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How Green are Ionic Liquids? – A Multicriteria Decision Analysis Approach

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ABSTRACT

Due to various desirable physicochemical properties, ionic liquids (ILs) are still gaining in popularity. ILs have been recurrently considered green solvents. However, environmental, health and safety assessments of ILs have raised certain doubts about their benignness, and their greenness status is currently unclear. To clarify the situation on their greenness, we perform a comprehensive assessment of more than 300 commercially available ILs. We apply multicriteria decision analysis, the tool that allows ranking many alternatives according to relevant criteria. They are toxicity towards various organisms, biodegradability, hazard statements and precautionary measures during their handling. We incorporated organic solvents to rankings, as their greenness is better described, so they serve as greenness reference points. The ranking results obtained considering the whole set of criteria show that ILs are placed between recommended polar solvents and problematic/undesirable non polar organic solvents in terms of greenness. However, the exclusion of toxicity data due to unavailability of endpoints results in assessment of ILs as greener than most of organic solvents.

Keywords: ionic liquids; green chemistry; solvents; green metrics; MCDA

Introduction

Ionic liquids (ILs) are a group of chemicals with melting points below 100 ºC that, in general, result from the combination of relatively large asymmetric organic cations and either organic or inorganic anions. ILs have received much attention in the last decades due to their unique properties, namely nearly negligible vapour pressure, high chemical and thermal stability, low flammability, large liquidus range, high ionic conductivity, large electrochemical window and excellent solvation ability of a wide range of compounds. (Chiappe and Pieraccini, 2005; Eshetu et al., 2016) ILs are considered designer materials since their properties can be tailored by suitable choice of ions from an almost countless number of cation/anion combinations. Thus, ILs with required features could potentially be designed for specific demands. Among the many applications of ILs, they have been used in energy production, storage and utilization (MacFarlane et al., 2014; Wishart, 2009), lignocellulosic biomass pretreatment (Brandt et al., 2013; Passos et al., 2014; Stark, 2011), organic synthesis and catalysis (Hubbard et al., 2011; Olivier-Bourbigou et al., 2010; Zhang et al., 2011), and extraction processes (Pena-Pereira and Namieśnik, 2014; Sun et al., 2012). Remarkably, a number of industrial processes involving ILs have also been reported (Plechkova and Seddon, 2008). From them, the BASIL™ (Biphasic Acid Scavenging utilizing Ionic Liquids) process implemented by BASF in 2002 represents the firstly publicly announced IL process (Rogers and Seddon, 2003).

Greenness of chemical processes and chemicals themselves is a challenging and very complex aspect. There are many greenness assessment systems, some of them, like E-factor (Sheldon, 2017), very widely used. These greenness metrics systems display different complexity, from simple scoring systems (Sheldon, 2017) to detailed multi-aspect systems like life-cycle assessment (Anastas and Lankey, 2000). What is unsuitable, authors overuse the term “green”, stating it even if their procedure, chemical or material meets only one or few of greenness aspects. These aspects include, but are not limited to, environmental benignness, operational safety, lack of toxicity (Poliakoff et al., 2002),biodegradability after use and the possibility to obtain feedstock from sustainable sources.

ILs have been recurrently considered to be green solvents, mainly because they show, in general, negligible volatility and non-flammability. The non-flammability of ILs offers additional safety when compared with many volatile organic solvents. Besides, the negligible vapour pressure of ILs results in no exposure to vapours and nontoxicity via inhalation, even though air pollution could still occur bearing in mind that some ILs could be distilled (Earle et al., 2006). It has been reported, however, that certain ILs produce a negative impact on humans and the environment (Amde et al., 2015; Costa et al., 2017; Cvjetko Bubalo et al., 2014; Pham et al., 2010). ILs may enter the environment by effluents or spills and, depending on their physicochemical properties, cause pollution in different compartments. Moreover, the decomposition of ILs in the environment can lead to additional environmental burdens (Ranke et al., 2007). Thus, aspects such as biodegradability and (eco)toxicity must also be considered before designating and specific IL as a green solvent. The unclear hazard status of ILs and many aspects of greenness assessment results in the need to apply dedicated tools for their full characterisation.

Multicriteria decision analysis (MCDA) is a group of techniques that are aimed at finding the most favourable solution and ranking all remaining ones (Huang et al., 2011). MCDA allows combining values of many assessment criteria into easy to be interpreted numbers – one for every single alternative. It is particularly desired when assessment criteria are contradictory to each other. In other words, MCDA allows ranking all available alternatives (such as ILs) according to the preference. We selected MCDA as assessment tool as was shown that can be successfully applied in sustainability assessment (Cinelli et al., 2014). Greenness rankings were performed for solvents (Tobiszewski et al., 2017a, 2015), derivatisation agents (Tobiszewski et al., 2017b) and nanoparticles (Cinelli et al., 2015; Naidu et al., 2008).

The aim of the study is to answer the question put in the title of the paper. To combine many assessment factors and to obtain full rankings we apply MCDA. The results of the study will give more comprehensive view on ILs greenness status and help researchers and practitioners in selection of safer alternatives.

Methods

Firstly, a dataset consisting of 319 ILs was prepared for analysis. We decided to focus on commercially available ILs only, since newly designed ILs applied for highly scientific purposes are very poorly characterised in terms of their potential hazards. We also wanted to take advantage of material safety data sheets (MSDS), which all commercially available chemicals have and extract as much of information as possible from them. Scientific publications were another source of information describing aspects related to safety – biodegradability or toxicity towards at least one organism. As a result, a dataset of ILs described by up to 14 criteria was prepared. Detailed procedure on data collection and transformation is described in section 1 of **SI**.

From few MCDA algorithms available we selected The Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS), since it allows ranking all alternatives and each alternative is characterised with the value of similarity to ideal solution ranged between 0 and 1.The value 0 is assigned to completely non-ideal alternative, meaning that it is characterised by the worst values for every single criterion and, oppositely, the value of 1 means that ideal solution is found, characterised by the best values for all criteria. Details of TOPSIS algorithm are presented in section 2 of **SI**.

Another desirable feature of MCDA is the possibility to assign weights to criteria, to differentiate the relative importance of criteria and, as a consequence, their influence on final ranking results. We gave higher weights to criteria that are related to toxicity factors than to biodegradability (which has little variance) and criteria taken from MSDS (because of subjective transformation of descriptions into points values). As a result, the weights applied in the ranking presented in the main body of the manuscript are as follows: Hazard statements - 0.1; Precautionary statements - 0.1; Signal wording - 0.025; Special hazards arising from the substance or mixture/Hazardous decomposition products - 0.05; Biodegradability in 28 day test - 0.025; Toxicity towards *Vibrio fischeri* - 0.25; Toxicity towards *Daphnia magna* - 0.25; Vapour pressure - 0.1; Toxicity towards rodents via inhalation - 0.1. Weights applied in other rankings are presented in **Tables S5**, **S7**, **S9** and **S11**.

Results and Discussion

To maximise the information derived from the analyses, we performed different rankings bearing in mind the missing points in the dataset. Thus, initial rankings were performed aiming at maximising the criteria amount (**Tables S6** and **S8**), whereas the last ones were aimed at maximising the number of ILs included in the analysis at the cost of reducing the number of criteria (**Tables S10** and **S12**).

To give the idea on the greenness of ILs we introduced in our analyses some organic molecular solvents previously characterised in solvent selection guides reported in the literature (Prat et al., 2014). Chemists are familiar with hazards related to their application and organic molecular solvents serve as reference points in our rankings. Organic solvents were not included in rankings presented in **Tables S6** and **S8** as their endpoints for toxicity towards rat leukemia cells were not available. The ranking of ILs obtained with the maximum number of criteria is provided in **Table 1**. Besides, the similarity to ideal solution values of those ILs and fifteen well-characterised organic molecular solvents are presented in **Figure 1**.

Table 1. The results of ILs ranking

Rank	IL	CAS number	Similarity to ideal solution value
1	1-ethyl-3-methylimidazolium tetrachloroaluminate	80432-05-9	0.99929
2	choline dihydrogen phosphate	83846-92-8	0.34805
3	1-ethyl-3-methylimidazolium methanesulfonate	145022-45-3	0.33891
4	1-ethyl-3-methylimidazolium tetrafluoroborate	143314-16-3	0.01866
5	1-ethyl-3-methylimidazolium tricyanomethanide	666823-18-3	0.01554
6	1-butyl-1-methylpiperidinium chloride	94280-72-5	0.01274
7	1-ethyl-3-methylimidazolium chloride	65039-09-0	0.00710
8	1-ethyl-3-methylimidazolium dicyanamide	370865-89-7	0.00568
9	triisobutylmethylphosphonium tosylate	344774-05-6	0.00475
10	1-ethyl-3-methylimidazolium nitrate	143314-14-1	0.00404
11	1-methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide	608140-12-1	0.00331
12	1-hexyl-3-methylimidazolium chloride	171058-17-6	0.00294
13	1-butyl-3-methylimidazolium hexafluorophosphate	174501-64-5	0.00286
14	1-octyl-3-methylimidazolium chloride	64697-40-1	0.00260
15	1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	223437-11-4	0.00223
16	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	174899-82-2	0.00221
17	1-butyl-3-methylimidazolium bromide	85100-77-2	0.00173
18	1-octyl-3-methylimidazolium bromide	61545-99-1	0.00165
19	1-butyl-3-methylimidazolium nitrate	179075-88-8	0.00165
20	1-decyl-3-methylimidazolium bromide	188589-32-4	0.00150
21	1-butylpyridinium chloride	1124-64-7	0.00128
22	tributylethylphosphonium diethyl phosphate	20445-94-7	0.00128
23	1-hexyl-3-methylimidazolium tetrafluoroborate	244193-50-8	0.00119
24	1-octyl-3-methylimidazolium tetrafluoroborate	244193-52-0	0.00117
25	1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	216299-72-8	0.00099
26	1-octadecyl-3-methylimidazolium chloride	171058-19-8	0.00091
27	1-butylpyridinium tetrafluoroborate	203389-28-0	0.00056
28	tetrabutylphosphonium bromide	3115-68-2	0.00050
29	1-butyl-3-methylimidazolium tetrafluoroborate	174501-65-6	0.00027
30	1-butyl-3-methylimidazolium chloride	79917-90-1	0.00025
31	1-butyl-4-methylpyridinium tetrafluoroborate	343952-33-0	0.00021
32	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	174899-83-3	0.00011

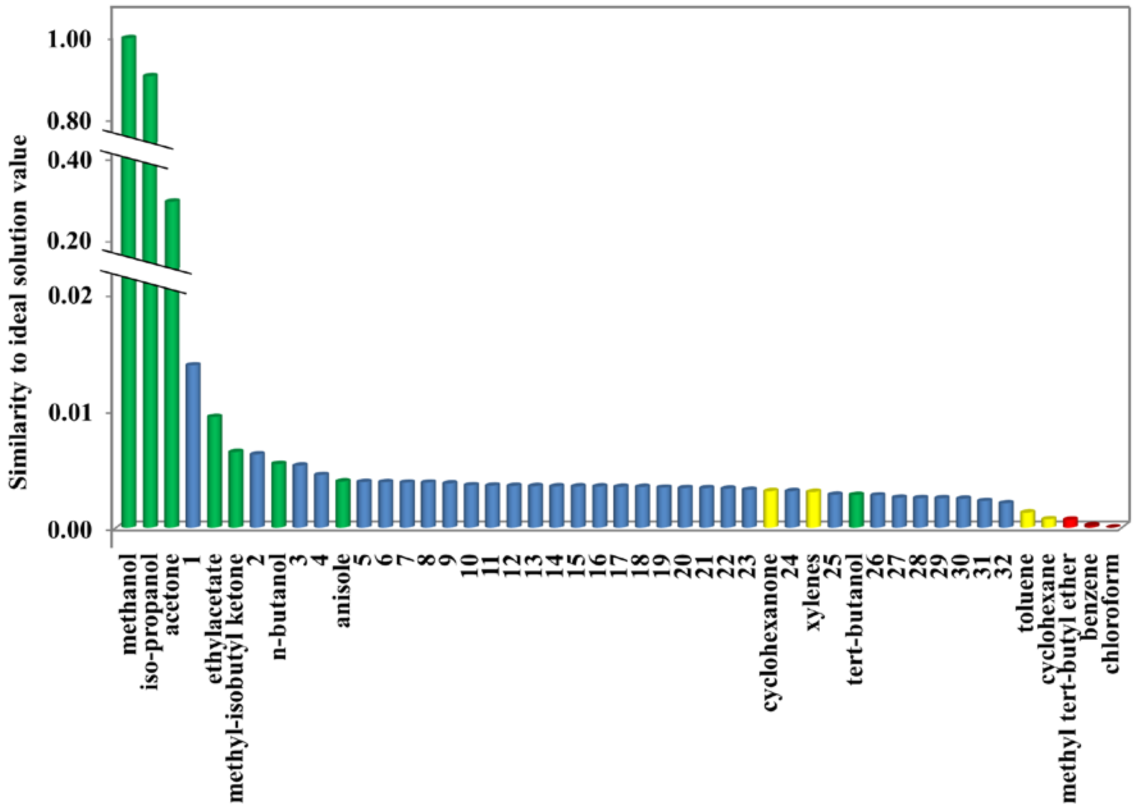

Figure 1. Results of the ranking of ILs and organic solvents as reference. ILs are coloured in blue and the numbering of ILs corresponds to the ranks shown in Table 1. Organic solvents are highlighted in dark green (recommended), yellow (problematic), red (hazardous) or dark red (highly hazardous) according to (Prat et al., 2016) rankings after discussion results.

The length of alkyl substituent in cation influences the greenness rank and the shorter alkyl chain the greener IL is (ranks 7, 12, 14, 26 but rank 30 does not fit this pattern; ranks 17, 18, 20; ranks 16, 25, 32; ranks 4, 23, 24 but butyl substituted IL ranked 29 again does not fit the pattern). Six out of top 10 ILs are short alkyl chain 1-ethyl-3-methylimidazolium ILs. 1-ethyl-3-methylimidazolium tetrachloroaluminate was the first rank for ILs(**Table 1**), and the first ranks in the assessments presented in **Tables S6** and **S8**were also scored by this chloroaluminate(III) IL. It is characterised by a significantly lower toxicity towards all organisms considered in toxicity assessments. It is notable that this IL has shown promise in a wide range of catalytic reactions (Estager et al., 2014; Pârvulescu and Hardacre, 2007) as well as in purification of fuels (Bösmann et al., 2001; Meindersma et al., 2010), even though its sensitivity to moisture has been identified as a limitation for its industrial applicability (Estager et al., 2014). In addition, ILs such as choline dihydrogen phosphateand 1-ethyl-3-methylimidazolium methanesulfonate received relatively high scores, being ranked second and third, respectively. Another remarkable finding was the low position in the ranking of 1-

propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide together with its 1-butyl-3-methylimidazolium analogue(ranks33 and 34, respectively). Both ILs are characterised by many hazard and precautionary statements. Furthermore, 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide is particularly toxic towards *Vibrio fischeri*, while 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide is toxic towards *Daphnia magna*.1-butyl-3-methylimidazolium cation has proved to be the most toxic in various tests when bis(trifluoromethylsulfonyl)imide is the anionic moiety (Matzke et al., 2007).This anion is less toxic than other ions towards *Lemna minor*, what is reflected in the ranking shown in **Table S6**. When compared with molecular organic solvents (**Figure 1**), all ILs were ranked within a narrow range of values of similarity to ideal solution (0.0021-0.0139), what makes them relatively non-diversificated group in comparison to polar solvents included in the ranking (considering assessment criteria). In general, ILs with available data for corresponding criteria were ranked between methanol, iso-propanol and acetone – three polar solvents commonly considered as green (Jessop, 2011; Prat et al., 2014), and toluene, cyclohexane, methyl*tert*-butyl ether, benzene and chloroform. The latter solvents are identified as causing major issues or are undesirable, except toluene, which is categorised as causing some issues or substitution is advisable (Byrne et al., 2016).It is also noteworthy that three ILs showed scores interleaved between the ones of organic solvents recognised as green, such as ethyl acetate, n-butanol and anisole, whereas eight out of the thirty two ILs considered showed similar but lower scores than xylenes, classified as problematic organic solvents (Prat et al., 2014).

Remarkably, the situation changed significantly when hardly available criteria on toxicities were not included in the assessment (see **Table S9**). The ranking presented in **Table S10** shows that more than 140 ILs were ranked higher than acetic acid, the first “reference point” in the assessment and they were very similar to ideal solution. There is a strong implication that if toxicity is neglected as a factor of greenness (or only inhalation toxicity is considered, bearing in mind their negligible volatility) ILs could be considered green solvents. Further reduction of assessment criteria to four (presented in **Table S12**) can give only very superficial information on ILs greenness. This assessment favours compounds that are biodegradable and do not form hazardous decomposition or degradation products. This means that compounds with only carbon and hydrogen are ranked much higher than others.

The problems related to obtained results reliability could be associated to the quality of input data and the subjectivity in transformation of descriptive criteria into numerical values. **Tables S13-S17** summarise the results of sensitivity analysis and proves that the rankings are not significantly different if the values for all criteria are randomly changed for ±10%.

Conclusions

The most comprehensive assessments that includes safety, biodegradability and toxicological criteria show that ILs can be placed in between molecular polar (methanol, iso-propanol and acetone) and nonpolar (toluene, cyclohexane, methyl *tert*-butyl ether, benzene and chloroform) solvents in terms of greenness. Comprehensive assessments can be performed for a limited amount of ILs in comparison to numbers appearing in literature or even these, comparably better described, commercially available ILs. It is hard to make definitive judgements but ILs with fluorine containing anions should be avoided. Lack of data is a serious problem in performing greenness assessments for ILs. In fact, apart from the comprehensive assessment criteria considered in this work, it would be worthwhile including additional information, such as environmental, health and safety issues of chemicals required in the preparation and purification of every single ILs and associated energy demands. Additional studies would be therefore essential to get a better picture of how a larger number of ILs behaves in comparison with well characterized solvents in terms of Green Chemistry. Notwithstanding the foregoing, our results clearly show that the flat assertions on ILs being green solvents are inappropriate and should be avoided.

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