF3CO2(CF3)]	KCF3(CF3)3CO2	Nonafluoro-1-butanefluoroborate potassium
[NO3]	AgNO3, NaNO3	Sodium and silver nitrates
[N(CH)2]	Ag N(CN)2	Dicyanamide of silver
[CB11H12]	AgCB11H12	Dodecaborate silver
[AuCl4]	HauCl4	Acid chloroauric

Challenges For Formulations of Ionic Liquids: (Ong et al., 2021)

The capacity to construct ionic species is considered to be a significant characteristic of ionic liquids (ILs). This feature enables the adjustment of ions via sidechain lengths on the cation and a variety of cation based ILs, including pyridinium, imidazolium, ammonium, choline, and so on. The production of biodiesel through ILs-catalysed conversion can be enhanced by combining ILs with (i) basic or acid catalysts, (ii) strong molecular interactions between cations and anions, (iii) providing supports or combining with enzymatic catalyst, (iv) mixed acid catalyst

(BAILs) or (v) their contaminations. In general, acidic type ILs (AILs) are employed more often than basic type ILs (BILs). The catalytic activity in esterification and transesterification increases with the acidity or basicity of the ILs in both AILs and BILs. BLAILs and BAILs with numerous acid sites shown better catalytic performance as compared to BAILs with a single acid site. IL creates a biphasic solution at the end of the process because it functions as a dual solvent catalyst. The organic phase (upper layer) is formed in this two-layered solution, and it is kept apart from the aqueous phase (bottom layer). This enables the separation of biodiesel from the IL residues and

the substrate that is retained at the bottom layer. In the meantime, it supports the reaction's forward shift. Additionally, the liquid-liquid, solid-liquid, solid-phase and induced precipitation extraction methods are the ones that are favoured when using IL. Recently, IRs have been employed to manufacture biodiesel in supercritical conditions. Using this supercritical technology aims to solve some of the challenges associated with the traditional heating process, such as the transesterification reaction time at standard pressure and temperature settings. But the evolution of the synthesis of biodiesel by supercritical IL-catalysed reactions is highly restricted. Even though ILs are frequently recognized as "green reaction media" in catalytic processes, they are not inherently green or ecologically beneficial like other catalysts. In particular, the most popular SFILs are extremely corrosive and acidic, with an acidic $[-SO_3H]$ functionalized group in the cation of ILs that has the potential to severely erode equipment. Designing a "greener" IL for the catalytic processes involved in the synthesis of biodiesel is difficult, and much research is required to improve our understanding of the catalytic activity of various IL. Consequently, since no harmful byproducts have been observed to form, acidic $[SO_4]^{2-}$ anion based ILs can be made "greener" by reacting with different alkyl sulphate groups such as hydrogen sulphate ($[HSO_4]$ -methyl sulphate ($[MeSO_4]^-$) and ethyl sulphate ($[EtSO_4]^-$). Furthermore, by forming a biphasic layer with the organic layer, these ILs are stable due to their reusability, which may facilitate the extraction of organic products. Among these, ILs based on $[HSO_4]^-$ anion have been extensively researched for diverse esterification reactions. Since the $[HSO_4]$ anionic component is the only acid site in the ILs, acidic protons on it are all that are required for the chemical process to be correctly activated. Furthermore, $[HSO_4]$ anion-based ILs improve the

digestibility of cellulose for later conversion, such as the synthesis of FAMES (biodiesel), by aiding in the efficient lignin/cellulose fractionation. As a result, using an ILs-catalysed method for the pretreatment stage and the subsequent one-pot catalytic conversions into biodiesel is a workable strategy. This approach inevitably reduces the amount of time, money, and energy needed for the conversions, which is a technological advancement in lowering the amount of solid waste and wastewater produced. Furthermore, the synthesis requires a cheap and simple feedstock, which makes $[HSO_4]$ – anion based ILs more affordable to produce. This is caused by a number of obstacles, including (i) the financial impact of the reusability of both enzyme catalysts and immobilization techniques for ILs in repeated operation cycles, (ii) the development of immobilization techniques for ILs that substituted costly commercial supports, and (iii) the high cost and instability of enzymes.

Properties:

Ionic liquids' critical characteristics, acentric factors, and typical boiling points are determined. Although they were unable to directly check this since there was a dearth of experimental data on the boiling points or critical properties of ionic liquids, they used the values they had obtained in a model to make a fairly accurate forecast of densities. Viscosity, a property of fluids related to internal friction caused by intermolecular interactions, is essential to all physical processes involving the movement of the fluid or components dissolved in it. Thus, the design of reactors, heat-transfer apparatus, distillation columns, process pipelines, and other devices utilized in various chemical and pharmaceutical sectors requires an understanding of the viscosity of fluids and their mixes. The use of volatile and dangerous solvents in these enterprises is a major environmental concern. (Ratti, 2014) It has recently been determined that the materials



listed below are appropriate for this use. All of the following, however, has pros and cons as well as limitations.

A. Supercritical CO_2 ;
Solvents that are fluorinated
Liquids with ions

In the first scenario, supercritical pressure and a temperature are applied to CO_2 gas to cause it to turn liquid and acquire liquid characteristics. The critical temperature and supercritical pressure for carbon dioxide gas are 31°C and 74 bar, respectively. Although it is a green solvent, hyper excitable carbon dioxide has two main issues. The apparatus required to apply supercritical pressure is needed in order to use this solvent. Furthermore, this solvent's range of solvency is extremely constrained. Another class of alternative solvents is fluoride solvents, which have the drawbacks of being costly and producing harmful fumes when heated. A class of substances known as ionic liquids is currently thought to be the greatest substitute for volatile solvents. (Ehsan Kianfar & Sajjad Mafi, 2020)

CONCLUSIONS:

Ionic liquids (ILs) have revolutionized chemical research and commercial processes, ushering in a new era. In spite of their modest origins in specialized research groups, ILs have developed into vital elements in a wide range of disciplines, driving advances in materials science, biology, and chemistry. They have significantly reduced the usage of harmful compounds and made previously inconceivable solutions in homogeneous systems and biocatalysis possible thanks to their exceptional adaptability, eco-friendly qualities, and distinctive physicochemical features. The potential of ILs in biocatalytic applications is being further unlocked by continuous study, despite constraints like enzyme denaturation. While the development of air- and water-stable versions has expanded their uses, from gas filtration to biological reaction media, the utility of

task-specific ILs has increased. Ionic Liquids (ILs) can be categorized into a variety of groups in order to get important understanding of their distinct structures and characteristics. This allows for the development of customized techniques for particular applications. Protic ILs show improved conductivity via proton transfer, whereas aprotic ILs have unique tunability and conductivity potential. Inorganic ionic liquids (ILs) utilize packing problems to generate compounds with low melting points, while solvate (chelate) ILs include multivalent cation salts with special characteristics. Extreme polarity and high electrical conductivity are only two of the many benefits that come with ILs, but there are drawbacks as well, like labour-intensive enzyme synthesis and batch-to-batch variability. Furthermore, issues including price, scalability, and suitability for use with delicate catalysts or reagents could prevent them from being widely used. But current studies to solve these issues are spurring creativity and extending the possible uses of ILs in various scientific and industrial contexts, indicating further progress in the field. Ionic species fine-tuning to maximize catalytic activity, particularly in the synthesis of biodiesel, presents a challenge in the formulation of ILs. Compared to basic ILs (BILs), acidic ILs (AILs) often show greater catalytic activity in esterification and transesterification reactions; multi-acid site ILs demonstrate the highest activity. Through pore structure optimization, supporting ILs on porous materials can increase catalytic activity. In the process of producing biodiesel, ILs operate as catalysts for dual solvents, allowing for biphasic solutions that improve reaction efficiency and product separation. However, as ILs are not widely used in supercritical conditions for biodiesel generation, there is still space for development. Synthesis techniques and optimization strategies need to be balanced in order to adjust the properties of ILs for a range of applications, while



simultaneously addressing problems with catalytic activity, waste minimization, and process efficiency. The goal of ongoing research is to get over these obstacles and realize the full potential of ILs in a variety of chemical and industrial domains.

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