IONIC LIQUIDS AS ALTERNATIVE SOLVENTS FOR ENERGY CONSERVATION AND ENVIRONMENTAL ENGINEERING

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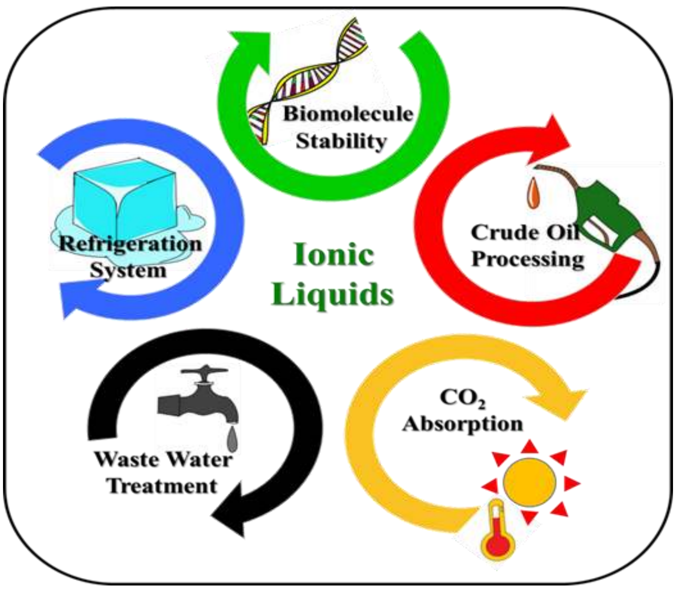
Article history: Received 2 February 2021, Received in revised form 21 February 2021, Accepted 21 February 2021, Available online 23 February 2021

Abstract

Because of industrialization and modernization, phenomenal changes have taken place in almost all spheres of life. Consequently, the consumption of energy resources and the cases of environmental hazards have risen to an unprecedentedly high level. A development model with due consideration to nature and an efficient utilization of energy sources has become the need of the hour, in order to ensure a sustainable balance between the environmental and technological needs. Recent studies have identified the suitability of ionic liquids (ILs), often labeled as 'green solvents', in the efficient utilization of energy resources and activities such as bio-extraction, pollution control, CO_2 capture, waste management etc. in an environmentally friendly manner. The advent of magnetic ionic liquids (MILs) and deep eutectic solvents (DESs) have opened possibilities for a circular economic approach in this filed. This review intends to analyze the environmental and energy wise consumption of a wide variety of ionic liquids and their potential towards future.

Key words
Ionic liquid; green solvent; energy resources; pollution control; bio-extraction; circular economic approach

Graphical abstract



Introduction

Development is the need of the hour, but proper planning and wise use of resources should be vital in minimizing the side effects and achieving the desired targets. The twenty-first-century witnesses a peak in the efforts to establish methodologies, technical support and socio-economic studies related to developmental activities [1]. The attempts to achieve the development envisioned inevitably results in the pollution of the environment. Non-sustainable utilization of energy resources has also aggravated the exploitation of nature and instances of pollution [2]. There is in fact a popular saying that 'any development which lacks its concern on nature is as good as being suicidal'. Even in recent times, our society is confronted by the detrimental impacts of industrialization and modernization which were preceded by globalization policies. Despite all the developments that we have achieved, we still struggle with unaddressed issues such as global warming, acid rains, air pollution, improper waste management and so forth. Therefore, one needs to note here that the method of development, efficient utilization of the energy resources and conservation of nature are interlinked to each other. An eco-friendly sustainable development model that maintains a holistic balance between these three aspects has undoubtedly become a necessity [3].

It is in this context the emergence of a new class of chemicals, namely ionic liquids (ILs), become vital [4]. Room temperature ionic liquids (RTILs) are a class of non-molecular compounds that are comprised of only ions with advantages in various physicochemical properties such as negligible vapor pressure, high thermal stability, high extraction capability, and tunability according to applications. Owing to these unique characteristics, ILs have the prospects to be a tool to achieve sustainable development and are often referred to as "green solvents". Due to their unique properties in comparison to conventional chemicals, RTILs have been extensively used in various fields including metal processing, bio-catalysis, environmental remediation and biological extractions [5–7]. New generation ionic liquids, which are a version of the above mentioned, incorporate transition metal or rare-earth metal ions in their structure and possess inherent magnetic properties. These ILs were categorized as magnetic ionic liquids (MILs) and have got advantages over conventional RTILs in thermal stability, vapor pressure, magnetic separation and recycling [8,9]. Similarly, as they share multiple properties and characteristics with ILs, deep eutectic solvents (DESs) are now commonly accepted as a new class of ionic liquid analogues. DESs are systems formed by a eutectic combination of Lewis or Bronsted acids and bases which could contain a number of anionic and cationic species. [10]. All these chemicals are categorized under 'ionic liquid chemistry'- the most explored branch of chemistry in recent years. The major increase in the number of publications in this field year by year indicates the importance and wide use of ILs in key areas (Fig. 1).

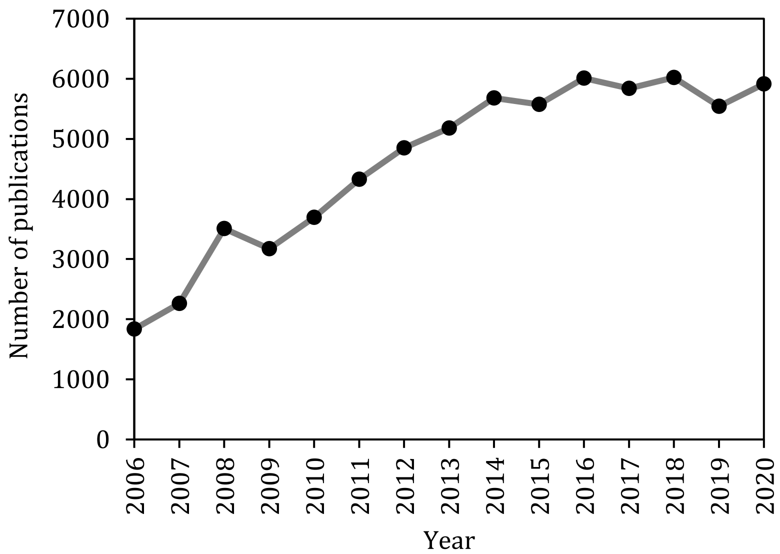


Fig. 1. Year wise publications on ionic liquids from 2006 to 2020. *Source: SCOPUS*

https://doi.org/10.32933/ActaInnovations.38.6• ISSN 2300-5599 •

The current review addresses the environmental concerns and inefficient energy resource utilization and analyzes the role of ionic liquid chemistry to tackle these hurdles. Conventionally, organic solvents have been extensively utilized for these applications. They are highly volatile, cytotoxic as well as ecotoxic. These disadvantages can be rectified by the use task-specific ionic liquids, as we can design them according to the desired application. As the area of interest is very vast, the main focal points were restricted to the role of ILs in crude oil industry, refrigeration process, CO_2 sequestration and wastewater management. This study also attempts to brief the application of ILs in the extraction and storage of biomolecules, which could unveil their importance as a bio-economic tool. The recent research trend in these fields is depicted (Fig. 2) and the constant increase in the number of publications towards this end indicates the unavoidable role of IL chemistry in our area of interest. Therefore, a deeper analysis of these results and a detailed study of the ionic liquids involved in them will obviously help to sharpen and reemphasize the goals of sustainable development. This can further help to improve the developmental efforts in the above-mentioned fields, as envisioned in this review.

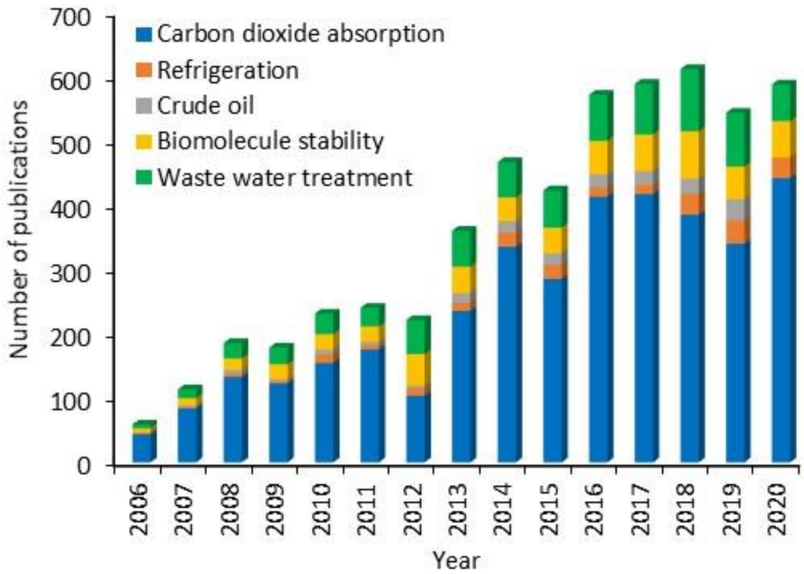


Fig. 2. Recent research trend in ionic liquids for the field of energy and environmental engineering. *Source: SCOPUS*

Role of green solvents in sustainable development

As mentioned in the introduction part, the role of ionic liquids and deep eutectic solvents in energy conservation and in environmental engineering is being discussed in detail under four subtopics.

Crude Oil Industry

The oil and gas industry forms the lifeblood of the global market and is one of the major contributors to the global economy. The economic framework of any nation is greatly influenced by the detection of oil fields, processing and production of oil. The dominance of oil as a potential energy source is attributed to its indispensability in the transport sector and the production of many everyday essentials. The refined products developed from oil constitute the key ingredients for the manufacture of almost all chemical products and other commercial goods [11]. The oil and gas industry can be broadly broken down into three segments based on their operational responsibilities: upstream, midstream and downstream. The primary responsibilities of upstream companies include exploration of reservoirs and drilling of oil and gas wells. Midstream and downstream companies are responsible for shipping crude oil from wells to refineries, refining and distributing oil products. Upstream oil industry can be classified into four categories: drilling operations, enhanced recovery of oil, non-conventional heavy oil recovery and flow assurance. The extreme conditions associated with these operations, such as high reservoir salinity, high temperature and heat, render the use of normal solvents undesirable.

Because of their unique chemical characteristics, especially the ease of tunability, ionic liquids have therefore emerged as a suitable alternative. Ionic liquids can function as an extraction agent during downstream refining processes to eliminate impurities from crude oil derivatives [12,13].

A fluid or mixtures of fluids, namely drilling fluid, is typically used in operations that involve the drilling of a borehole into the earth. According to the composition, these drilling fluids can be classified as water-based, non-aqueous based and pneumatic. A critical challenge in drilling applications is the development of cake buildup, resulting from the leakage of the drilling fluid into the formation matrix. Although cake build up to a certain degree is desirable, the excess formation of the same can result in stuck pipe issue and other drilling problems. Fluid-loss additives are generally used to control this process and avoid potential reservoir damage [14]. Recent literature studies show that ionic liquids can be used prospectively to control this fluid loss. A study on the feasibility of the use of ionic liquids as a potential drilling fluid additive for high-temperature wells has been envisaged by Ofei et al. [15]. The study validates the use of ionic liquids as a drilling fluid additive and their capability to maintain the rheological properties of water-based mud at high operating temperatures. The rheological and filtration behaviors of water-based drilling mud have been studied by using 1-butyl-3-methylimidazoliumchloride (BMIM-Cl) as the model compound, over a temperature ranging from room temperature to 200 °C and to a pressure limit of 1000 PSI. The study indicates that the addition of BMIM-Cl stabilized the viscosity of the mud, solid suspension capacity and filtration behaviors up to 180 ° C. Further, the suitability of 1-methyl-3-octylimidazolium tetrafluoroborate (OMIM-BF_4) was evaluated as a possible additive to polymer-water based mud [16]. The results from this study reveal that OMIM-BF_4 has effectively improved the rheological properties as well as the consistency index of the polymer-water based mud. The key factor which attributes to this improved behavior is the presence of long alkyl chain in OMIM-BF_4 and thereby the possibility of hydrophobic adsorption. Another example of the fact related to drilling fluid additives has been established by Yang et al. Their main focus was on bentonite/water-based drilling fluids, which were characterized by a significant fluid loss due to high temperature-pressure levels and divalent cation concentrations. The filtration control was achieved through free radical copolymerization in presence of 1-vinyl-3-ethylimidazolium bromide [17]. The in-depth studies on the rheological and hydration inhibition potentials have provided systematic guidelines to design novel sets of drilling fluid- IL combinations for the drilling of gas hydrate rocks [18–20].

In addition, ILs and DES have also been used as clay stabilizers and shale hydration inhibiters. Clay swelling is a type of damage that results in the reduction of formation permeability due to the alteration of clay equilibrium. The influx of water-based filter fluids into the forming matrix and ion exchange are two major factors for the occurrence of the clay swelling. To solve this issue, it is very important to understand the structure of the clay and its chemical condition at the moment of contact. Chemical additives (clay stabilizers) may be used as a measure to reduce clay swelling. The filtrate fluid's charge and electrolytic properties can be efficiently controlled by the clay stabilizers and the clay platelets can be held in place. Imidazolium-based ionic liquids have been identified as a possible inhibitor of clay swelling and research in this area is progressing at a brisk pace [21]. Shale oil is the unconventional oil extracted from a class of fine-grained classic sedimentary rocks known as shale rocks. Shale hydration results from the interaction between the exposed shale formation and water-based drilling fluids during reservoir exploration. Therefore, the research on shale hydration inhibitor is worthwhile. Luo et al. initiated the studies on the potential of ionic liquid as shale hydration inhibitor. They have prepared a model drilling fuel by mixing distilled water, sodium montmorillonite and sodium carbonate. Through various tests, they have proved the greater affinity of the drilling fluid towards the inhibitor ionic liquid 1-octyl-3-methylimidazolium tetrafluoroborate [22]. Yang et al. synthesized 1-vinyl-3-ethylimidazolium bromide and analyzed its performance as a shale hydration inhibitor in detail [23]. Later, the effect of alkyl-chain lengths on the vinylimidazolium group on hydration inhibition activity was analyzed by the same group. The efficiency of IL inhibition decreased with increase in alkyl-chain length. When alkyl chain length increases, IL molecular volume increases while the hydrophilicity and solubility of the IL decreases. This minimizes the interlayer space and thereby the hydration inhibition activity. [24]. The effect of 1-octyl-3-methylimidazolium bromide (OMB)

https://doi.org/10.32933/ActaInnovations.38.6• ISSN 2300-5599 •

as shale hydration inhibition agent has been explored by Xu et al. Compared to conventional shale inhibitors, superior shale hydration inhibition properties were observed in the case of OMB. [25].
Ionic liquids have an undisputed role in the enhanced oil recovery (EOR). Enhanced oil recovery (improved oil recovery), which generally happens in the third stage of oil recovery, restores formation pressure and improves oil displacement in the reservoir. The oil recovery enhancement method using sophisticated techniques alters the original properties of the oil. Ionic liquids can alter the wettability and interfacial tension accordingly to the required levels and are stable under high temperature and high saline conditions within the reservoir [26]. Therefore, ILs were identified as the right candidates EOR processes. In a detailed review on surface-active ionic liquids used in surfactant-based enhanced oil recovery processes, Nandwani et al. analyzed recent trends in this particular field. Their review focuses on the efficiency of surface-active ionic liquids (SAILs) to reduce interfacial tension (IFT) between oil and water under prohibitive environmental conditions. The study compares different SAILs used in EOR applications till date and lists out their advantages and disadvantages [27]. Prathibha et al. studied the advantages of polyionic liquids (PILs) in the field of EOR. Their primary focus was on the EOR properties of poly [1-hexadecyl-3-vinyl-imidazolium bromide]. The study analyzed the interaction of the synthesized PIL with aqueous injection fluids and crude oil with respect to different properties such as interfacial tension, wettability alteration and dynamic light scattering (DLS). IFT values were decreased with increase in temperature and salinity. The importance of poly ionic liquids in the EOR process is underscored by the positive observations obtained during the wettability and DLS studies [28,29].

Unconventional heavy oil recovery field has also started utilizing the services of ionic liquid chemistry in recent times. Unconventional recovery is the recovery of oil other than conventional method. This unconventionality can occur in resource characteristics, production technologies, economic environment or the scale of production. Coal bed methane, gas hydrates, shale gas, fractured reservoirs and tight gas sands are considered as unconventional resources. The major application of ionic liquids in this field is that they could act as a viscosity reduction agent of heavy crude and as an effective kerogen extractant (kerogen is the portion of naturally occurring organic matter that is non-extractable using typical organic solvents) [30]. Flow assurance, which involves design, techniques and principles for ensuring uninterrupted hydrocarbon supply from the reservoir to the point of sale, is another crucial task in the crude oil industry. As they move into the processing plant, fluids undergo changes in pressure and temperature and result in multiple fluid phases. In consequence, the formation, accumulation and dispersal of inorganic and organic solids can occur. Major disadvantages of this process are asphaltene precipitation, wax deposition and gas hydrate formation. According to recent studies, ionic liquids have the capacity to control asphaltene precipitation, wax deposition and they act as methane gas hydrate inhibitors [31].

Processing of crude oil is essential from economic and environmental perspectives. Contemporary research shows that dispersion of crude oil, oil acidity reduction, bitumen extraction, carbonate mineral separation and many other related processes can be carried out using ionic liquids [32–35]. Removal of hazardous particles has greater significance because it will increase the efficiency of the fuel as well as decrease harmful emissions during burning. For example, air pollution and even acid rain is caused by the emission of toxic sulfur and nitrogen oxides during fuel combustion. Therefore, its removal from the fuel is significant. Recently, ionic liquids have been developed to extract sulfur and nitrogen compounds from petroleum and fuels. Ionic liquids are used to extract S- and N- compounds either combined or selective. ILs were found to be far better option than classical desulfurization and denitrogenation agents due to their enhanced efficiency and selectivity [36]. Wang et al. have examined over the ability of oxidative desulphurization of coal, as the sulfur dioxide and soot which emerges out during the combustion of coal are the main sources of air pollution. In their investigation, they have used imidazolium based ILs, namely, 1-butyl-3-methylimidazolium bisulfate and 1-carboxymethyl-3-methylimidazolium bisulfate to extract sulfur from coal [37] Patra et al. analyzed the effect of nitro groups

https://doi.org/10.32933/ActaInnovations.38.6• ISSN 2300-5599 •

on desulfurization efficiency of benzyl substituted imidazolium-based ionic liquids. The liquid-liquid microextraction approach was adopted and the parameters influencing extraction efficiency, such as the effect of IL volume, concentration and rotation period, were extensively studied. The analysis focused on the effect of Lewis acidity, the availability of the Lewis acid site and the π-π interaction on the efficiency of desulphurization of ILs. [38]. However, its main disadvantage lies in the sessions of regeneration and recycling. The limitations of ILs such as environmental biodegradation, bioaccumulation and corrosivity have to be addressed and the researchers have to focus on the ways to overcome it.

Majority of studies on the application of ionic liquids in the crude oil industry are based on microscale laboratory experiments. Therefore, recommending them instead of conventional chemicals for the field application has to be done after extensive large-scale testing. However, the growth and development of ionic liquid in this domain is remarkable. Recent article on the role of ionic liquid catalysts in trans-esterification of different feedstock oils to biodiesel [39] is opening up a possibility of an eco-friendly economy. Scientists are even experimenting with ionic liquids to develop it as an alternate fuel by modifying the chemical structure. Though it is too early to predict the effectiveness of ionic liquids in large scale crude oil production, laboratory experiments are offering hope towards an eco-friendly sustainable development.

<u>Refrigeration systems</u>

Refrigeration is the process of cooling a space or a substance below room temperature, which indeed is an energy consuming process. Compression and absorption refrigeration systems are the two most common refrigeration systems used for household and industrial applications [40]. In compression cycles, gaseous refrigerant is compressed at low temperature and pressure in the compression chamber and is entered to the throttling valve. Here it expands and releases the pressure, consequent to which the temperature of the surrounding drops down. Whereas, in the case of absorption refrigeration systems, a liquid refrigerant gets evaporated at low partial pressure with the help of renewable heat energy sources or waste heat, drawing away some amount of heat with it giving rise to a cooling effect. Later, this refrigerant in gaseous form is absorbed by another fluid from refrigerant- saturated liquid solution having low partial pressure. The refrigerant-saturated liquid is then heated, causing the evaporation of refrigerant [41].

Hydrofluorocarbon (HFCs) and hydrofluoroolefins (HFOs) have been proposed as the new generation refrigerant in refrigeration and cryogenic process, which creates low temperature spaces, nearly cryogenic temperature range (-150 ˚C to -273 ˚C). However, they cause a lot of environmental problems like global warming and ozone layer depletion [42]. Therefore, the research on designing more efficient and environment friendly refrigerants and refrigerant/absorbent pairs with improved cooling capacity and coefficient of performance (COP) is essential. Considering the properties of the refrigerant, it should have high enthalpy of vaporization, low molar mass and high solubility in the selected absorbent to minimize the operating and investment costs [43]. The coefficient of performance (COP) of the refrigerator depends on the solubility of refrigerant in corresponding absorbents. The absorbent must be a fluid with a low vapor pressure to avert its evaporation. In addition, it should possess a low freezing temperature. Low viscosity of absorbent reduces the energy spent during transport and improves flux of mass and energy [44]. Finally, it is essential that both refrigerants and absorbents should be thermally and chemically stable over a range of temperatures.

Water, though non-toxic and non-flammable and shows high enthalpy of vaporization per unit mass, is not a well preferred choice as a refrigerant at temperatures below 0 ˚C and atmosphere pressure, owing to its high triple point temperature and low vapor pressure [43]. Use of H_2O with LiBr as absorbent in absorption refrigeration cycle is an example of a conventional refrigerant/absorbent pair, showing high performance due to their high solubility and the high-water mass cooling capacity. The major disadvantage of H_2O-LiBr systems is the

https://doi.org/10.32933/ActaInnovations.38.6• ISSN 2300-5599 •

crystallization of absorbent rich solution at low temperatures [45]. Alternatively, NH_3/H_2O system can work as a refrigerant/absorbent pair at temperature -77 ˚C and pressures near 4-20 bar. The limitation of this mixture is the small difference in volatility between the compounds [46].

Recent studies have explored the use of Ionic liquids (ILs) as an alternative to the traditional absorbents, by virtue of their high absorption capacity of gases, very low vapor pressure and good thermal stability. Low volatility of ILs allows the separation of refrigerant in refrigerant/ absorbent mixture [47]. Solubility of NH_3 on imidazolium ILs with different chain length have been studied by Li et al. and is concluded that NH_3 solubility increases with increase in cation chain length [48]. In order to improve the solubility of ammonia in ILs, Bai et al. proposed a new idea of introducing Na^+ ions into ILs for the first time [49]. Since the refrigeration experiments are more expensive and sometimes dangerous, theoretical approaches have also been envisaged to correlate the gas solubility in various ionic liquids. Karakatsani et al. used the tPCPSAFT association model [50] to tackle the task while Shiflett and Yokozeki used the Redlich-Kwong EoS model for the same. Later studies by Yokozeki et al. approached the task through a generic van der Waals EoS [51] while Freitas et al. used two cubic equations of state (PR and SRK) with van der Waals 2-parameter mixing [52] rules (vdW-2) to test the theoretical probabilities. The more promising approach in this field was carried out by Shojaeian et al., where they have used Peng Robinson-two State equation of state in order to correlate the gas solubility in various ionic liquids [53]. Moreno et al. studied different combinations of refrigerant/IL pairs out of 8 refrigerants in 900 ionic liquids using Henry's constant as the key thermodynamic parameter and COSMO-RS molecular simulations [40]. All theoretical models mentioned above, successfully predicted the solubility of refrigerant gases in ILs in the absorption cycle for different cooling temperatures.

Apart from this, ILs have been proposed as mass separating agent called entrainer for the separation of azeotropic or close-boiling point blends of refrigerant gases (HFCs and HFOs) and provide selective solubility [42]. HFCs solubility in different ILs is associated with their ability to form hydrogen bonds and different HFC compounds show different solubility due to their differences in molecular masses [54]. Delgado et al. studied the selectivity of [C_2mim] [SCN], on the separation of HFCs and HFOs, due to its low molar mass and low viscosity [55]. Shiflett et al. have correlated the solubility behavior of refrigerants with the electric dipole moment and have inferred that more the value of dipole moment, higher is the solubility [47]. Morais et al. studied the vapor-liquid equilibrium (VLE) of HFC-32 and HFC-125 in fluorinated and non-fluorinated imidazolium based ILs and HFC compounds have shown more affinity towards fluorinated ILs [55]. Delgado et al. studied solubility and diffusivity of HFC-32, HFC-134a, and HFO-1234yf in less viscous ILs and concluded that solvation is enthalpically favorable and entropically unfavorable [56].

In nutshell, to date, the major studies on the role of ILs in refrigerant chemistry is analyzed from a theoretical perspective. Once the theoretical data looks convincing, scientists can proceed to the micro-scale laboratory level and then to a large-scale industrial level. The hopeful fact is that some of the research groups have preceded to the second stage which focuses on the practical applicability of the developed refrigerant/absorbent combination based on ILs to wet lab conditions. In addition, studies have also been carried out to develop ionic liquids that can be operated in cryogenic conditions without losing the fluid properties. Another developing area of research is towards developing ionic liquids with improved ammonia solubility, which can be prospective substitute for HFC based refrigerants used in household applications.

Environmental Applications

The whole world is striving to achieve the ultimate development in each sector, but unfortunately, it is happening at the expense of environment. It is imperative to reduce the number of processes that are hazardous to the nature, but the fact is that most of these processes are the bedrock of the global economy. This contradiction is the main point to address, especially in the current circumstances. This is where the concept of eco-friendly

https://doi.org/10.32933/ActaInnovations.38.6• ISSN 2300-5599 •

sustainable development comes into the picture. Proper treatment of industrial effluent, controlling the smoke from vehicles and industries, waste management, reducing biomagnifications and a multitude of such herculean tasks are out there in front of the human community. Latest studies illustrate that ionic liquids have the potential to address some of these environmental issues and some are capable of pollution control. The numerous structural modifications possible on the anionic and cationic moieties in ILs allow us to synthesize compounds with desired characteristics. These special properties of ILs have the benefit in the environmental engineering as we can design a particular ionic liquid to address a particular environmental issue.

Greenhouse gas emission, especially from natural gas sweetening and flue gas treatment, causes global warming. CO_2 is a well-known greenhouse gas that contributes significantly to climate change and global warming. A report published in 2018 by the Intergovernmental Panel on Climate Change (IPCC) titled "Global Warming of 1.5" states that global temperatures are expected to rise by 1.5˚C in 2030 [57]. To minimize global warming and ocean acidification, it is very important to control the excessive concentration of CO_2 in the atmosphere. Several techniques such as absorption, adsorption, membrane separation and bio fixation have been developed in this field. But they are inadequate in terms of efficiency. Therefore, researchers in this area have been motivated to develop efficient, cost-effective and novel materials for capturing greenhouse gases and ionic liquids are at the forefront of contemporary research in this field. Blanchard et al. reported that CO_2 is highly soluble in 1-butyl-3-methyl imidazolium hexafluroborate ([BMIM][BF_6]) [58]. Later studies were conducted to improve the solubility range of CO_2 in ILs. The solubility of CO_2 seemed to be increased by amino-functionalized task-specific ILs with imidazole or pyridine ring. Based on the interaction of the CO_2-amine group, ILs containing multiple amine sites were developed [59]. A new dual functionalized IL containing amine and amino acid groups in the imidazolium ring was prepared by Lu et al. High CO_2 absorption capability, thermal tolerance and regeneration capacity were exhibited by these ILs [60]. Recently, Martin et.al proposed a study on selection and characterization of non-ideal ionic liquids in CO_2 capture [61]. A novel absorbent medium comprised of amino-functionalized ionic liquids (AFILs) dissolved in ethanol-water solvent was developed by Huang et al. The solution gets separated into two phases after CO_2 absorption and this phase transition behavior depends on the water-ethanol ratio [59]. In addition to the effect of functional group, the nature of cations and anions plays a key role in the capture of CO_2. Aki et al. reported that with the increase in alkyl chain length from butyl to octyl, CO_2 solubility is getting increased [62]. A series of amine-functionalized imidazolium cation-based ionic liquids with different anions were studied by Sharma et al. and found that anions containing fluorine had a stronger affinity for CO_2 capture [63]. Ramkumar et.al conducted the studies on CO_2 absorption capacity of guanidinium based carboxylate ionic liquids and found to be highly efficient [64]. Another method that is extensively used for the selective isolation of CO_2 is membrane separation. A membrane technology called supporting ionic liquid membrane (SILM), is used in this technique to achieve gas separation. Poly-ILs were observed to have greater absorption capacities and faster rates of absorption/desorption rate than monomers of ILs, and can thus be considered as very promising candidates for membrane material [65]. The suitability of deep eutectic solvents (DESs) as a possible solution to ILs has also been explored in recent studies. This has many favorable benefits compared to normal ILs, such as biocompatibility, biodegradability and recyclability. The primary drawback of ILs and DES is their high viscosity. Ren et al. synthesized DES based on hydrophilic polyols such as L-arginine and glycerol for CO_2 solubility to address this issue [66].

The significance of ionic liquid in wastewater treatment is another field that has been extensively studied. The dispersive liquid-liquid extraction method is used to perform most of these studies [67]. As they are directly discharged to the river or any other aquatic reservoirs, improper treatment of industrial effluents may cause a plethora of problems. This can have a negative impact on the life cycle of marine animals and can alter the equilibrium of the existing ecosystem. The removal of heavy metal from activated sludge and wastewater is of prime importance since many terrible incidents have already happened in our world, such as the Minamata incident. Removal techniques for heavy metals like cadmium and lead from drainage samples and activated

https://doi.org/10.32933/ActaInnovations.38.6• ISSN 2300-5599 •

sewage using quaternary ammonium and phosphonium ILs were demonstrated by Fuerhacker et al. in 2012 [68]. Heavy metal removal from activated sludge has proven to be more efficient than conventional approaches such as incineration and extraction by acid. Proper and scientific management of textile wastewater containing colorants and other chemicals is of great importance. With the use of activated carbon modified ionic liquid, Afrin et al. have put forward an innovative approach for handling wastewater from the textile industry [69]. In contrast with traditional methodologies, this approach yielded good results and demonstrated advantages in terms of selectivity, stability and adsorption capability. According to Tangatova et al. certain ionic liquids can influence microorganisms present in the activated sludge and accelerate the rate of biological wastewater treatment [70]. The removal of various forms of organic contaminants such as pesticides, insecticides, micro-pollutants and other chemical components from the water resources is a sub-area of the same field, and the advancement of research in this area is also worth noting. Jingying et al. have conducted studies on the separation, recycling and management of a large variety of organic contaminants with ILs. Phenolic agents, toxins, solid waste and some waste gases were in this list of pollutants [71].

With the introduction of magnetic ionic liquids and deep eutectic solvents, research related to wastewater treatment has been elevated to the next level. A wide range of MILs and DESs have been synthesized for the extraction of pollutants. Hydrophobicity, structure and Lewis acidity of MILs/DESs play a key role in the extraction efficiency. Their significant advantages are recyclability and reusability. Florindo et al. have put forward a circular method using hydrophobic deep eutectic solvents to purify water polluted with micro-pollutant drugs. Ciprofloxacin, classified as one of the top ten important micropollutants, has been isolated using DESs comprising quaternary ammonium salts and natural fatty acids. A circular method has been developed by the group to recycle and reuse hydrophobic DES through the use of activated carbon [72]. Sas et al. focused on the elimination of phenolic pollutants from water reservoirs using organic acids and DESs based on menthol. The findings obtained from similar RTILs were compared with the experimental data and was shown to be more advanced [73]. Silva et al. employed magnetic ionic liquids to identify organic pollutants in river water samples [74]. The detection and elimination of pesticides from water sources is also of primary importance. Since the advent of ionic liquid chemistry, research in this field has found a new vigor. Liu et.al, conducted a series of experiments to detect, extract and analyze organophsophorous pesticides from water samples with imidazolium ionic liquid and the findings were promising [75]. A similar method was explored by Tatjana et al. in which the imidazolium ionic liquid-based vortex-assisted liquid-liquid microextraction method was used to determine the presence of four pesticides in an industrial wastewater sample [76]. Wilms et al. recently performed a detailed study on the potentials and possibilities of herbicidal ionic liquids. This study objectively analyzes both the merits and demerits of ionic liquids in the view of herbicidal properties and adds their thoughts to improve the contemporary research methodologies [77].

Modern research studies concentrate on the development of new ionic liquids that are more eco-friendly and efficient for the extraction of contaminants [78]. For the aforementioned reason, efforts have also been made to design biocompatible polymeric ILs. In addition, experiments based on magnetic ionic liquids are proceeding in the right direction, and this can deliver a groundbreaking result in terms of reusability. Recently researchers are also showing interest in the designing of IL-coated membranes that are biocompatible for the same application. Scientists are also in pursuit of developing methods for regenerating the absorbed CO_2 in order to produce fuel out of it which is a big hope in the field of renewable energy and engineering.

Biomolecule extraction

Production, extraction, purification and storage of bioactive compounds are getting much attention in modern day research because of their unavoidable role as a biochemical and nanotechnological tool. The existing methods to extract and purify biomolecules incorporate environmentally hazardous chemicals and have several other drawbacks such as low extraction efficiencies, poor selectivity and lack of cost effectiveness. Most of the

https://doi.org/10.32933/ActaInnovations.38.6• ISSN 2300-5599 •

existing methodologies require multiple and nonconventional operations which could affect the molecule's inherent biological nature and properties. To rectify these disadvantages, scientists were in active quest for an alternative solvent and it resulted in the incorporation of ionic liquid in the field of biomass extraction. Applications of ionic liquids in the biological and biomedical field are getting explored rapidly in recent times as they possess improved solvation ability, easily tunable nature and environmental benign behavior. They are task specific solvents, the quality which improves the extraction efficiency and relaxes the hectic purification procedures. To analyze the growth in this area of research a wide range of bioactive compounds can be considered, but our area of focus is restricted to the field of amino acids, proteins and nucleic acid chemistry where the ionic liquid related research is at top gear. [79–82]

Proteins are macromolecules of structural units called amino acids *and they* are very much essential in the vital functioning of an organism. In addition, proteins have got huge impact in different industrial sectors. The isolation and storage of proteins are, therefore, very important in biological and economic sense. The ability of ILs to enhance the stability of the native states of proteins, to gear up their refolding capacity and to subdue the irreversible aggregation pattern have provided a new outlook to the protein related research. Amino acid extraction and storage is also very much essential as they are the building blocks of any protein. According to the literature, there are four main techniques used in amino acid and protein extraction namely solid phase extraction (SPE), liquid-liquid extraction (LLE), IL-based three-phase partitioning (TPP) and IL-based aqueous biphasic systems (ABS) [79].

IL-based SPE methods aimed at extracting amino acids and proteins was mainly done through IL modified materials – such as IL immobilized silica and ILs on the molecularly imprinted polymers (MIPs). Direct extraction technique was also attempted by various groups of scientists, but in general, SLE is less explored due to the relative difficulty to establish the experimental setup and lower extraction efficiency. Liquid-liquid extraction emerged as an effective substitute due to its advantages in experimental pattern, selectivity and extraction efficiency. The pioneering study in the amino acid extractions based on LLE approach was done in 2003 where 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF_6) as the extractant. Tryptophan, glycine, alanine and leucine were amongst the amino acids and some of them were not directly soluble in this ionic liquid. To have similar extraction efficiencies for both hydrophilic and hydrophobic amino acids, the ionic liquid structure was modified by adding the crown ether [dibenzo-18-crown-6] at acidic pH [80]. Following this, Smirnova et.al attempted the extraction of a wide variety of amino acids by using the same ionic liquid. The extraction was from aqueous solution to the IL phase with dicyclohexano-18-crown-6 as an additive (pH range 1.5- 5.5). The most hydrophilic amino acids were extracted as efficiently as the less hydrophilic and the extraction efficiency was above 90 percent. The influence of pH, amino acid and crown ether concentration and volume ratio in this process were studied in depth [81]. The synthesis of hydrophobic ILs by tuning the cationic and anionic moieties was achieved later in the decade since hydrophobicity was the key property which influenced the flow of majority of amino acids to the IL rich medium. Imidazolium based long chain ILs were widely used for this application [82–84]. Back extraction was done mainly by specific buffers. In Parallel, the efforts to extract a wide variety of proteins were also flourishing. But the scope of the studies was restricted by the fact that the dissolution of protein required the presence of hydrated ionic liquids. Still, many proteins including lysozyme, cytochrome-c and heme were extracted successfully by LLE method [85].

The biggest drawback of LLE lies in the use of organic solvents, which may have a detrimental effect on biomolecules, human health and the environment. As an alternative to conventional extraction methods, aqueous biphasic system (ABS) has been researched due to the aforementioned reasons. Aqueous biphasic systems (ABS) are also a class of liquid-liquid extraction systems which, due to their potential use as alternatives for organic solvents in extraction and separation systems, have gained considerable interest in the research community. The main benefit of using ABS is that it is composed of two water-soluble solutes that separate into

https://doi.org/10.32933/ActaInnovations.38.6• ISSN 2300-5599 •

two co-existing phases at their optimum concentration. Since the major constituent is water, ABS is more biocompatible and also provides benign media for the extraction of various biomolecules. Here the extraction takes place based on the various interaction between extractant and biomolecules such as hydrogen bonding, π-interactions, electrostatic interaction and hydrophobic interactions by which biomolecules get separated to either IL rich phase or salt-rich phase. The studies on amino acid extraction with IL based ABS by Ventura et al. is worth mentioning. In their work, a wide range of imidazolium- based ILs were studied in detail. The extraction capacity of the ABS was evaluated through the extraction of amino acid L-tryptophan. Extraction capability was analyzed by setting different kind of cation anion combinations. As the hydrogen bond acidity of the IL anion plays a crucial role in the formation of ABS, the anion effect on ABS formation was found to be pivotal [86]. The amino acid extraction efficiency of ABS in the presence of biodegradable organic salt has been studied by Ferreira et al. The organic salt potassium citrate was conjugated with imidazolium-, pyrrolidinium-, phosphonium- and ammonium based ILs for L-typtophan extraction. The study underlined the fact that hydrophobic interaction has a major role to play in the whole process. They also observed that the separation of biomolecules between the ABS phases depends on their affinity for each other, which further depends on parameters such as pH, temperature and composition of the system. [87]. Following this many groups investigated the amino acid extraction through ABS technique. An interesting one to mention is by Priyanka et al. In the presence of different potassium salts at 298.15 K, they analyzed the phase activity of benzyltrimethylammonium chloride and benzyltributylammonium chloride. The effect of substitution of the benzyl group on the IL cation and the nature of different potassium salts on the phase activity were studied. In the presence of different potassium salts, these IL-based ABS have been systematically scrutinized for their efficacy in tryptophan extraction. For the examined combinations of ILs and inorganic salts, improved extraction coefficients were achieved [88]. Many studies on IL based ABS for protein extraction were also reported. Since protein is a larger moiety in comparison with amino acid, the factors influencing the stability of proteins in IL medium was analyzed in prior. It is found that the selection of constituent ions and the chemical nature of the ILs play a critical role in the stability. ILs containing high kosmotropic anions and cations with enhanced chaotropicity showed a higher efficiency. The observations made by Du et al. is of prime importance. To directly isolate proteins from human body fluids, the group used the IL-ABS system based on 1-butyl-3-methylimidazolium chloride (BMIM-Cl) and K2HPO4. In the IL-rich upper phase, proteins present at low levels were quantitatively extracted. The K_2HPO_4 addition to the IL rich phase (after separation) has resulted in a further phase separation and an elevation in enrichment factor was also observed. After the whole process, protein's natural structure and properties were found to be unaltered [89]. A detailed review on recent trends in protein extraction using ABS was done by Lee et al. in 2017. The review listed out almost all the studies during the last decade on IL-ABS systems for protein extraction and separation. A broad variety of cations (e.g., imidazolium, cholinium, ammonium, phosphonium and guanidinium) and benign anions (e.g., carboxylic acids, amino acids and biological buffers) were also examined for their relevance in the process. The review underlined the role of chemical structure of IL on protein partition and stability [90]. In the partition of proteins in IL-ABS, hydrophobic and electrostatic interactions as well as salting-out effects were also dominant variables. Apart from pure protein sources, several studies on separation of value-added proteins from complex media are gearing up. Latest review by Anusha et.al. on the role of ABS in sustainable extraction and separation analyzes the advancement of IL based ABS technology in the last two decades [91]. The quest and growth of research is in the right direction and will provide a new outlook to this area of research in both commercial and economic sense.

Nucleic acids are known to be the unique identity molecule of any organism and have emerged as powerful biological tool. They are carriers of genetic information and can act as a digital data storage medium in, with potential benefits such as high density, high efficiency of replication, long-term longevity and long-term stability. In molecular biology, nucleic acid extraction plays a crucial role as the primary stage for many downstream applications. Developing novel methods to extract and purify nucleic acids from various types of cells and their storage are therefore crucial. Traditionally, the purification of deoxyribonucleic acid (DNA) and ribonucleic acid

https://doi.org/10.32933/ActaInnovations.38.6• ISSN 2300-5599 •

(RNA) was based on liquid−liquid extraction techniques involving solvents like phenol and chloroform. These solvents are highly volatile and carcinogenic. Recent studies suggest that the efficiency of extraction and purification of nucleic acids from biological samples were increased by IL addition in comparison with conventional methods. Moreover, nucleic acids in ILs showed long-term stability and enhancement in nuclease resistance.

Zaho et al. in 2014 studied the interaction pattern between ILs and DES with DNA by analyzing the available literature in the field till then [92]. According to their analysis, in the case of ILs and DESs, organic cationic part is intruding into the minor groves of DNA. Electrostatic attraction is a prominent interaction between organic cations and the DNA phosphate backbone which provides additional support for hydrophobic and polar interactions between ILs and grooves. Anions may form hydrogen bonds with cytosine, adenine and guanine bases.

Moreover, nucleic acids have got structural speciality as they are viable for electrostatic interaction, formation of hydrogen bonds as well as van der Waals interactions. These strong interactions help the DNA molecules to maintain a double helical structure in most ionic solvent system. Shi et al. analyzed the polymerized chain reaction amplification of DNA by bicyclic imidazolium ionic liquid and found that nucleic acids in ILs can be used directly in polymerase chain reaction and gene expression analysis with high efficiency [93]. Based on the unique changes in the stability of nucleic acids in ILs, highly sensitive DNA sensors have been developed. The recent trends in IL-DNA interactions got a new complexion by the emergence of magnetic ionic liquid. Incorporation of MILs has made the extraction easier and the magnetic recovery of DNA enriched IL droplet is comparatively effortless. The reusability of MILs to different cycles was also an important achievement. Jared L Anderson and coworkers deserve a special mention for their contribution in this field. In their recent study, hydrophobic magnetic ionic liquids (MILs) with long chain tetra alkyl ammonium cations and metal chloride incorporated anions were synthesized and used as solvents for the extraction of DNA from aqueous solution. After extraction the DNA-enriched microdroplet was manipulated by applying a magnetic field [94]. Very recently magnetic ionic liquids with phosphonium cations and cobalt metal in the anion sphere has been proved to be efficient for RNA extraction in aqueous solution [95]. Cations and cobalt metal in the anion sphere have been proved to be efficient for RNA extraction in aqueous solution [95]

Apart from the discussed, many other biomolecules and bioactive components including lipids, fats, vitamins, carotenoids were successfully extracted and preserved with the help of ionic liquid assisted chemical processes [96–99]. The important hurdle to pass in the biomolecule extraction is the modification of separation strategies and the lack of techniques in IL recyclability and reuse. Emergence of MILs and new developments in DES related research have addressed this issue to an extent. Application of the mentioned techniques to an industrial scale is also important. Large scale separation and storage of biomolecules is necessary in commercial and economic sense. Once it comes to a bigger picture, a lot of practical issues can be dealt including cost effectiveness, storage capacity and purification strategies. In conclusion the development of cost-effective and more sustainable extraction and separation processes is the crucial step toward the recovery and commercialization of new and low-cost bioactive products for different chemical industries. While envisaging their widespread use in the near future to boost the quality of modern society, and in which ILs could have a remarkable role as alternative solvents and materials.

Impact

Human needs to open a myriad of dimensions in the advancement of research, which may also have detrimental effects on both the environment and social health. This has prompted scientists to pursue various strategies to mitigate environmental issues, especially through the use of green chemicals. In this sense, ILs have been introduced as a green solvent in different engineering areas, gas abstraction, fuel technology, cooling

https://doi.org/10.32933/ActaInnovations.38.6• ISSN 2300-5599 •

strategies etc. Nowadays, ILs are being used in the fuel industry in the different stages of oil production which were found to improve the efficiency of the crude oil extraction process. Similarly, the use of ILs have proved to be effective in wastewater treatment and CO_2 capture. These studies are the blueprints to prove the environmental and social impact of ILs. Apart from this the growth of ILs as a bio-extraction tool underlines their commercial impact. In short, the ILs, on account of being an environmentally friendly and cost-effective green solvent, is capable of improving the effectiveness of several processes which are much essential in modern circumstances. A detailed review of such applications and utilities of ILs can therefore be helpful for the further exploration of their uses and to unveil their hidden potential.

Conclusions

Throughout this review, we have appraised the advantages of implementing ionic liquid chemistry towards the field of environmental remediation and efficient energy consumption. These studies are highly promising and encouraging for the scientific community in a futuristic perspective. Needless to say, the effective utilization of energy sources and efficient conservation of nature form the life breath for the generations to come. Consequently, the progress of research in this domain has become an indispensable need of our society itself. While enumerating the advantages of ionic liquids, there had been some issues which were not really addressed. One major aspect among them is the toxicity study of ionic liquids. Although there have been a few studies carried out for assessing the extent by which the chemical compounds involved in them are detrimental to the nature [100,101], the focus towards this sector is not seems to be deep enough. There is still scope for a deep-level analysis in these aspects. Another major concern is that all the advantages which have been listed above are validated only on a laboratory scale. Very few ionic liquids have been tested and validated on a bulk scale and in industrial environments. As a result, we have not been able to identify the possible disadvantages which are likely to occur in the case of practical implementation of the same. Industrial level consumption of these chemicals may lead to several issues which may not even be present in a micro-level laboratory utilization, and therefore, a careful study of these issues is of utmost importance. Another important concern is their recyclability. Even though the advent of magnetic ionic liquids and deep eutectic solvents gives a new momentum to this concern, room temperature ionic liquids and other hydrophilic ionic liquids are observed to fail in delivering the intended functionality within one cycle of operation. It raises the question about the cost effectiveness of these classes of ionic liquids and may also be portrayed as indicator of a non-constructive utilization. Keeping all these shortcomings aside, one should appreciate the fact that ionic liquid chemistry, as an innovation, has greatly contributed to the field of energy and environmental engineering. It has opened a wide new window of opportunities for sustainable development. Cunning studies, evaluations, scientific analyses and discussions in this area are imperative in the future, in order to make the utilization of ionic liquids more eco-friendly and more economic.

Conflicts of interest

There are no conflicts to declare.

Acknowledgement:

The authors would like to acknowledge Indian Institute of Technology Madras, Chennai, for financial support through Institute Research and Development Mid-Career Level Award (IRDA) Project: CY/20-21/069/RFIR/008452. Authors acknowledge Dr. Anu Aravind Thoppil and Mr. Pranav U S for the discussion and a few suggestions during the interpretation of data.

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