A Review of Ionic Liquids, Their Limits and Applications

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ABSTRACT

Since environmental pollution caused by chemical and energy industries has increased for several decades, there is a social expectation that scientists and engineers try to design sustainable chemical processes, to generate less hazardous materials and more environmentally friendly sources of energy production. In this review the roles of Ionic Liquids (ILs) and IL based solvent systems as proposed alternative for conventional organic solvents are described. Since there are already many reviews on benefits of ILs, after a very brief review of ILs we focus mostly on aspects that are not covered in other reviews, in particular the known limits of these solvents. In addition, different methods to measure the physicochemical properties relevant to their use in energy storage applications such as fuel cells and batteries are introduced. The physicochemical properties that are reviewed are thermal properties, conductivity and chemical reactivity. The focus of the review is on the literature after 2008, with the exception of some important historic articles on ILs.

KEYWORDS

Technology; Preference for Quality; Volume of Trade; Vertical Intra-Industry Trade

1. Introduction

One of the major sources of waste is solvent losses that end up in the atmosphere or in ground water [1-6]. Solvent use has been reported to account for about 60% of the overall energy in pharmaceutical production, and it has been responsible for 50% of post-treatment greenhouse gas emissions [7,8]. Therefore, solvent selection should be considered systematically to improve synthesis conditions within the framework of green chemistry principles.

Various methods and tools have been developed for the identification and selection of appropriate solvents for synthesis. Consequently, there are a number of solvent selection guides available in the literature [1-8]. We have categorized the common solvents in three different classes of preferred, usable, and undesirable (Table 1) [1-8]. The first three items in the preferred column are the most desired solvents and ILs on their own are a large class of solvents. However not all ILs are green solvents.

The focus of this review is on the literature after 2008, with the exception of some important historic articles. We will first have a very brief review of ILs and then we will discuss the limits of these solvents. Most of the limits in the literature are reported for non protic ILs therefore in our review of protic ionic liquids instead of discussion of their limits we focused mostly on their applications in energy industry. Consequently several methods to measure the physicochemical properties relevant to their use in energy industry applications are reviewed.

2. Ionic Liquids

Room-temperature ILs, organic salts that are liquid below 100°C, have received considerable attention as substitutes for volatile organic solvents. Since they are nonflammable, non-volatile and recyclable, they are classified as green solvents. Due to their remarkable properties, such as outstanding solvating potential [9], thermal stability [10] and their tunable properties by suitable choices of cations and anions [11], they are considered favourable medium candidates for chemical syntheses.

ILs are usually categorized into four types based on their cation segment: 1) alkylammonium-, 2) dialkylimidazolium-, 3) phosphonium- and 4) N-alkylpyridinium-based ILs (Figure 1).
Table 1. Guide for solvent selection.

| Preferred         | Usable           | Undesirable         |
|-------------------|------------------|---------------------|
| Sc-CO₂            | Cyclohexane      | Pentane             |
| ILs               | Heptane          | Hexane(s)           |
| Water             | Toluene          | Diisopropyl ether   |
| Acetone           | Methyl cyclohexane| Diethyl ether       |
| Ethanol           | Isooctane        | Dichloromethane     |
| 2-propanol        | Acetonitrile     | Dichloroethane      |
| 1-propanol        | 2-MeTHF          | Pyridine            |
| Ethylacetate      | THF              | Dioxane             |
| Isopropanol       | Xylenes          | Dimethoxyethane     |
| Methanol          | DMSO             | Benzene             |
| 1-Butanol         | Acetic acid      | Carbon tetrachloride|
| tert-Butyl alcohol| Ethylene glycol  |                     |
|                   | Methyl Ethyl Ketone|                    |

Note: Sc-CO₂ is referred to Supercritical-CO₂.

Figure 1. Alkylammonium, phosphonium, dialkylimidazolium and N-alkylpyridinium cations.

Although these ILs are used successfully as solvents and catalysts in many reactions, there are some limitations in their use. In the following, we will describe the known advantages and disadvantages of each class of ILs.

The first synthesized IL was an ammonium-based one (ethanolammonium nitrate, EOAN), which was reported by Gabriel in 1888 [12]. Ammonium-based ILs have been used widely as electrolytes in high-energy electrochemical devices owing to their good electrochemical cathodic stabilities, low melting points and low viscosities [13-15].

Popular imidazolium-based ILs are among the most studied ILs. Selection of the imidazolium ring as a cation (Figure 2) is often due to its stability within oxidative and reductive conditions [16], low viscosity of imidazolium ILs and their ease of synthesis [17]. There are also several reports regarding the application of imidazolium-based ILs as catalysts for the improvement of reaction time, yield and chemoselectivity of many organic reactions [18-21].

However, Olofson et al., in 1964 [22], reported on a kinetics study demonstrating that the proton sandwiched between the two nitrogen atoms (H₂) in the imidazolium cation undergoes deuterium exchange in deuterated solvent because of its acidic nature. Two later studies reported that deprotonation of the imidazolium cation to the highly reactive carbene and hence showed the non-innocent nature of imidazolium-based ILs under basic conditions [23,24].

In another investigation [25], the low yield of a base-catalyzed Baylis-Hillman reaction in the presence of imidazolium-based ILs was attributed to a side reaction involving the imidazolium-based IL (Scheme 1). This observation also confirmed that using this type of IL under basic conditions needs to be considered with more precaution to avoid unexpected side reactions (Scheme 2).

Pyridinium-based ILs are more novel in comparison with their imidazolium-based counterparts, and research on their stability, reactivity and catalytic role in organic synthesis is still in progress. Although they show poor regioselectivity in palladium-catalyzed telomerization of butadiene with methanol [26], and they have a negative effect on the rate of some Diels-Alder reactions [27], applications of this type of ILs are quite successful in reactions such as Friedel-Crafts [28] and Grignard [29].

The catalytic role of pyridinium-based ILs has been shown to be remarkable in the synthesis of some pharmaceutical agents such as 1,4-dihydropyridine [30], dihydropyrimidinones [31] and 3,5-bis(dodecyloxycarbonyl)-1,4-dihydropyridine derivatives [32].

Phosphonium-based ILs are more novel than the imidazolium- and pyridinium-based ILs. They are more thermally stable (in some cases up to nearly 400°C!) [33] in comparison with ammonium and imidazolium salts, and this remarkable property makes them suitable for reactions that are carried out at greater than 100°C. Phosphonium-based ILs are used as the catalyst and solvent for hydroformylation [34], palladium-catalyzed Heck re-
actions [35] and palladium-mediated Suzuki cross-coupling reactions [35]. In addition, they are also powerful phase-transfer catalysts for the Halex reaction [36].

Recently, phosphonium-based ILs have been used for CO₂ capture [37]. Along with their application in the synthesis of a novel polystyrene-based material [38], the styrenic derivatives of phosphonium-based ILs are used as monomers in the synthesis of phosphonium-containing random copolymers [39]. Thicyclohexadienylradical in trihexyl (tetradecyl) phosphonium chloride (IL101) [40] has been studied, and the effects of temperature and solvent on the reaction have been investigated using muon techniques at the TRIUMF National Laboratory of Canada [41]. These studies showed [40,41] reactive free radicals do not react with phosphonium ionic liquids.

Although phosphonium-based ILs showed good stability in the presence of bases (even in reactions involving strong bases such as Grignard reagents [42]), they are still susceptible to reaction with small bases [43] (Scheme 3).

Unlike ammonium-based ILs, which undergo Hoffman or -elimination in the presence of a base at high temperature, phosphonium-based ILs tend to decompose to tertiary phosphine oxides and alkanes under alkaline conditions [44] (Equation (1)).

$$\text{R}_3\text{P-CH}_2\text{-R}^+\text{OH}^- \rightarrow \text{R}_3\text{P=O+CH}_2\text{-R}^-$$  \hspace{1cm} (1)

3. Protic ILs

ILs can be divided into two broad categories: protic ILs (PILs) and aprotic ILs (APILs). PILs are produced through proton transfer from a Brønsted acid to a Brønsted base.

Historically, the first PIL, EOAN was reported in 1888 by Gabriel [12]. There are a large number of reports on the properties of APILs and their applications in different fields [9,45-51]; however, there are few reviews on PILs [52,53].

In comparison with APILs, PILs often have higher conductivity and fluidity as well as lower melting points [54]. They are also cheaper and more convenient to prepare as their synthesis does not involve the formation of byproducts [52]. However, there are several reports of the ability of PILs to form a hydrogen bond network, which can limit the ionicity of PILs in comparison with APILs [55-57]. The hydrogen bonding of PILs has been identified by NMR [55], X-ray diffraction [58] and neutron diffraction [59]. The most studied example of the ability of a PIL to form supramolecular networks through hydrogen bonding is related to ethyldiammonium nitrate (EAN) [59-61].

Normally, PILs are prepared through the neutralization of a base by an acid [62,63] or the mixture of equimolar amounts of acid and base [54,55]. Ideally, the proton transfer is completed from Brønsted acid to Brønsted base, but, in most cases, a neutral species is formed owing to incomplete proton transfer. Aggregation or the formation of ion complexes also can happen to prevent complete proton transfer, which limits the ionicity of the PILs [51]. Although there is still no standard method to measure the ionicity of PILs, some qualitative techniques such as NMR spectroscopy [56,64], changes in thermal properties as a function of stoichiometry [56,64], IR spectroscopy [64], Raman spectroscopy [64] and ionic conductivity by using Walden plots [65,66] have been used to provide information about the ionicity of PILs. Obviously, proton transfer improves by using stronger acids and bases.

PILs have wide applications in biological systems [52] and chromatography [52,67]. In addition, they have been applied as proton-conducting electrolytes for polymer membrane fuel cells [68-72], because of the advantage of having a defined proton activity as well as high proton conductivity, allowing the fuel cell to operate under non-humidified and high-temperature conditions. PILs also have been widely used as a Brønsted acid or base [72] in many acid-base-catalyzed organic reactions such as Knoevenaglecondensation [73], the Diels-Alder reaction [74], aldol condensation [75], Fischer esterification [76] and pinacol rearrangement [77] owing to their non-corrosive, non-volatile and recyclable nature in comparison with mineral acids.

Since ILs, including PILs, are great microwave absorbents, they are good candidates for application as a medium or catalyst in many microwave-assisted reactions. Henderson and Byrne [77] used several ammonium-based PILs as potential mediators for pinacol rearrangements under microwave irradiation; complete conversion was observed in optimized conditions in a pinacol rearrangement of hydrobenzoin (Scheme 4).

Esterification of benzoic acid with a variety of alcohols and a variety of acids with benzoic alcohols are also reported to be efficient when used with some types of imidazolium- or pyridinium-based PILs under microwave irradiation [78] (Scheme 5).

The solvent-free synthesis of coumarins [79], the esterification of salicylic acid [80] and the dehydration of D-fructose and glucose [81] are other examples of using PILs as acidic catalysts under microwave irradiation.

Compared to the disadvantages of ordinary ILs (mostly their reactivity under certain reaction conditions where ILs are used as medium for reaction) there are limited disadvantages of PILs including side reactions during the planned reactions. On the other hand PILs have been considered mostly for their applications in energy industry not as medium for chemistry. For such applications knowledge of their physicochemical properties is important.
3.1. Physicochemical Properties of PILs

Different potential applications of PILs rely on their physicochemical properties, which vary based on the structures of the cation and anion used in the system. In the following sections, different methods for the investigation of thermal and ionic properties of PILs are described briefly.

3.1.1. Thermal-Phase Behaviour

Differential scanning calorimetry (DSC) is one of the thermoanalytical techniques used to study phase transitions of materials (Figure 3). In DSC, both the sample and the reference are maintained at the same temperature ($\Delta T = T_s - T_r = 0$) and any heat transfer between the sample and reference materials is recorded against the temperature [82,83]. The reference in the DSC method is a material that does not show phase change over a wide temperature range, Alumina (Al$_2$O$_3$) and silicon carbide (SiC) are mostly used as the reference materials in DSC. The DSC trace usually is plotted as the heat flow versus temperature; deviation from the baseline of the DSC trace is representative of a phase change such as melting of the sample. Steps in the baseline position of the DSC curves usually refer to the glass-transition temperature ($T_g$) of the materials, which is a transition that happens for amorphous and semi-crystalline materials including some ILs. For ILs, the $T_g$ indicates the cohesive energy within the salt which is decreased by repulsive Pauli forces and increased through attractive Coulomb and van der Waals interactions [52]. Therefore, it is feasible to reach a lower $T_g$ by decreasing the cohesive energy of the ILs through the modification of the cations and anions.

Usually the dependence of logarithm of viscosity on inverse temperature, $i.e.$ $\log(\eta)$ vs. $T_g/T$ are used to show the fragility of materials. More deviation from a linear trend indicates more fragility, which means that as the temperature goes up, the viscosities will decrease at a faster rate than the Arrhenius relationship. Almost all the data on room temperature PILs provide evidence that they show fragile behavior [52,84-88].

3.1.2. Thermal Stability

Thermogravimetry analysis (TGA) is a type of thermal analysis that examines the mass loss of the sample as a function of temperature in a controlled atmosphere [83] (Figure 4).
It has been established that PILs with large proton-transfer energies decompose before reaching their boiling points [52,84,89]. The decomposition temperature varies between 100°C and 360°C [52,68,85,90]. PILs with a bis(trifluoromethane) sulfonamide anion (TFSI) with alkylammonium cations, the imidazolium cation, and a variety of heterocyclic cations are known as the most stable PILs with decomposition temperatures of >200°C [52,90].

3.1.3. Viscosity

Viscosity is an important property of ILs for different applications. Normally, materials with greater van der Waals interactions and hydrogen bonding have higher viscosities [52,86,87,90]. Although it has been observed that the size of the PIL components has little effect on viscosity, the structure of the anion has a large effect on the viscosity and usually more than the structure of the cation [88]. This is an interesting observation that needs to be further substantiated by theoretical modeling. Specific structural features can affect viscosity of ILs. E.g. in substituted imidazolium PILs, stacking of the aromatic rings leads to higher viscosity [52,90]. Increasing the cation size by increasing the ring number in lactam-based PILs increases the viscosity by enhancing the cation-anion interactions [68]. Analysis of the temperature dependence of viscosity for PILs with different glass transitions, \( T_g \), suggests that PILs in general are among fragile material and the PILs with higher fragility have lower viscosity (Figure 5) [90].

3.1.4. Conductivity

The ionic conductivity, which depends on the available charge carriers and their mobility (which depends on viscosity), varies with the molecular weight, and size of the ion. The conductivity of PILs is limited usually by their ion mobility resulting from aggregation [52,88]. Therefore, less ionic interaction and more delocalized charge lead to higher conductivity; therefore, high ionic conductivity values will be expected for the stronger Brønsted acids and bases [69,89]. Ion conductivity decreases by increasing the size of the cation (less mobility); consequently, the conductivity of PILs with longer alkyl chains decreases [52]. Therefore, the higher ionic conductivity of the 1-methyl-2-methyl imidazolium-based PILs compared with the 1-benzyl-2-methyl imidazolium-based PILs [81], and the higher conductivity value for methyl formate over butyl ammonium formate [84], should be due to the increase in the size of the cation. The ionic conductivity of heterocyclic PILs increases with less symmetrical cation structure and smaller molecular weight [52,68]. No obvious trend can be found for the anions used in the system: as an example, nitrate has the highest ionic conductivity in ethyl ammonium-based PILs in comparison with formate, acetate, butrate and lactate anions, but in the series of ethanol ammonium-based PILs, nitrate has the lowest ionic conductivity compared with the same anions [84]. There are a few alkylammonium-based PILs, such as methylammonium-formate (MAF), EAN, ethylammonium acetate (EAA),
and ethylammonium formate (EAF), that have a high ion conductivity over 10 mS·cm⁻¹ at 25°C [52].

A Waldon plot, which is of the equivalent conductivity against the log of the fluidity (inverse viscosity), is a good indication of the ionicity of the ILs. The Walden rule is shown in Equation (2), where λ is the molar conductivity and η is the viscosity.

\[ \Delta \eta = \text{Constant} \quad (2) \]

Negative deviation from the straight line can be representative of an incomplete proton transfer or aggregation of PILs [65] (Figure 6). The solid ideal line corresponds to a dilute aqueous KCl solution in which the system is known to be fully dissociated and to have ions of equal mobility. The presence of parent acid and base molecules in the system can be indicated by vertical deviation from the Walden line as well. The PILs are usually categorized as poor ILs, except for those with a BF₄ anion, which have good ionicity [52].

4. Conclusions

Over the past five years, ILs have continued to be used significantly as a medium and catalyst for many reactions. Despite the significant potential of ILs in this regard, there are reports that show in some cases ILs react with reactants and therefore they cannot be considered as inert solvents. Therefore synthetic chemists should be cautious when designing reactions in ILs depending on reactions they want to do. Overall PILs are less studied compared to aprotic ILs, however among PILs that have been studied so far there is no report of reactivity of PILs with reagents used for chemical reactions. Moreover PILs have an easily tunable and interesting range of physicochemical properties that make them potential candidates for applications in alkaline and alkaline earth ion batteries and fuel cells.

There is a significant need for modelling IL and PIL chemical and physicochemical properties to guide the applications of these materials more efficiently. On the experimental side, the least understood reactions in ILs and PILs are the free radical reactions. There is a need for a microscopic understanding of free radical chemistry in ILs and PILs.

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