

Ionic Liquids towards the Supercritical Fluid: A Review Paper

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ABSTRACT: *Ionic liquids (ILs), which are regarded a new magical chemical owing to their unusual characteristics, offer a wide range of uses in the chemical sector. Electrolytes as batteries, lubricants, plasticizers, solvents and catalysis in synthesis, matrices for mass spectrometry, solvents for manufacturing nano-materials, extraction, gas absorption agents, etc are some of the applications. Their common characteristics of non-volatility and non-flammability provide materials an edge in a variety of applications. When combined with the ability to tune the physicochemical characteristics of ILs by altering the anion-cation combination, this common advantage provides a fantastic opportunity to create task-specific ILs for a wide range of applications. Many research have been published in the literature on the unique characteristics, preparation techniques, and various uses of ILs. The primary emphasis of this study, however, is on how ILs might be utilized in the chemical processing industry. Thus, the major application areas are investigated and fundamental applications such as fluid replacement, gas purification, homogeneous and chemical processing, biological response media, and metal ion removal are thoroughly addressed. Not only are the benefits of ILs discussed, but also the key obstacles and opportunities for utilizing ILs in the chemical sector. In many applications, ILs have replaced scCO₂, and the majority of research in the literature have focused on the interplay of such two green solvents, ILs and scCO₂. The chemistry of the ILs has indeed been discussed in a number of previous publications. As a result, the primary goal of this review article is to give an overview of the chemical and physical characteristics of ILs, as well as to look into the IL-scCO₂ systems in more depth. Solute recovery from ILs with CO₂, separation of ILs from organic solvents with CO₂, phase behavior of IL-scCO₂ systems, solubility of ILs in CO₂ phase, and IL-scCO₂ system interactions at the molecular level are all covered.*

KEYWORDS: *Ionic Liquids, Green Solvents, Low Melting Temperature, Physio-Chemical Properties, Supercritical,*

INTRODUCTION

Ionic liquids (ILs) have indeed been hailed as a new green chemistry revolution that has piqued the interest of both academics and industry. Because of its unique properties, this novel chemical group may decrease the usage of toxic and damaging organic solvents while also participating in a variety of new syntheses. These salts in the liquid state have been referred to as room temp ionic liquid (RTIL), water immiscible ionic liquid, liquid metals, liquid organic salt, and fused salt. In contrast to the high molten salts, ILs are salts that really are liquid at room temperature. They offer a unique set of physico-chemical characteristics that make them ideal for a variety of applications when traditional organic solvents are ineffective or unavailable. Short noted that there were just few patent applications for ILs in 1980, but that by 2000, the number had risen to 100, and by 2004, there were even more than 800. This is an ample proof of academia's and industry's strong ties to ILs.[1]

Although ILs have indeed been known for decades, their widespread application as solvents in chemical synthesis & catalysis has only lately become apparent. ILs are not new, according to Welton, and some of them, such as [EtNH₃][NO₃], were originally characterized in 1914. The first IL in the research was developed for nuclear weapon batteries in the 1970s. At temperatures of hundreds of degrees Celsius, aluminum iodide molten salts were used for electroplating in the 1940s. Wilkes attempted to create battery technology for nuclear weapons and space missions that needed molten salts to function in the early 1970s. The molten salts were hot enough to cause harm to the materials around them. As a result, the scientists went on a quest for salts that remained liquid at lower temperatures, ultimately finding one that is liquid at ambient temperature. Wilkes and his colleagues proceeded to develop their ILs used as battery electrolytes, and a tiny group of researchers followed suit. ILs were among the most promising compounds as solvents in the late 1990s.[2]

As they were unstable to air and water, the earliest ILs, such as organo-aluminate ILs, had a restricted range of uses. These ILs were also not inert to a variety of chemical substances. The variety of air and water stable ILs has been quickly increasing since the initial publications on the synthesis and uses of air stable ILs such as 1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) and 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]). Researchers recently discovered that ILs can be used for a variety of purposes, including replacing volatile organic substances, creating new materials, successfully conducting

heat, supporting protease reactions, going to host a variety of catalysts, purification of gases, homogeneous and heterogeneous catalysis, biological reaction media, and removal of contaminants.[3]

Researchers are currently evaluating some of the fundamental physical characteristics of ILs, such as viscosity and density, since IL research is still in its early stages. In the literature, the number of studies on ILs and its particular uses is constantly growing. For example, until 2001, the cation 1-n-ethyl-3-methylimidazolium was the most extensively explored, but today, 1-3-dialkyl imidazolium salt are the most frequently utilized and researched class of ILs. The goal of research for the future of ILs is to commercialize them so that they may be used as solvents, reagents, catalysts, and nano materials in large-scale chemical application.[4]

DISCUSSION

1. The fundamental characteristics of ILs:

Water and organic solvents like toluene and dichloromethane are made up of molecules, while ILs are made up of positive and negative ions. ILs have a structure comparable to table salt, such as sodium chloride, which is formed up of crystals of positively charged sodium negative ions chlorine ions rather than molecules. While salt do not melt at temperatures below 800 degrees Celsius, most ILs stay liquid at normal temperature. Sodium chloride and lithium chloride have melting temperature of 801 and 614 degrees Celsius, respectively. The use of traditional molten salts as solvent in application is severely restricted due to their high melting temperatures. RTILs, on the other hand, are liquid up to 200°C. ILs have a broad range of liquids. Extremely high melting ionic systems are known as molten salts, and the accepted highest melting limit for the categorization as 'IL' is known as 100 C. Because the ions need not pack effectively, ILs stay liquid at ambient temperature, according to researchers. A regular structure, meaning a liquid phase, is formed by the combination of heavy and asymmetrical cations with uniformly structured anions. The chemical makeup of ILs contributes to their low melting points. The melting temperature of the resultant ionic medium is lower due to the mix of bigger asymmetric organic cations and smaller inorganic equivalents. Even the anions, in certain instances, are quite big and contribute to the melting point being lowered.[5]

- ILs are extremely polar and have the capacity to dissolve a wide range of organic, inorganic, and organometallic compounds.
- ILs are made up of tightly coordinating bulky ions with extremely low vapor pressures, thus they don't evaporate.
- ILs are thermostable up to 300 degrees Celsius.
- ILs have a fluid window of up to 200 degrees Celsius, allowing for broad kinetic control;
- ILs have excellent thermal conductivity and a big electrochemical window; and
- ILs are immiscible with a wide range of organic solvents.
- In nonaqueous polar phase transfer procedures, ILs are used.
- It is possible to adjust the solvent characteristics of ILs for a ILs and CO₂ scrubbing systems

Green chemistry, also known as renewable chemistry, is the pursuit of minimizing or even abolishing the use of chemicals that are harmful to human health and the environment in the manufacture of industrial chemicals and reactions. Green chemistry's aim is to develop a cleaner, more sustainable chemistry, and it has gotten a lot of press in recent years. Green chemistry strives for faster reaction speeds, lower reaction temperatures, and higher selectivities while searching for alternative, ecologically acceptable reaction media to conventional organic solvents. The ideal scenario for a safe and environmentally friendly chemical process is to avoid employing any solvents; nevertheless, solvents are used in the majority of chemical processes. Since some of these compounds are water soluble, they must be removed from the water before it exits the process, not only for environmental but also economic reasons. For a process to be economically feasible, solvents must be collected for recycling and reuse.[6]

2. ILs and scCO₂ systems:

Alternative solvents for green chemistry include water, perfluorinated hydrocarbons, and supercritical fluids (SCFs). ILs and scCO₂ are two of the most promising green chemistry elements. The stability of ILs is one of the main characteristics that distinguish them as green solvents. This benefit, however, creates a difficulty for product removal and recovery. There are many methods for recovering solutes from ILs: volatile products may

be recovered from ILs using distillation or simple evaporation. Nonvolatile or thermo-sensitive compounds, on the other hand, cannot be isolated from ILs using these techniques.

Water-soluble solutes from ILs that are immiscible with water may be recovered with water to separate them from the aqueous phase, however this technique is not appropriate for hydrophilic ILs. Organic solvents like hexane and toluene may be successful in recovering goods from IL, but this method clearly undermines the ultimate aim of "green" technology. Cross pollution between the stages is also a concern. Finally, supercritical fluids are found as a green solvent that overcomes all of the issues and recovers different types of solute molecules from ILs with cross contamination (SCFs).[7]

2.1 Phase behavior of IL–CO₂ systems at high pressures:

scCO₂ extraction has been proven to be a feasible technique for recovering solutes from an IL in preliminary studies. However, understanding the phase formation of IL–CO₂ systems is critical to this approach. In the IL phase, scCO₂ dissolution is not only required for interaction with the solute, but it also lowers the viscosity of the IL, improving the mass transfer. Early research on the phase behavior of IL–CO₂ systems revealed that they are extremely uncommon biphasic systems. Although a significant quantity of CO₂ dissolved in the IL-rich phase, decreasing the viscosity of IL, no detectable amount of [bmim][PF₆] was accessible in the CO₂-rich phase. Even at pressures up to 400 bar, Blanchard and Brennecke found that the system maintained two separate phases. As a result, the high-pressure phase behaviour of [bmim][PF₆]–CO₂ differs significantly from that of other organic liquid–CO₂ systems. The fundamental phenomenon that makes CO₂ removal of solutes from IL appealing is the distinct phase behavior.[8]

2.2 Other IL–CO₂ systems:

Different kinds of ILs have comparable high-pressure phase behavior to [bmim][PF₆]. Blanchard et al. used six different ILs to study CO₂'s high-pressure phase behavior: 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), 1-n-octyl-3-methylimidazolium hexafluorophosphate ([C8-mim][PF₆]), 1-n-octyl-3-methylimidazolium tetrafluoroborate ([N-bupy][BF₄]). They looked studied CO₂ solubility in various ILs at 40, 50, and 60 degrees Celsius and pressure up to 93 bar. The goal of this research was to get a better description of the physiological interactions among CO₂ and ILs with various cation–anion combinations. Continuing the pattern of [bmim][PF₆] and [C8-mim], CO₂ solubility in the IL-rich phase was highest for ILs containing fluorinated anions. [PF₆] > [C8-mim][BF₄] > [N-bupy][BF₄] > [bmim][NO₃] > [emim][EtSO₄] [70]. [PF₆] > [C8-mim][BF₄] > [N-bupy][BF₄] > [bmim][NO₃] > [emim][EtSO₄] CO₂ solubility was found to be highest in ILs containing the PF₆ anion, while the IL with the lowest CO₂ solubility was [emim][EtSO₄].[9]

3. CO₂ solubility of IL:

While the bulk of study focuses on CO₂ solubility in IL, the content of IL in the CO₂-rich phase is equally significant. The absorption of [bmim][PF₆] in the CO₂-rich phase was measured using a dynamic equipment with a high-pressure cell. At 40°C and 137.9 bar, the solubility of [bmim][PF₆] in CO₂ was measured by passing 0.5866 mol of CO₂ through a cartridge containing [bmim][PF₆]. UV–visible examination revealed no discernible IL absorption peak, suggesting [bmim][PF₆] solubility in the CO₂ phase of less than 5 10⁻⁷ (mole fraction of [bmim][PF₆]). Because CO₂ does not dissolve any detectable IL, a solute dissolved in an IL may be readily retrieved with scCO₂ without risk of cross contamination. The difficulty of CO₂ to properly believe that when it comes ions in the gaseous phase is due to two factors: IL's very low vapor pressure and CO₂'s incapacity to believe that when it comes ions inside the gaseous phase.

4. Solute recovery from ILs with scCO₂:

Researchers discovered that nonvolatile organic molecules may be recovered from ILs using scCO₂, a popular method for extracting big organic compounds with little pollution. CO₂ was employed by Blanchard et al. to extract acetonitrile, a high volatility modeling solute, from an IL. They created [bmim][PF₆], a stable compound in the case of moisture and oxygen. The model chemical naphthalene was soluble in both [bmim][PF₆] and CO₂ (maximum mobility of 0.30 molar concentration at 40 C). Their research looked at the phase behavior of [bmim][PF₆] in the presence of CO₂, naphthalene, and the [bmim][PF₆]–CO₂–naphthalene ternary system. The findings revealed that IL did not substantially pollute the CO₂-rich phase, as would be anticipated when CO₂ is in contact with any typical organic solvent.[10]

CONCLUSION

The goal of this paper is to collect and explain the data regarding ILs and IL–CO₂ systems that has been published in the literature. Many studies studied the rising phase behavior of IL–CO₂ systems and came to the conclusion that CO₂ is extremely soluble in most ILs, while ILs are not demonstrably soluble in scCO₂. Various research' findings on the effects of temperature, temperature, anion type, and cation alkyl chain length on CO₂ solubility are addressed and summarized here. The volatile and nonpolar scCO₂ has shown to be an excellent companion for nonvolatile and polar IL, and this novel system has been used to extract chemical molecules from ILs using scCO₂. ILs are gaining popularity in scientific research and commercial applications, and they seem to be a viable alternative to volatile organic solvents. However, because of the ILs' limited physical, chemical, and toxicological data, there is some debate regarding their greenness. Although there are some questions about the particular characteristics of ILs, it appears that the majority of researchers would keep working with this novel solvent, and the number of new applications using ILs will quickly grow, as will the number of publications. In many possible commercial uses, the current prices of ILs are prohibitive. However, it is hoped that throughout the near future, the cost-benefit ratios of ILs would make their widespread usage economically viable.

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