

Wonder of Chemistry: Ionic Liquids

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Abstract

Ionic liquids are the liquidsalts which exist in the liquid state even at room temperature. Their properties like low volatility, less toxicity, their viscosity,and other properties have found to be very attractive for their application in various sectors such as separation of uranium from radioactive waste, as a catalyst, to extract CO₂ or to extract solvent or solute from solution as extracting solvent. This paper will reviewmuchsuch reported application of Ionic Liquids (ILs).

Keywords: Ionic liquids, room temperature ionic liquids, green solvent,

Introduction

What are Ionic Liquids?

Ionic liquids (ILs) are the organic or may be inorganic salts, generally consisting of organic cations and a polyatomic organic or inorganic anions, that are in the form of liquid phase below 100°C. Their negligible vapor pressure is the main attractive property. Their physical & chemical properties can be sufficient selection of cation&anion constituents. The ionic liquids (ILs) are recognized as environmental being alternative to the organic solvents which are volatile in nature. Application of the ionic liquids (ILs) in the chemical processes has increased within the last decade. [1-3]

Typical cation-anion combinations for Ionic liquids are:

- Cations: Imidazolium, Pyridinium, Ammonium, Phosphonium...
- Anions: Halides, BF₄-, NO₃-, AlCl₄-, Al₂O₇-...

Physical and Chemical Properties

Ionic liquids are good solvents for a large variety of organic as well as inorganic compounds. Ionic liquids are mostly polar solvents and they are weakly coordinating. Ionic liquids are immiscible with several commonly used solvents. They are having a low vapor pressure. They are having a low melting point. Ionic liquids are non-toxic. They are highly thermal stable. (300-400 oC). Ionic liquids are nonflammable in nature. The viscosity of the ionic liquids is much higher than that of conventional solvents. [2-3,5]

Because of these all attractive properties, ionic liquids can be used in various sectors such as to extract uranium from radioactive waste, in catalysis, in the separation of CO₂, in batteries and fuel cells, etc. [6]

Some wonder applications:

1. Removal of radioactive waste and separation of the Uranium metal from the transition metal using Ionic Liquids:

Uranium is a natural, radioactive and toxic heavy metals. Uranium is very hazardous and dangerous which is affected our life. Uranium is a raw material for nuclear energy production. [7] In nuclear industry most of the metals or other waste material like tissue paper, cotton cloth generated and which contains uranium and other radioactive metals, this waste is called radioactive waste. This waste can't be disposed of directly in the environment so uranium can be separated by this radioactive waste. [4, 9]

Different methods are available for recovery of uranium and its oxides from the radioactive waste like precipitation and liquid-liquid extraction, adsorption, electro-chemical recovery, membrane separation, etc. But all these methods are technically and economically ineffective. [12]

Uranium can be removed from metals by using the spent solution with organic diluents. And it is completely dissolved in the spent acid solution using the organic diluents. Then uranium can be recovered by electrolysis but the disadvantage of these techniques we have to keep very high temperature. It's cost is effective too. Radioactive waste such as tissue-paper, cloths, and other cellulose-based waste are easily dissolved in the 1-butyl-3-methylimidazolium (BMICl), ionic liquid at room temperature. [10] Uranium and palladium contamination are completely soluble with ionic liquid and after uranium and palladium can be recovered by the

electrolysis of the solution. Radioactive metal waste with uranium contamination can be easily removed by using the ionic liquid. Metal waste uranium and its oxide UO_2 , U_3O_8 dissolved in ionic liquid. The commonly used ionic liquid is 1-butyl-3-methylimidazolium (BMICl) and after the dissolving, uranium can be separated by electrolysis method. But this method can't be used due to environmental issues and its cost.[11]

In today's time, uranium can be separated by using nonfluorinated ionic liquids, not by any organic solvent. In this method morpholinium based undiluted ionic liquid is used. Uranium feed solution dissolves in (1-butyl-1-methylmorpholinium butyl phosphate). Uranium(VI) (UO_2^{2+}) dissolving capacity increases by adding the nitric acid solution. Separation and extraction of UO_2^{2+} from a solution of the concentrated nitric acid including transition metals such as Fe^{3+} , Cu^{2+} , Ni^{2+} , Cd^{2+} without the necessity of any mild organic solvent. [7] Distribution ratio and extraction efficiency of uranium are mainly depended on extraction time, the acidity of the aqueous phase, length of the alkyl chain in the ionic liquid, aqueous feed concentration and molar-quantity of the ionic liquids. So this method through we can separate the uranium from the transition metals.[12]

2. Application of Ionic liquids (ILs) in Batteries and Fuel Cells:

Ionic liquids offer a suite property so it is an important candidate for an energy application. [13] We all are using energy storage application in our daily life for e.g.: Inverter, Remote Cell, Fuel Cell, Batteries, etc. Because of the attractive properties of Ionic liquids like low flammability, high electro stability, low vapor pressure, etc. Ionic liquids are used as an electrolyte in all types of batteries. [14, 15]

Why water can be replaced by Ionic liquids in batteries?

Water can be replaced by ionic liquids in batteries because the ionic liquid has low vapor pressure, increasing battery life. Ionic liquids have a high electrochemical window (5-6 V) compare to water (1-2 V). [14, 46]

In Batteries, ionic liquids are used as an electrolyte in rechargeable batteries in huge quantity. Ionic liquids are used nowadays in Metal-air batteries. For e.g.: Aluminum-based batteries, Lithium based batteries, etc...

In aluminum batteries, Al is used as anode and graphite as the cathode and which is low cost and low flammable. So aluminum based batteries possess at low cost and higher safety. Imidazolium salts (eg: [EMIm] Cl) can be used in aluminum based batteries to form ionic liquid electrolytes. These ionic liquids are used as an ideal in aluminum batteries. When it is mixed with AlCl_3 these electrolytes contain redox active chloroaluminate anions (such as AlCl_4^- and Al_2Cl_7^-). [14, 15]

In fuel cells:

In proton exchange membranes fuel cell (PEM-FC) reaction of hydrogen and oxygen presence of water and produce energy. In a fuel cell, PTFE-backbone type polymer membrane is used but the presence of water proton conductivity is less. Ionic liquids have a good proton conductivity so ionic liquids are used in the fuel cell. [16]

3. Application of Ionic liquids in the oil and petroleum industries:

In oil and petroleum industries ionic liquids are used in many applications due to their attractive properties. [17, 18, 20]

i. CO_2 capture and sequestration:

Main three processes for CO_2 capture in different ways:

1. Post Combustion: In these process separation of CO_2 after the combustion of fuel.
2. Pre Combustion: In these process separation of CO_2 before the combustion of hydrocarbon fuel using the CO shift converter.
3. Oxyfuel combustion: In this process oxygen used as an oxidant and creating a flue gas mainly consisting high concentration of CO_2 and separation of CO_2 . [18, 19]

In Today's time, post-combustion techniques are widely used for CO_2 capture. Adsorption and adsorption are mainly used in post-combustion. Amines absorber are used for the post-combustion process. Mono ethylamine (MEA), Diethyl amine (DEA) and Triethylamine (TEA) mainly used as an absorber in the post-combustion process for CO_2 capture. [19, 21-23]

Why do we use ionic liquids by replacing amines?

Some disadvantage of amines such as high vapor pressure, it's corrosive nature, a high amount of energy is required for the regeneration. The properties of ionic liquids are having low vapor pressure, less toxicity, high reactivity, high electrochemical window, tunable nature to makes as green so ionic liquids use as capturing carbon dioxide. [21, 24, 25]

Advantage of using ionic liquids as a solvent for CO₂ capture [20, 26]

- CO₂ capture efficiency is high compared to other solvents or amines.
- Less energy required to regenerate ionic liquids from captured CO₂.
- Ionic liquids have high thermal stability and chemical stability and it does not react with any other gas or impurities and avoid the corrosion. [27]

Process:

The first mixture of gases passes into the absorption process in the absorption tower. In absorption tower, ionic liquid is used as a solvent and CO₂ gas is soluble in ionic liquids and other gases are insoluble in ionic liquids which is removed from the absorber. Then CO₂ rich gas stream passes into a stripper. [28] In stripper, regenerated ionic liquids from the CO₂ stream using high temperature or inert gases. 1-Butyl-3-methylimidazolium chloride [BMIM][Cl] ionic liquid is commonly used for the CO₂ capture. [21, 27]

ii. Desulfurization of fuel oils:

There are many sulfur compounds aliphatic and aromatic (thiophene and its derivatives) can be found in crude oils 7-8%. Sulfur compounds generate a problem and affect the performance of crude oils. Many methods are available to remove the sulfur content which is present in crude oils. But we will discuss the method of desulfurization of the crude oil by using the ionic liquid. [29- 32]

4. Ionic liquids (ILs) used as an extractant in the desulfurization of Crude oils:

Ionic liquids are used as an extracting solvent in the desulfurization process because of properties like the good extractive capacity of sulfur and its derivatives compound, insolubility in the oil or its products, recoverability from sulfur compounds, reusability, recycle-ability, catalyst solubility.

In extractive desulfurization of fuel oils, mainly two methods are there.

1. use of liquid-liquid equilibrium data
2. conductor like screen model

The main step of desulfurization process is to choose an important extracting solvent. The best solvent is in which sulfur and nitrogen compounds are soluble and it's not soluble in fuel oils. In the desulfurization process, select smaller cation size because it will extract only sulfur compounds, not any hydrocarbons. So in this process, used imidazolium-based cations instead of others. For e.g. 1-alkyl-3-methylimidazolium cation is used for the desulfurization of fuel. [31, 33 - 35]

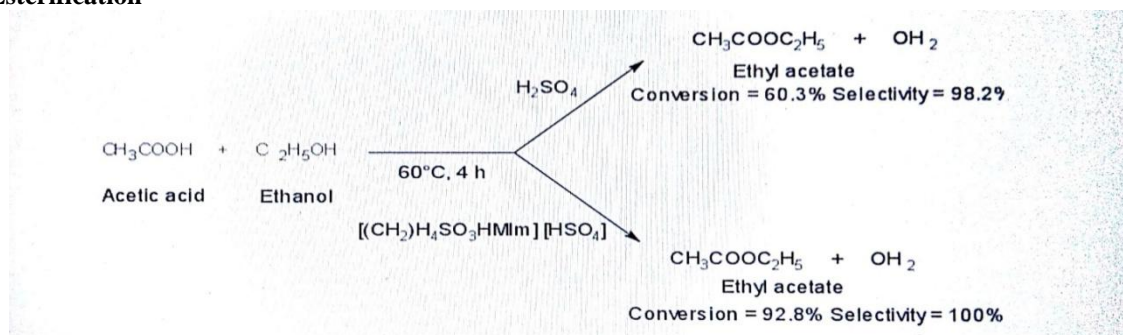
5. Ionic liquids as Catalyst:

Ionic liquids are come out as alternative green reaction media due to their attractive physical & chemical properties. [20, 35]

As Acid Catalyst: Acidic ionic liquids are used as a catalyst in the chemical reaction instead of using mineral acids such as sulfuric acid or hydrochloric acid. [29, 36]

E.g.: 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate [(CH₂)₄SO₃HMIm][HSO₄] [23, 30, 31, 32]

1. Esterification

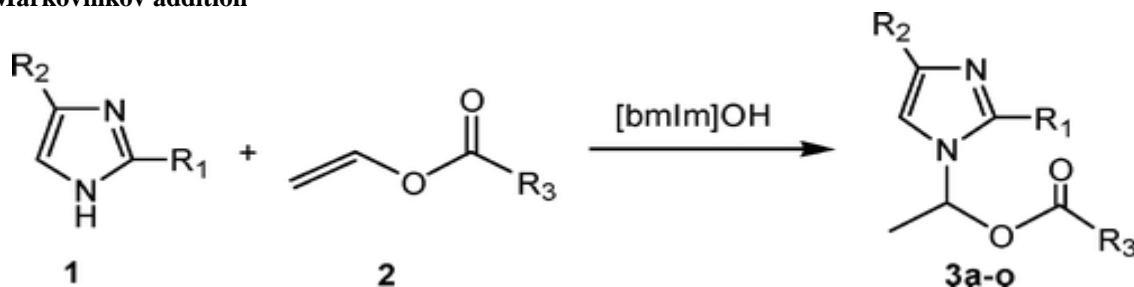


The 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate is more beneficial catalyst than the conventional catalysts (sulfuric acid H₂SO₄). [32, 34]

As Base Catalyst: Basic ionic liquids are used instead of KOH, NaOH, NaOAc because they are nonvolatile, flexible, immiscible and noncorrosive with several organic solvents. [32]

E.g.: 1-butyl-3-methylimidazolium hydroxide [BMIm][OH]

2. Markovnikov addition



6. Ionic liquids in liquid-liquid extraction:

Nowadays Ionic liquids (ILs) are being used as an extracting solvent instead of organic solvents in liquid-liquid extraction. Ionic liquids (ILs) can be applied to separate two liquids by using a liquid-liquid extraction method of the metal cations, large biomolecules or small organic molecules as proteins.[37]

Examples of liquid-liquid extraction: [38-42]

1. Using liquid-liquid extraction, to separate the glycerin from bio-diesel we can use the ionic liquid as extracting solvent.
2. The ionic liquid can be used in the extraction of metals into their mixtures using liquid-liquid extraction.

Conclusion:

One can conclude that due to the attractive properties of ionic liquids, they are applicable in various sectors. [6] Ionic liquids are being used by major industries instead of using organic/inorganic solvents. Therefore, ionic liquids are a green solvent. In the area of polymers, Ionic liquids are employed in various ways like the grafting of the chain, as a solvent for polymerization reactions, as polymer morphology modifiers and as polymer unusual component.[43] Ionic liquids are also finding applications in many diverse but unusual areas like drug delivery,[44-45] nanomaterials, electrodeposition, and recovery of metals, liquid-liquid extraction for metal salt recovery, optical materials, fuels for propulsion, lubricants, vitamin recovery [46], etc. As diverse as this list of topics is, it does not even begin to truly represent the wide array of areas impacted by ionic liquids. Rightly said, "as more and more scientists become aware of the potential of ionic liquids, one can expect their applications to expand even further".

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