

Revisiting Characteristics of Ionic Liquids: A Review for Further Application Development

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ABSTRACT

In literature concerning ionic liquid (IL) applications, the commonly accepted properties of ionic liquids are frequently mentioned. For example, ionic liquids are described as possessing immeasurably low vapor pressure, being “green material”, non-coordinating, physically and chemically stable, and non-toxic, to name a few. However, all these descriptions are deemed “not exact” [1] as intensive research on ionic liquid properties continues. This review highlights the most recent developments in IL chemistry where the “well-known” description of IL properties sometimes proves to be inaccurate. However, in the authors’ opinion, all these new research developments concerning ionic liquid properties serve to update knowledge on the typical physical and chemical properties of ILs, which is significant to both theoretical research and industrial applications. This review presents an opportunity to understand IL through a more complete and accurate view. It seeks to pave the way for further studies on IL application in various fields.

Keywords: Ionic Liquids, Functionalized Ionic Liquids, Volatility, Polarity, Green Chemistry

1. Introduction

Scientific and technical research on ionic liquid (IL) application has progressed over the last 20 years. Interest has been derived from ILs’ unique advantageous properties, such as non-volatility, versatile solubility, and stability, to name a few. These properties present ILs as a promising alternative to environmentally undesirable volatile organic solvents, especially chlorinated hydrocarbons. Successful industrial processes using ionic liquids appear to confirm such advantages [2].

Another important feature on the cap of ILs is the ability of their molecular structure to be tailored according to application requirements. This has spurred the rise of task-specific ionic liquids, or the so-called functionalized ionic liquids [3-5].

Existing studies on ILs, especially the earlier ones, reiterated the following advantageous properties:

- 1) No measurable vapor pressure or non-volatility
- 2) Low toxicity
- 3) High polarity
- 4) Non-coordination
- 5) Physical and chemical stability

The above-mentioned description appeared at a time when only limited kinds of ionic liquids were available,

especially those based on imidazolium salts. In-depth investigations were not carried out. Nevertheless, as research progressed and a number of new ILs were synthesized, the said properties were proven to be non-standard.

Various results obtained from newer research works offered counterexamples to the said properties. For example, IL vapor pressure can now be measured and ILs can be distilled. Further, the toxicity tests of commonly used ILs in bioassays prove that they are considerably toxic. Furthermore, the commonly used “stable” 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf₂N]) was even tested as a propellant for space shuttle. Based on these, the authors conclude that the traditional description has been rendered incomplete and inappropriate. In addition, the IL varieties that trigger property change are, to a certain extent, ignored and not realized systematically.

To date, there is a significant number of high-quality reviews on IL research activities, from the early ones that generally focused on catalysis [6-13], to current detailed descriptions of specified applications such as coordination chemistry [14], physicochemical properties [15], analytical chemistry [16], polymer materials [17], fluorine chemistry [18], and nanotechnology [19]. All these reviews contribute largely to the rapid rise and stimulation of research interest on ILs.

This review attempts to highlight the new findings concerning ionic liquid properties, specifically those indicating that the ILs' "well-known" descriptions should be updated and even corrected. The authors believe that a careful recognition of IL properties based on recent discoveries is essential to research and application. Instead of nullifying the unique value of ionic liquids, this will provide an opportunity to explore new avenues for research and application. Without a doubt, a more complete and accurate understanding of IL properties will be beneficial for further studies concerning these "magic" liquids.

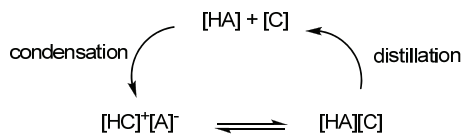
2. Can Ionic Liquids be Distilled?

"Negligible", "immeasurable", "extremely low", "vanishingly small", and "virtually nonexistent" are among the most common descriptions ascribed to vapor pressure of ionic liquids. It was therefore logical to assume that ionic liquids are non-volatile and impossible to distill, especially since they are composed completely of ions [20].

Early investigations of ionic liquids' thermal properties using thermogravimetric analysis (TGA) [21] proved that they possessed minimal vapor pressure up to their thermal decomposition temperature. This property is considered an advantage when applied to the distillation process because the azeotrope formation between the solvent and products does not occur. In addition, this characteristic is expected to ease manipulation and purification, and facilitate multiphasic application and recycling [22]. Vapor pressure research related to ILs was almost refined in the binary or multimixed system of ILs and other volatile liquids [23-29]. There were reports on the theoretical estimation of ILs' thermodynamic properties, including the calculation of vapor pressures [30-32].

However, this feature led to certain limitations such as problems in distilling ionic liquids to achieve extreme purity or the almost-impossible use of the ionic liquids in the gas phase. One exception is the protic ionic liquids written as $[HC]^+[A]^-$, which can be vaporized like equilibrium forming $[C][HA]$, which are both volatile [33] (**Scheme 1**). However, the reverse protic transfer is found recently can be controlled by changing cation type, for example, superbase cations by which the thermal stability is greatly enhanced [34].

Information purporting that "ionic liquid cannot be distilled" and "their vapor pressure cannot be measured" has been nullified only recently. A report on one-stage



Scheme 1. Distillation process of protic ionic liquids

distillation of imidazolium ionic liquid of $[Tf_2N]$ anion under reduced pressure at moderate temperature was published [35]. The authors used experimental surface tension and density measurement, as well as Eötvös or Guggenheim empirical equations, to estimate the critical points related to the IL's normal boiling points. According to the study's results, measuring ILs' vapor pressure is possible, owing to a wide window of possible experimental working temperature of obtained boiling point data. Ionic liquids, $[C_{10}mim][Tf_2N]$, and $[C_{12}mim][Tf_2N]$ were found to be readily distilled under 450 K and 1 Pa pressure. Shortly after, the experimental vapor pressure data were measured via the Knudsen method. Within the temperature range of 458-517 K, the relationship between vapor pressure and temperature was obtained [36, 37].

More recently, studies proved that a broader series of ionic liquid of $[Tf_2N]$ anion could be distilled at 473-573 K under low pressure using the Kugelrohr apparatus [38]. Protic ionic liquids of trifluoroacetate or formate anion, however, can be distilled more easily using the standard method under normal pressure and temperature [39]. As mentioned above, the Lewis acidity/basicity is believed to produce the main effect on protic ionic liquids' volatile property [33].

From assuming a "non-distillable" property to discovering a large number of distillable ionic liquids, it is needless to predict that the non-volatile advantage of ionic liquids is diminishing. However, all these observations broaden the field of ionic liquid property research and may lead to wider applications.

3. Are Ionic Liquids Really that Green?

Because of ionic liquids' "immeasurably" low vapor pressure under normal conditions [10], they are considered as "greener" solvents rather than volatile organic compounds (VOCs) that emit pollution to the atmosphere. This "greenness", however, merely satisfies certain parts of the 12 principles of Green Chemistry [40] if ionic liquids are used in chemical processes. Unfortunately, this has been misinterpreted as possessing broader green properties such as low toxicity and biodegradability. It should be noted that a considerable number of precursors to ionic liquids were labeled as toxic and environmentally hazardous, and the toxicity and biodegradability of ionic liquids generated thereof require further investigation.

Looking into the hazards involved in using ionic liquids was not attempted until 2003 [41]. The authors of the study theoretically used the structure-activity relationship to discuss the toxicity and ecotoxicity of a selection of commonly used ILs. The direct toxicity analyses of ILs followed thereafter, mainly using bacteria or cells as targets. Examples included *vibrio fischeri* and WST-1 cell [42,43], human tumor cell line HeLa [44], lactic acid-producing bacteria as *lactobacillus rhamnosus* [45,46],

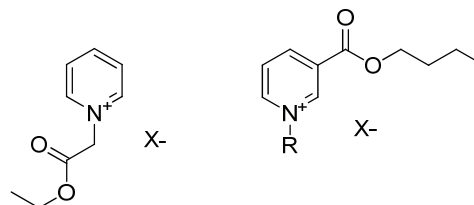
Escherichia coli, *Pichia pastoris* and *Bacillus cereus* [47], *Caenorhabditis elegans* [48], and acetylcholinesterase [49].

The acute toxic effects of ILs on various high forms of organisms, plant or animals, were likewise tested; these included algae,[50] *Daphnia magna* [51], zebrafish (*Danio rerio*) [52], rabbits [53], fresh water snails [54], and zebra mussel (*Dreissena polymorpha*) [55]. Different ionic liquids displayed diverse toxicity to the bio subjects used in the said research. In addition, various methodologies were developed and investigated for better understanding of this toxicity issue, such as the quantitative structure-property relationship modeling [56], lipophilicity, and metabolic pathway prediction of ILs [57].

Despite various efforts to discover whether or not ionic liquids are toxic, as well as the possible extent of toxicity, researchers have yet to arrive at a clear answer because of acceptors' and ILs' variability. In certain reports, for example, compared with traditional solvents, imidazolium-based ionic liquids are reportedly more toxic to microorganisms [43]. However, a number of reports claim that the lactic acid-producing bacterium still grows faster in the presence of imidazolium-based ionic liquids than in hexane [45]. Certain primitive trends on the commonly used ionic liquids were found, such as an increase in toxicity of aquatic organisms as the number of nitrogen atoms in the cation increases [56].

The biodegradability of ILs are similarly an object of research interest, and the Closed Bottle Test (OECD 301D) is commonly used to administer the biodegradability test. At present, the biodegradability of traditional non-functionalized ILs, such as those based on $[C_4mim]^+$, are hard to be biotic-degraded [58]; and the abiotic degradation is found to be impossible for $[C_4mim][BF_4]$ [59].

Despite the fact that many ionic liquids exhibit toxicity and create a negative impact on the environment, it should be remembered that certain parts of toxic ILs are not necessarily indicating that all the ILs are toxic. Furthermore, ionic liquids in principle can be modified to be non-toxic. Previous studies have reported that ILs can be obtained from biodegradable and renewable resources [60-68]. With infinite possibilities for designing ionic liquids, the authors of this study are optimistic that IL can be designed to be non-toxic, readily degradable, and even edible. For example, the following shown ionic liquids can be classified as "readily biodegradable" [69] (Scheme 2). It is also possible to design ionic liquid possessing a toxicity level that serves a specific need. For instance, ionic liquids extraction of Para Red and Sudan dyes from chilli powder, chilli oil and food additive combined with high performance liquid chromatography has been reported very recently [70], which shows application potentials of ILs in food industries, especially in analytical applications [71,72].



Scheme 2. Biodegradable pyridinium ionic liquids

Until now, the toxicity related investigation is still a hot topic concerning safety issue of ionic liquids, among which detailed research activities are carried out continuously [73-75]. A Agar Diffusion Test has also been developed for clarification of biocompatibility of water-miscible ionic liquids [76].

4. Do Ionic Liquids have high Polarity?

Polarity is a physical property of compounds related to other physical properties such as melting and boiling points, solubility, and intermolecular interactions [77]. Ionic liquids have been considered as polar solvents, such as those suitable for charged compounds, possibly because of their ionic nature.

The first polarity investigation of ionic liquids using the solvatochromic dye method emerged in 2000, postulating that imidazolium-based ILs possess a polarity similar to lower alcohols [78]. Various methods were subsequently developed to determine the polarity of ILs, such as fluorescent dye method [79,80], EPR spectroscopy [81], 2-nitrocyclohexanone tautomerism method [82], microwave spectroscopy [83], FT-IR spectroscopic probe ($Fe(CO)_5$) [84], and FT-IR combined with density functional calculations (DFT) [85]. These different methods resulted in accordance, but a definitive standard has not been established for ionic liquid polarity. However, all these tests revealed that ILs were not as polar as expected. On the contrary, they demonstrated considerably low polarity [86].

The polarity of ILs is responsible for their ability to dissolve solutes. The solubility of many non-polar substances in ILs, including hydrogen [87], carbon monoxide [88], and fullerene [89], has been tested. It has been found that hydrogen and carbon monoxide possessed solubility that is quite higher than what was initially expected. In the case of ionic liquid of cation with long alkyl chain, the solubility of H_2 is higher than non-polar organic solvents like benzene. C_{60} can likewise be dissolved in ILs at concentration of up to 0.1 mg/ml. There are as well reports on the CH_4 dissolution into low-polarity designed ILs [90].

It is reasonable to state that ILs can dissolve not only polar solutes or charged solute via ionic liquid structure design, but also various non-polar compounds. However, a more comprehensive investigation on solute-solvent interactions has yet to be performed.

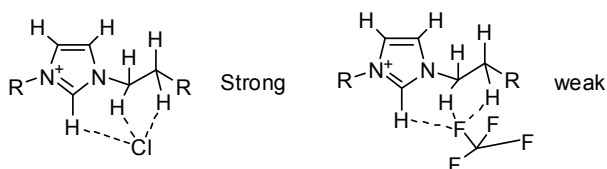
5. Can Ionic Liquids Coordinate?

A decade ago, ILs were generally perceived as non-coordinating, which implied that their anions were non-coordinating as well [6-13]. Various scientific publications have postulated that ILs were “poorly coordinating” or “weakly coordinating” [91]. However, recent reports have claimed that ILs are indeed coordinating [92-94].

The coordinating ability is a tendency to donate electron(s) to form a chemical bond [95]. In traditional imidazolium IL systems, the cationic part displays minor coordinating ability, thus the coordinating abilities are determined by the anionic part [96]. The chloride or bromide displays strong coordinating abilities, and this is reflected in many crystallographic studies as well as NMR and IR studies [97,98]. For other anions, however, especially those that reduce the viscosities and melting points of ionic liquids (e.g., $[\text{BF}_4]^-$, $[\text{SO}_3\text{CF}_3]^-$), there is little evidence obtained from X-ray crystallography. Delocalization of the negative charge within the anionic core structure (e.g., O-S-N-S-O for $[\text{Tf}_2\text{N}]^-$, O-S-O for $[\text{SO}_3\text{CF}_3]^-$) accounts for the weak coulombic attraction between the anion and the weakly acidic organic cations (*i.e.*, low lattice energy and low melting points). They are assumed to be non-coordinating because the negative charge is highly delocalized over electron-negative fluorine atoms.

However, as the chemistry of ILs continued to advance, there rose evidences that even the above-mentioned ILs demonstrate coordinating abilities towards main group metals and transition metals. Recent studies of several commonly used ILs through *in situ* re-crystallization suggest that the intermolecular C-H...F interactions are likewise commonly present in these ILs. The hydrogen bonding network differs depending on the anions, from $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, to $[\text{Tf}_2\text{N}]^-$, $[\text{SO}_3\text{CF}_3]^-$ [99]. Prior to this work, C-H...F interactions were equally found in other ionic liquids with $[\text{SO}_3\text{CF}_3]^-$ anion [100]. From the fact that these ILs can donate electrons to H atoms, it is reasonable to imply that they can likewise coordinate to Lewis acidic metals and exhibit a coordinating property.

The coordinating abilities of ILs have been utilized in various processes as well. An interesting example is that $[\text{BF}_4]^-$ anion exhibits a coordinating ability towards BF_3 ; this process has been successfully used in the storage and



Scheme 3. Anion coordination of imidazolium ionic liquids

transport of highly toxic gases such as BF_3 [101,102]. It is believed that the fluorine atoms in the anion can interact as donor to the boron atom of the BF_3 molecule, and a Lewis acid and base complex can be formed through this process. In another example, the $[\text{CH}_3\text{BF}_3(\text{CH}_2)_2\text{CN}]^-$ anion displays coordination ability towards potassium [103] (Scheme 3).

The coordinating abilities of $[\text{PF}_6]^-$ anions was investigated and compared with the molecular solvents dichloromethane [91]. Owing to the coordinating behavior of the $[\text{PF}_6]^-$ anion, the IL of $[\text{PF}_6]^-$ can be successfully used as both catalyst and solvent for olefin polymerization and ethane oligomerization to higher α -olefins by cation catalysts [91]. The mechanism is believed to be the coordination of F atoms in the $[\text{PF}_6]^-$ anion, which activates the olefin. Polymerization can thus be induced in the presence of a nickel catalyst (Scheme 4).

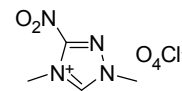
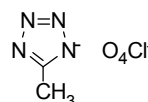
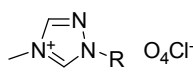
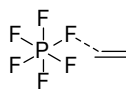
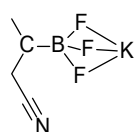
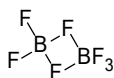
Anion $[\text{Tf}_2\text{N}]^-$ has been frequently used as ionic liquid anion to reduce IL viscosity; this can improve ionic conductivity as well. To date, its rich coordination chemistry remains unexplored. However, recent studies suggest that $[\text{Tf}_2\text{N}]^-$ is a versatile coordinating anion that can interact with transition metals in various modes. For example, N-methyl-N-propylpyrrolidinium bis (trifluoromethanesulfonyl) imide [92] reacts with YbI_2 , creating a complex in which the $[\text{Tf}_2\text{N}]^-$ anions coordinate with the Yb center in a chelating mode using the two oxygen atoms as donors. The cation was included in the final structure to balance the charge. The O-Yb distances were between 241.0 to 251.7 pm, the latter being the longest among all complexes with Yb-O bonds. All the ligands showed cissoids conformation with respect to the CF_3 groups (Scheme 5).

With transition metals, Ti, Fe, Ru, and $[\text{Tf}_2\text{N}]^-$ anions can use its donor O or N to coordinate metal centers forming η^2 -O, O, or η^2 -O, N, chelating or η^1 -N, η^1 -O, mono-complexes [104,105] (Scheme 6).

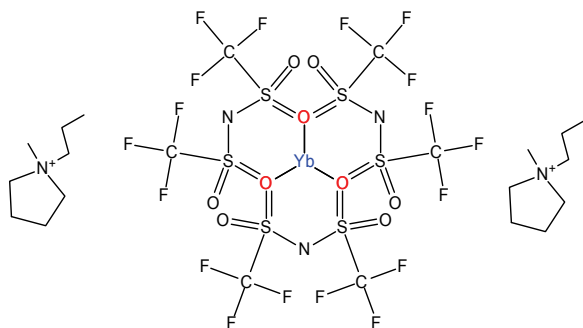
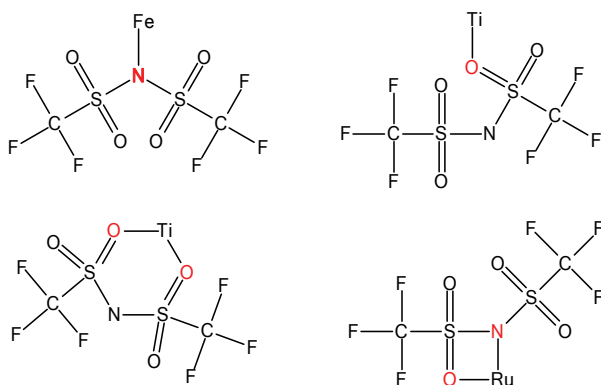
Ionic liquids appear to coordinate from birth and it should be noted that ionic liquids can be designed to coordinate deliberately by incorporating coordination groups. Ionic liquids containing various coordinating functionalities that can coordinate to main group metals and transition metals were reported.¹ This has evoked a change in ionic liquid chemistry. These functionalized ionic liquids have been successfully used in catalysis, coordination polymers, and gas-absorption. This aspect had been reviewed previously [4]. Apart from the cation coordinating ILs, a number of ILs bearing coordination groups in the anion have likewise been reported [106].

6. Stable Versus Energetic

The stability of a very limited number of ionic liquids has been misleadingly accorded to all ionic liquids. In fact, the earliest examples based on $[\text{AlCl}_4]^-$ anions were extremely air-sensitive, so much so that their application has been very limited [107,108].

Scheme 4. Coordination of BF_4 , R-BF_3 and PF_6

Scheme 7. Energetic ionic liquids

Scheme 5. Yb complex with $[\text{Tf}_2\text{N}]$ anionScheme 6. Coordination modes of $[\text{Tf}_2\text{N}]$ anion with transition metals, $\text{M} = \text{Fe}, \text{Ti}, \text{Ru}$

The stable generation ILs represented by 1, 3-dialkyl imidazolium salts with $[\text{BF}_4]$, $[\text{PF}_6]$ anions are indeed thermally stable compounds that will not decompose below 300°C . The high thermal stability has been an ad-

vantage in many applications. However, there have been reports alleging that they decompose when heated in the presence of water, thus emitting HF [109].

Detailed stability studies on ILs have been extensively reported and reviewed [66,110,111]. Imidazolium-based ILs are not stable under basic conditions. In the presence of strong bases, they decompose to produce Manich-elimination products [112]. Phosphonium ILs are more inert against strong bases, so that reactions using strong bases, such as Grignard reagents, can be carried out among phosphonium ILs. The results, however, are not better than molecular solvents such as THF [113]. In fact, stability can also be obtained through ionic liquid structure design. For example, a series of geminal dicationic ionic liquids were reported, among which the stable range can be -4 to 400°C [114].

Meanwhile, ILs can be designed as unstable yet energetic [100,115-119]. For example, Shreeve *et al.* have designed and synthesized a series of triazolium, tetraazolium-based ILs, especially those with $[\text{ClO}_4]$ and $[\text{NO}_3]$ anions (Scheme 7) that can be exposed at considerably low temperature so that they can be used as energetic materials [120-123]. These works have been covered in a recent review [124]. It is important to emphasize that in general, organic nitrates and perchlorates are potentially explosive, especially when rigorously dried. Although no problems have been reported to date, care should be taken at all times when handling these. It has been reported that a large number of ILs, including commercially available ILs, are combustible owing to the positive heat formation, oxygen content, and decomposition products [125].

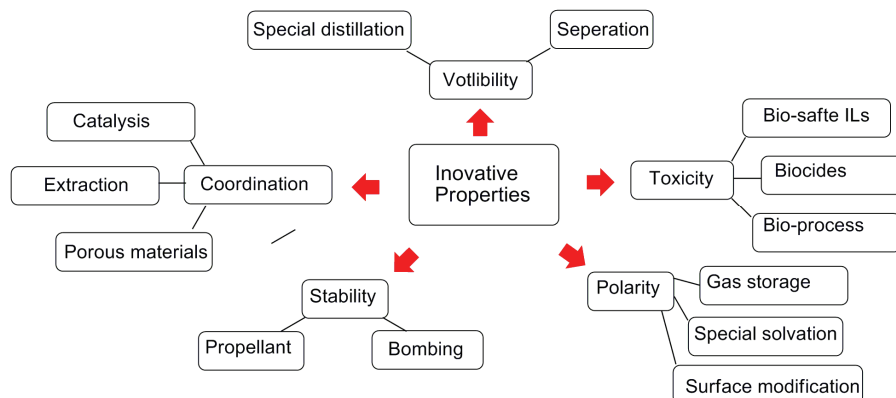


Figure 1. Discovery of innovative properties of IL-inducing novel applications

It is important to note that there is a significant number of functionalized ILs that are now available, though their stability has not been routinely investigated.

7. Perspectives

This review aims to arrive at a gradual understanding of the following knowledge on IL properties, which is continuously being updated:

- 1) Some ionic liquids can be readily distilled.
- 2) Some ionic liquids are proven toxic and environmentally hazardous.
- 3) Some ionic liquids are low polar.
- 4) Ionic liquids are normally coordinating.
- 5) Ionic liquid stability can be controlled through molecular design.

All these changes demonstrate a quiet but ongoing transformation in our understanding of IL properties. Instead of arresting the development of IL applications, the realization and deeper understanding of IL properties can lead to innovation and application to more fields, as illustrated in **Figure 1**.

8. Acknowledgements

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