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A Preliminary Assessment of the 'Greenness' of Halide-Free Ionic Liquids—An MCDA Based Approach

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Abstract: With the growing interests in non-aqueous media for diversified applications, ionic liquids (ILs) are frequently considered as green solvents. While the environmental, health, and safety assessments of the commercially developed ILs and their 'greenness' status are in debate, research focus is shifting towards the application of halide-free ILs for diversified applications. To clarify the situation on their greenness, and to understand if they really possess safe characteristics, we performed an initial assessment of 193 halide free ionic liquids composed of four groups of cations (imidazolium, pyridinium, pyrrodilinium, piperidinum) and 5 groups of anions (acetate, propionate, butyrate, alkanesulfonates, alkylsulfates). The 'Technique for Order of Preference by Similarity to Ideal Solutions' (TOPSIS), a multi-criteria decision analysis (MCDA) tool that allows ranking many alternatives is applied by carrying out the assessment against 14 criteria that includes hazard statements, precautionary statements, biodegradability, and toxicity towards different organisms. The ranking results obtained against the set of criteria considered show that the halide free ILs placed between recommended polar solvents: methanol and ethanol can be considered to be safer alternatives in terms of 'greenness'. The study in this work provides an initial assessment of the halide-free ionic liquids evaluated against 14 criteria in terms of their safety characteristics ("green character") using the MCDA-TOPSIS approach.

Keywords: ionic liquids; MCDA; TOPSIS; green chemistry; chemometrics; electrodeposition

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1. Introduction

Ionic liquids (ILs) are a class of compounds with melting temperatures below 100 °C that are made up of large asymmetric organic cations and either organic or inorganic anions. ILs have changed dramatically since their discovery in 1912, and their unusual physio-chemical features have attracted a lot of attention in recent decades [1,2]. Low vapour pressure, superior chemical and thermal stability, low flammability, high ionic conductivity, wide electrochemical window, and excellent solvation ability of a wide spectrum of chemicals are examples of such properties. Furthermore, they are commonly used as designer solvents for a wide range of applications, including chemical unit operations and processes, renewables, and electrochemical engineering [3]. Electrodeposition of metals from aqueous solutions is one of the key areas of metallization in automotive and aerospace industries.

Despite the attractive properties of aqueous electrolytes, such as high metal salt solubility, high conductivity, etc., industrial metal plating suffers from common problems such as hydrogen embrittlement and low coulombic efficiency [4]. In addition, the spent process solution must be treated before recycling and reuse, which necessitates the addition of chemicals and contributes to recycling costs. Furthermore, certain complexing agents present in the aqueous plating/deposition solution are subjected to anodic oxidation and tend to form breakdown products during the electrolysis. Such products may not only impact the plating process but also pose an environmental hazard [5,6].

Electrodeposition of metals, metal-alloy combinations from ionic liquids has gained significant attention in the past two decades. They provide a different environments/electrolytes for metal and metal-alloy electrodeposition, wide electrochemical windows, high thermal stability, good ionic conductivity, and better mass transport. In addition, employing ionic liquids (ILs) can eliminate or minimize the hydrogen gas evolution at the cathode and prevent the base metal substrates (such as high strength steels) from hydrogen embrittlement. While aqueous-based technology is established and used for the production of commercial metal and metal-alloy coatings, ILs have attracted much interest as promising electrolytes for metal electrodeposition [7].

Though there are significant developments on the metal, metal-alloy electrodeposition from ILs, there are certain issues that remain critical. Issues associated with the use of ILs include the Registration, Evaluation, Authorisation, and Restriction of Chemicals (REACH) approval costs associated with the development of new compounds and their listing under the European rules: end-of-life vehicles (ELV), waste electrical and electronic equipment (WEEE), and restriction of hazardous substances (RoHS). Transferring the technology from academia to the industry and translating it into products with commercial value will boost the possibility of ILs entering more markets in the near future [1,7].

ILs have frequently been regarded as "green" solvents, owing to their low volatility and low flammability. On comparison with majority of the volatile organic solvents, the relatively low flammability of ILs provides additional safety. Besides, the low vapour pressure of ILs results in negligible exposure to fumes, exhibit relatively low toxicity during inhalation. However, air pollution may still occur from few ILs due to the release of certain vapours in small concentrations during their distillation [3,8]. Despite their wide range of applications, however, claims about their safety, harmfulness, toxicity, and biodegradability remain unclear. Certain ILs, however, have been reported to have a negative impact on humans and the environment [9,10]. ILs, for example, may enter the environment through effluents or spills and, could cause pollution in various regions and sectors, depending on their nature and interaction with the environment. Furthermore, the breakdown of ILs in the environment might result in additional environmental burdens [11]. Several studies have found that the majority of ILs are not easily biodegradable and are relatively toxic. Consequently, the lack of data on the biodegradability of ILs poses a serious problem in determining the hazard status and safer characteristics of the ILs when performing environmental evaluations to determine their greenness [12–14]. In order to assess the 'green' credentials of the ILs, a strategy must be implemented that takes into account market demands as well as health, safety, and environmental concerns.

To understand and assess the greenness of the ILs, certain estimations were performed by Marta et al. using multi-criterion decision approach (MCDA) algorithms such as the Technique for Order of Preference by Similarity to Ideal Solutions (TOPSIS) methodology [15–18]. Multicriteria decision analysis (MCDA) is a collection of methodologies aimed at identifying the most favourable alternative while ranking all the remaining ones [19,20]. MCDA helps to integrate the results of multiple evaluation criteria into a single, easily interpreted number—one for each alternative. It is especially useful when the assessment criteria are at odds with one another. MCDA methods have already been used to evaluate the greenness of organic solvents (polar and non-polar), derivatization agents [21], ionic liquids [17], and deep eutectic solvents [16], successfully. With regards to the ILs, the greenness assessments were successfully applied focusing on commercially available ILs only. With the research focus shifting towards halide-free ILs (HF-ILs), claims pertaining to their low harmfulness and toxicity, or high biodegradability are not clearly understood.

The commercially available and newly designed HF-ILs that could be applied for industrial and scientific purposes are very poorly characterised in terms of their potential hazards. Though the debate on the 'greenness' of the HF-ILs continues, estimation of their greenness should be performed to understand the preliminary safety characteristics. The aim of the study is to assess the greenness of HF-ILs against a variety of criteria besides toxicity. The MCDA, via TOPSIS methodology, is used to combine different

assessment factors and obtain full rankings for the alternatives chosen. To the best of authors' knowledge, this is the first study that considers a range of criteria (not only toxicity) to rank the commercial and laboratory-developed halide free ILs according to their environmental impact. The results of this study may be useful for fields such as electroplating, CO_2 reduction, biomass energy conversions, other chemical/electrochemical processes, and so on, in selection of safer alternatives.

2. Materials and Methods

2.1. Data Collection and Selection of Halide-Free Ionic Liquids

Firstly, a dataset consisting of 193 halide-free ILs (HF-ILs) consisting of combination of imidazolium, pyrrolidinium, pyridinium, piperidinium cations, and carboxylic acid (acetic acid, propionic acid, butyric acid), alkyl sulfate (methyl, ethyl), sulfonate (methane, ethane) anions was prepared for analysis. Since the primary focus was on the development of HF- ILs for electrodeposition, CO_2 reduction and other electrochemical processes, alkyl groups for the cations were restricted up to butyl. Increasing the cationic chain length with higher alkyl group will increase the viscosity drastically and affect the overall process performance. A combination of HF-ILs that are commercially available and designed through machine learning methods (artificial intelligence) was chosen for the analysis. The cation-anion combinations for HF-ILs are chosen considering the guidelines on selection of safer ILs by Costa et al. [9]. Since the safety data on the commercially available HF-ILs and be-spoke HF-ILs are quite limited, safety information on the raw materials that are used for the synthesis were collected along with commercially available HF-ILs. The raw materials required for the synthesis of HF-ILs were taken from the literature [22–47]. Safety data sheets (SDS), research publications, The European Chemicals Agency (ECHA) register database [48], Pubchem [49], Chemspider [50], and the European Commission funded projects website were used to extract as much information as possible. The details of the HF-ILs and the raw materials required for their synthesis are listed in Table S1 (supplementary information).

2.2. Ranking Methodology-TOPSIS Algorithm

MCDA is an assessment tool which allows to prioritise all the alternatives (such as ILs) based on the ranking through TOPSIS methodology. Hwang and Yoon [51] developed TOPSIS algorithm which helps to identify the best alternative by transforming all the criteria into a numerical matrix, and calculate the shortest and longest distance from the ideal and non-ideal solution. The key advantage with TOPSIS method is that it ranks all the alternatives by combining different criteria to obtain a single value, which is based on the similarity to the ideal solution ranging from 0 to 1. "0" represents a completely non-ideal (or negative ideal) option, indicating that it is characterised by the worst values for each and every criterion, furthest from the completely ideal (or positive ideal) solution. On the contrary, "1" indicates that an ideal solution has been identified, indicating that the best values have been obtained for all the criteria, and has attained the shortest distance from the completely ideal solution.

Prior to assessing the greenness of the HF-ILs, the greenness of the raw materials that are used for the synthesis of HF-ILs are assessed via the TOPSIS algorithm. For TOPSIS analysis, numerical values are required. Therefore, the collected information were transformed into numerical values by adopting the procedure reported by Marta et al. [16,17]. Sensitivity analysis is also carried out to investigate how changes in input values and/or weights affect the final ranking results. The input values are changed at random for $\pm 10\%$, and the results are analysed to see if the differences in ranking are significant.

The TOPSIS algorithm is outlined briefly in the Supplementary Information (https://www.mdpi.com/article/10.3390/pr9091524/s1). One of the desirable features of MCDA is the ability to assign weights to criteria, thereby differentiating the relative importance of criteria and providing an insight into their impact on final ranking results. Higher weights are assigned to criteria that are related to toxicity factors followed by biodegrad-

ability and criteria taken from SDS. Table 1 lists the weightage that has been applied to each criterion for the TOPSIS ranking. The criteria and the relevant source of information that was chosen for the study are shown in Table S2 (Supplementary Information).

Table 1. Table showing the criteria and the weightage employed in the study for the TOPSIS Ranking.

Criteria	Weightage
Signal wording	0.02
Hazard statements	0.06
Precautionary statements	0.06
Special hazards arising from the substance or mixture/Hazardous decomposition products	0.02
Biodegradability	0.1
Toxicity towards Daphnia Magna	0.13
Toxicity towards algae	0.13
Toxicity towards fish	0.13
Toxicity towards rodents (rats, mice)	0.13
Flash point	0.04
Vapor pressure	0.06
Partition coefficient	0.04
pH	0.04
Carcinogenity	0.04

3. Results and Discussion

To understand the greenness of the HF-ILs, the greenness of the raw materials that are used for the synthesis are evaluated initially by assessing against 14 criteria, as mentioned in Section 2 and in the Supplementary Information (https://www.mdpi.com/article/10.3390/pr9091524/s1). In this context, it is important to note that certain halide containing ILs are used for the synthesis of HF-ILs and as a result, these ILs are assessed along with the raw materials used for the synthesis of HF- ILs. As can be seen in the supplementary file, methylguanidine is identified as the most safe alternative (Ci* = 0.62834), owing to its non-toxicity to all evaluated organisms, and relatively less hazard statements (5 statements). There is no foreseeable risk of serious hazardous products being formed during its decomposition (except oxides of carbon and nitrogen). The values of similarities to ideal solutions then decrease from 0.20 to 0.12 for the next ten compounds, with the majority of them being imidazolium-based ILs, followed by other raw materials. To assess the reliability, a sensitivity analysis was performed by randomly changing the input data by $\pm 10\%$.

Based on the data set of raw materials, it is observed that toxicity, hazard, and precautionary statements are observed as the major influencing factors. Therefore, these values were changed randomly, and the relative closeness to ideal solutions are evaluated. Results of sensitivity analysis rankings and their differences are presented in Table S3 of the Supplementary Information (https://www.mdpi.com/article/10.3390/pr9091524/s1). From the table, it is evident that there are no significant differences in the overall ranking indicating that the ranking results are reliable and considered to be accurate. The HF-ILs mixture that could be synthesized from these basic ingredients (as mentioned in Table S1) is expected to function similarly, guided by the same mechanism/mode of action, and differ solely in potencies, according to general principles of mixture toxicology [52].

Considering such a scenario, effects can be calculated simply from the sum of doses/concentrations, adjusted for relative toxicity (dose/concentration addition) for mixtures of similar acting substances (such as HF-ILs) using

$$E(Cmix) = \sum_{i=1}^{n} aE(Ci) \quad (1)$$

where $E(C_{mix})$ is combined effect at the equimolar mixture concentration of raw materials (C_{mix}). $E(C_i)$ represents the similarity value to ideal solution that are calculated for different raw materials with TOPSIS and represent the individual HF-IL mixture component (i) applied at the concentration (C_i). In principle, concentrations of the individual raw materials are multiplied by a scaling factor "a" followed by their summation. The scaling factor takes into account the differences in the potency of the individual substances. In our analysis, we have assumed a = 1 considering an equimolar ratio of the raw materials for the preparation of HF-ILs.

The combined greenness results of HF-ILs, calculated with Equation (1), and their rankings are presented in Table 2. The complete list of the HF-ILs and their rankings are presented as Table S4 in the Supporting Information (https://www.mdpi.com/article/10.3390/pr9091524/s1). The assessment results show the HF-ILs that are placed between the two polar molecules: methanol and ethanol are relatively close to the ideal solution compared to the other HF-ILs. The short alkyl chain imidazolium based ILs, with the 2 same cations (diethyl), are identified to be the best alternatives amongst the first set. N,N'-alkyl imidazolium cations was shown to exhibit toxicity in various tests by researchers. When coupled with halide-free anions such as propionate, acetate, butyrate, sulfonates, and sulfates, the results show that these ILs exhibit the 'green' character. Similar results were obtained by [53] when tests were conducted with bis(trifluoromethylsulfonyl)imide anion and were reflected in the ranking analysis studied by Marta et al. [17]. These suggest that the selection of cation and anion could also play a critical role in controlling the toxicity besides tailoring the physico-chemical properties required for an intended application. The results signify that replacing the halide anions with halide-free ions (such as propionate, acetate, butyrate, bisulfates/methyl sulfates, methane/ethane sulfonates) could make them environmentally friendlier and help achieve the 'green' character. The results also confirm that the greenness rank is influenced by the length of the alkyl substituent in the cation, with shorter ones being predominant (dialkyl imidazolium) and [E2BPyr][HSO_4] being an exception. It is notable that imidazolium-acetate based ILs have shown promise for CO_2 conversion through electrochemical route [54] as well as in biomass [55], despite their sensitivity to moisture and being a limitation for its industrial applicability [56]. In addition, ILs such as guanidinium-based, choline based ILs (acetate, propionate, butyrate) and other dialkyl, trialkyl imidazolium/pyrrolidinium based ones received relatively high scores.

Table 2. Table showing the TOPSIS ranking of halide free ILs.

Ranking	Name of the Ionic Liquid	Abbrevation	Similarity to Ideal Solution Value $E(C_{mix})$
1	methanol	[MeOH]	0.62834
2	1,3-diethyl imidazolium acetate	[EE'Im][OAc]	0.46447
3	1-ethyl-2-butyl pyridinium bisulfate	[E2BPyr][HSO_4]	0.46441
4	1,3-diethyl imidazolium propionate	[EE'Im][C_2COO]	0.46025
5	1-propyl-1-methyl piperidinium bisulfate	[PMPip][HSO_4]	0.45638
6	1,3-diethyl imidazolium butyrate	[EE'Im][C_3COO]	0.45439
7	1,3-dimethyl imidazolium bisulfate	[MM'Im][HSO_4]	0.44969
8	1-propyl-2,3-dimethyl imidazolium bisulfate	[PMM'Im][HSO_4]	0.44879
9	1,3-diethyl imidazolium bisulfate	[EE'Im][HSO_4]	0.42599

Table 2. *Cont.*

Ranking	Name of the Ionic Liquid	Abbrevation	Similarity to Ideal Solution Value $E(C_{mix})$
10	2,2-diethyl-1,1,3,3-tetramethyl guanidinium ethyl sulfate	[EE′TMG][$EtSO_4$]	0.41882
11	1,3-diethyl imidazolium methane sulfonate	[EE′Im][CH_3SO_3]	0.41720
12	1,3-diethyl imidazolium ethane sulfonate	[EE′Im][$C_2H_5SO_3$]	0.41503
13	1-butyl-1-ethyl pyrrolidinium acetate	[BEPyrl][OAc]	0.41328
14	1-butyl-1-ethyl pyrrolidinium propionate	[BEPyrl][C_2COO]	0.40906
15	1-butyl-1-ethyl pyrrolidinium methane sulfonate	[BEPyrl][CH_3SO_3]	0.40903
16	1-ethyl-2,3-dimethyl imidazolium bisulfate	[EMM′Im][HSO_4]	0.40766
17	1-butyl-1-ethyl pyrrolidinium butyrate	[BEPyrl][C_3COO]	0.40320
18	1-butyl-2,3-dimethyl imidazolium bisulfate	[BMM′Im][HSO_4]	0.40032
19	1-butyl-2,3-dimethyl imidazolium methyl sulfate	[BMM′Im][$MeSO_4$]	0.39949
20	1-ethyl-2,3-dimethyl imidazolium methyl sulfate	[EMM′Im][$MeSO_4$]	0.38581
21	1-butyl-2-methyl pyridinium bisulfate	[B2MPyr][HSO_4]	0.38369
22	1-ethyl-2-butyl pyridinium acetate	[E2BPyr][OAc]	0.37927
23	1-propyl-1-methyl piperidinium acetate	[PMPip][OAc]	0.37015
24	1-ethyl-2-butyl pyridinium butyrate	[E2BPyr][C_3COO]	0.36918
25	1-propyl-1-methyl piperidinium propionate	[PMPip][C_2COO]	0.36701
26	1-butyl-1-ethyl pyrrolidinium methane sulfonate	[BEPyrl][CH_3SO_3]	0.36601
27	1-butyl-1-ethyl pyrrolidinium ethane sulfonate	[BEPyrl][$C_2H_5SO_3$]	0.36384
28	1-propyl-2,3-dimethyl imidazolium acetate	[PMM′Im][OAc]	0.36364
29	1-propyl-1-methyl piperidinium butyrate	[PMPip][C_3COO]	0.36007
30	1-propyl-2,3-dimethyl imidazolium propionate	[PMM′Im][C_2COO]	0.35942
31	Choline acetate	[Ch][OAc]	0.35756
32	ethanol	[EtOH]	0.35613
33	1-propyl-3-methyl imidazolium propionate	[PMIm][C_2COO]	0.35396
34	1-propyl-2,3-dimethyl imidazolium butyrate	[PMM′Im][C_3COO]	0.35356
35	Choline propionate	[Ch][C_2COO]	0.35333
36	1,1-dimethyl pyrrolidinium acetate	[MM′Pyrl][OAc]	0.35101
37	Choline butyrate	[Ch][C_3COO]	0.34748
38	1,1-dimethyl pyrrolidinium propionate	[MM′Pyrl][C_2COO]	0.34679
39	1-propyl-3-methyl pyridinium acetate	[PMPyr][OAc]	0.34379
39	1-propyl-3-methyl pyridinium butyrate	[P3MPyr][C_3COO]	0.34379
41	1,1-dimethyl pyrrolidinium butyrate	[MM′Pyr][C_3COO]	0.34093
42	1-propyl-3-methyl pyridinium propionate	[PMPyr][C_2COO]	0.33957
43	1-propyl-1-methyl pyrrolidinium propionate	[PMPyrl][C_2COO]	0.33648
44	1-ethyl-2-butyl pyridinium methane sulfonate	[E2BPyr][CH_3SO_3]	0.32982
44	1-ethyl-2-butyl pyridinium ethane sulfonate	[E2BPyr][$C_2H_5SO_3$]	0.32982
46	1-propyl-3-methyl pyridinium methyl sulfate	[PMPyr][$MeSO_4$]	0.32609
47	1,3-dibutyl imidazolium Propionate	[BB′Im][C_2COO]	0.32516
48	1-propyl-1-methyl piperidinium methane sulfonate	[PMPip][CH_3SO_3]	0.32396
49	1-ethyl-2,3-dimethyl imidazolium acetate	[EMM′Im][OAc]	0.32251
50	1-propyl-1-methyl piperidinium ethane sulfonate	[PMPip][$C_2H_5SO_3$]	0.32179

Santos and co-workers [57,58] recently reviewed the aquatic toxicity of ILs and underlined the case of cholinium-based ILs as less toxic and more sustainable. Our study also confirms that the cholinium based ILs with different halide-free ions are relatively less toxic and can be considered as less hazardous. Though bisulfate based ILs are shown

to be safer, their applicability in electroplating and other similar applications are limited due to the hydrogen gas evolution. This could not only affect the process performance but also influence the safety. Another notable finding was the low ranking of methane/ethane sulfonates and their pyridinium, pyrrolidinium analogues. These ILs are characterised by many hazard and precautionary statements because of the additive effect resulting from the mixture of raw materials.

In short, the initial assessment shows that it is possible to customize the biological properties of ILs besides physical and chemical properties. Through careful selection of cation/anions and tailoring their combination, it is possible to develop less hazardous HF-ILs. Based on all the contributions from many researchers on the toxicity assessments of ILs, it is clear that the toxicity effects of ILs are significantly influenced by their structural properties. While imidazolium-based ILs are the most widely studied, followed by pyridinium, cholinium-based ILs, few HF-ILs have already achieved the REACH licensing. [EMIm][OAc], [BMIm][OAc], [EMIm][C_2COO], choline acetate are few of the examples that achieved the REACH status and have been licensed to Sigma, Proionic company [59]. Among these, [EMIm][OAc] has shown high potential and predominantly employed in a variety of applications such as zinc electrodeposition [60], dissolution of biomass, biopolymers (cellulose, chitin) [61], and electrochemical conversion of CO_2 to useful chemicals [54]. Despite their widespread use, and numerous studies on the toxic effects [EMIm][OAc], there is still a lack of reliable toxicological information on this topic [62].

The issue with assessing the greenness of ILs is that reports and safety data sheets typically refer to physicochemical properties such as density and viscosity [9,10,13]. Unfortunately, data related to toxicity, biodegradability, and other environmental parameters are still scarce. As a result, ILs are poorly characterized on these criteria. We anticipate that this work will provide a basic overview on the safer characteristics of the HF-ILs and help to screen the alternatives depending on the intended applications.

4. Conclusions

Halide-free ionic liquids (HF-ILs) were assessed based on safety, toxicology criteria, available physical properties, and bio-degradability by adopting the TOPSIS methodology. The TOPSIS algorithm is initially applied for the raw materials and is combined with the general principles of toxicology to evaluate the combined 'greenness' of the be-spoke and commercially available HF-ILs. While the attempts to substitute the halide-containing ILs continue, initial assessment on the greenness of the HF-ILs showed that acetate, butyrate, sulfate (hydrogen, methyl), propionate, and sulfonate, based with short cationic length, seem to be environmentally advantageous and can be considered as potential electrolytes for the electrodeposition of metals and metal-alloys. The assessment can be used as an initial screening of the electrolytes for metal electrodeposition and other associated electrochemical/chemical processes.

The study in this work clearly demonstrate that the assertions about HF-ILs being green solvents can be considered in preliminary screening for electroplating or related electrochemical/chemical processes. Because of the lack of data, the greenness of the HF-ILs are assessed by extracting the information from the raw materials that are used for the synthesis and combining their effects to predict the greenness. The assessment results show the HF-ILs that are placed in between the two polar molecules (methanol and ethanol) are relatively close to the ideal solution compared to the other HF-ILs. In addition to the initial assessment criteria, it is critical to understand the health, safety, and environmental issues of chemicals required in the preparation and purification of each individual HF-IL. Additionally, the preparation, suitability, and compatibility of HF-ILs for the intended applications needs to be understood prior to their testing. Additional research would be required to gain a better understanding of how a large number of the designed HF-ILs behave in comparison to well-characterized ILs, solvents in terms of Green Chemistry.

The methodology described in this work provides basic information on the greenness of HF-ILs and enables easy comparison of the greenness performance of a variety of other

ILs and solvents. The proposed assessment procedure, however, could only be used as a screening tool for preliminary selection of a safer alternative. Incorporation of the newly obtained data (toxicology, biodegradability, and environmental fate) into the performed algorithm will aid the better understanding of IL's biodegradability. In addition, it will also enable to perform a comprehensive assessment of their hazardous nature and analyse their safety aspects from large industrial scale process point of view. Overall, this study evaluated the ILs' safer character by assessing them against the 14 criteria and considering different combinations of cations and halide-free anions.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/pr9091524/s1, Table S1: Table lists the HF-ILs that were studied for analysis in this work and their corresponding raw materials, Table S2: Criteria, parameters describing the ionic liquids along with their weighting factors, Table S3: Table showing the results of TOPSIS analysis for raw materials, comparison with traditional organic solvents and ionic liquids combined with sensitivity analysis for changes in range of ±10%. For the sake of brevity, the relative closeness to the ideal solution, ranking, ranking difference for ±10% sensitivity changes are represented separately. Table S4: Overall ranking of the halide free ILs.

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