

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 °C that, in general, result from the combination of relatively large asymmetric organic cations and either organic

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

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

63 ILs have been recurrently considered to be green solvents, mainly because they show,
64 in general, negligible volatility and non-flammability. The non-flammability of ILs offers
65 additional safety when compared with many volatile organic solvents. Besides, the negligible
66 vapour pressure of ILs results in no exposure to vapours and nontoxicity via inhalation, even
67 though air pollution could still occur bearing in mind that some ILs could be distilled (Earle et
68 al., 2006). It has been reported, however, that certain ILs produce a negative impact on
69 humans and the environment (Amde et al., 2015; Costa et al., 2017; Cvjetko Bubalo et al.,
70 2014; Pham et al., 2010). ILs may enter the environment by effluents or spills and, depending
71 on their physicochemical properties, cause pollution in different compartments. Moreover, the

72 decomposition of ILs in the environment can lead to additional environmental burdens (Ranke
73 et al., 2007). Thus, aspects such as biodegradability and (eco)toxicity must also be considered
74 before designating and specific IL as a green solvent. The unclear hazard status of ILs and
75 many aspects of greenness assessment results in the need to apply dedicated tools for their full
76 characterisation.

77 Multicriteria decision analysis (MCDA) is a group of techniques that are aimed at
78 finding the most favourable solution and ranking all remaining ones (Huang et al., 2011).
79 MCDA allows combining values of many assessment criteria into easy to be interpreted
80 numbers – one for every single alternative. It is particularly desired when assessment criteria
81 are contradictory to each other. In other words, MCDA allows ranking all available
82 alternatives (such as ILs) according to the preference. We selected MCDA as assessment tool
83 as was shown that can be successfully applied in sustainability assessment (Cinelli et al.,
84 2014). Greenness rankings were performed for solvents (Tobiszewski et al., 2017a, 2015),
85 derivatisation agents (Tobiszewski et al., 2017b) and nanoparticles (Cinelli et al., 2015; Naidu
86 et al., 2008).

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

91

92 **Methods**

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

102 From few MCDA algorithms available we selected The Technique for Order of
103 Preference by Similarity to Ideal Solution (TOPSIS), since it allows ranking all alternatives
104 and each alternative is characterised with the value of similarity to ideal solution ranged
105 between 0 and 1. The value 0 is assigned to completely non-ideal alternative, meaning that it is

106 characterised by the worst values for every single criterion and, oppositely, the value of 1
107 means that ideal solution is found, characterised by the best values for all criteria. Details of
108 TOPSIS algorithm are presented in section 2 of **SI**.

109 Another desirable feature of MCDA is the possibility to assign weights to criteria, to
110 differentiate the relative importance of criteria and, as a consequence, their influence on final
111 ranking results. We gave higher weights to criteria that are related to toxicity factors than to
112 biodegradability (which has little variance) and criteria taken from MSDS (because of
113 subjective transformation of descriptions into points values). As a result, the weights applied
114 in the ranking presented in the main body of the manuscript are as follows: Hazard statements
115 - 0.1; Precautionary statements - 0.1; Signal wording - 0.025; Special hazards arising from the
116 substance or mixture/Hazardous decomposition products - 0.05; Biodegradability in 28 day
117 test - 0.025; Toxicity towards *Vibrio fischeri* - 0.25; Toxicity towards *Daphnia magna* - 0.25;
118 Vapour pressure - 0.1; Toxicity towards rodents via inhalation - 0.1. Weights applied in other
119 rankings are presented in **Tables S5, S7, S9** and **S11**.

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121 **Results and Discussion**

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

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

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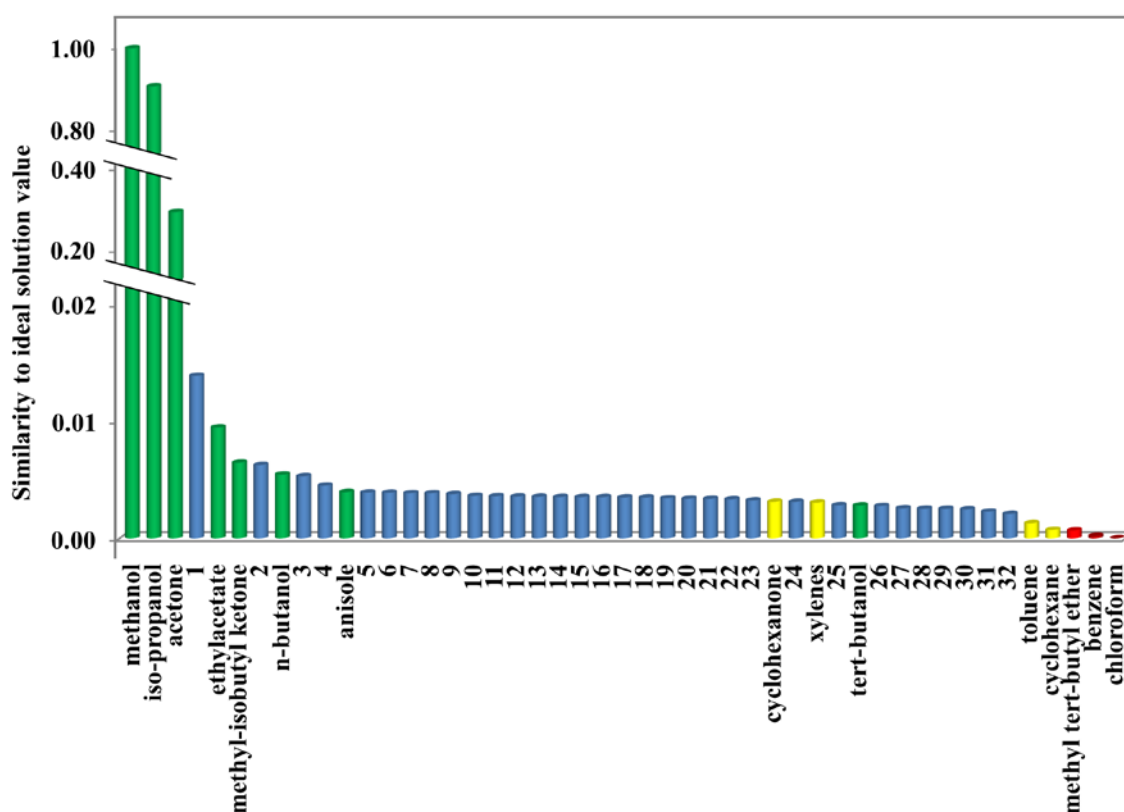
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Table 1. The results of ILs ranking

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





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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.

148 The length of alkyl substituent in cation influences the greenness rank and the shorter
149 alkyl chain the greener IL is (ranks 7, 12, 14, 26 but rank 30 does not fit this pattern; ranks 17,
150 18, 20; ranks 16, 25, 32; ranks 4, 23, 24 but butyl substituted IL ranked 29 again does not fit
151 the pattern). Six out of top 10 ILs are short alkyl chain 1-ethyl-3-methylimidazolium ILs. 1-
152 ethyl-3-methylimidazolium tetrachloroaluminate was the first rank for ILs(**Table 1**), and the
153 first ranks in the assessments presented in **Tables S6** and **S8**were also scored by this
154 chloroaluminate(III) IL. It is characterised by a significantly lower toxicity towards all
155 organisms considered in toxicity assessments. It is notable that this IL has shown promise in a
156 wide range of catalytic reactions (Estager et al., 2014; Pârvulescu and Hardacre, 2007) as well
157 as in purification of fuels (Bösmann et al., 2001; Meindersma et al., 2010), even though its
158 sensitivity to moisture has been identified as a limitation for its industrial applicability
159 (Estager et al., 2014). In addition, ILs such as choline dihydrogen phosphate and 1-ethyl-3-
160 methylimidazolium methanesulfonate received relatively high scores, being ranked second
161 and third, respectively. Another remarkable finding was the low position in the ranking of 1-

162 propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide together with its 1-butyl-3-
163 methylimidazolium analogue (ranks 33 and 34, respectively). Both ILs are characterised by
164 many hazard and precautionary statements. Furthermore, 1-propyl-3-methylimidazolium
165 bis(trifluoromethylsulfonyl)imide is particularly toxic towards *Vibrio fischeri*, while 1-butyl-
166 3-methylimidazolium bis(trifluoromethylsulfonyl)imide is toxic towards *Daphnia magna*. 1-
167 butyl-3-methylimidazolium cation has proved to be the most toxic in various tests when
168 bis(trifluoromethylsulfonyl)imide is the anionic moiety (Matzke et al., 2007). This anion is
169 less toxic than other ions towards *Lemna minor*, what is reflected in the ranking shown in
170 **Table S6**. When compared with molecular organic solvents (**Figure 1**), all ILs were ranked
171 within a narrow range of values of similarity to ideal solution (0.0021-0.0139), what makes
172 them relatively non-diversificated group in comparison to polar solvents included in the
173 ranking (considering assessment criteria). In general, ILs with available data for
174 corresponding criteria were ranked between methanol, iso-propanol and acetone – three polar
175 solvents commonly considered as green (Jessop, 2011; Prat et al., 2014), and toluene,
176 cyclohexane, methyltert-butyl ether, benzene and chloroform. The latter solvents are
177 identified as causing major issues or are undesirable, except toluene, which is categorised as
178 causing some issues or substitution is advisable (Byrne et al., 2016). It is also noteworthy that
179 three ILs showed scores interleaved between the ones of organic solvents recognised as green,
180 such as ethyl acetate, n-butanol and anisole, whereas eight out of the thirty two ILs considered
181 showed similar but lower scores than xylenes, classified as problematic organic solvents (Prat
182 et al., 2014).

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

193 The problems related to obtained results reliability could be associated to the quality
194 of input data and the subjectivity in transformation of descriptive criteria into numerical
195 values. **Tables S13-S17** summarise the results of sensitivity analysis and proves that the

196 rankings are not significantly different if the values for all criteria are randomly changed for
197 $\pm 10\%$.

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199 **Conclusions**

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

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