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Role of the chemical structure of ionic liquids in their ecotoxicity and reactivity towards Fenton oxidation

*Macarena Munoz^{*a}, Carmen M. Domínguez^a, Zahara M. de Pedro^a, Asunción Quintanilla^a, Jose A. Casas^a, Sónia P.M. Ventura^b and João A. P. Coutinho^b*

^a Ingenieria Quimica, Universidad Autonoma de Madrid, Crta. Colmenar km 15, 28049 Madrid, Spain

^b Departamento de Quimica, CICECO, Universidade de Aveiro, Campus Universitario de Santiago,
3810-193 Aveiro, Portugal

*Corresponding author phone: +34 91 497 3991; fax: +34 91 497 3516; e-mail:

macarena.munnoz@uam.es

Abstract

The production and application of ionic liquids (ILs) is often associated with the formation of aqueous effluents. Due to the well-known toxicity and poor biodegradability of those compounds, effective treatments for their removal from aqueous solutions are required. In this work, the Fenton oxidation methodology under optimum operating conditions ($50 \text{ mg L}^{-1} \text{ Fe}^{3+}$, stoichiometric dose of H_2O_2 , 70°C and $\text{pH}_0=3$) was investigated in eleven different ILs, based in the imidazolium, phosphonium, quaternary ammonium, pyridinium and cholinium families, conjugated with various inorganic and organic anions such as chloride, cyanoborate, cyanamide, thiocyanate, dimethylphosphate and tosylate. The efficacy of the process was evaluated by the analysis of the chemical oxygen demand (COD), total organic carbon (TOC), the acids formed by ILs oxidation and the toxicity of the non-treated and treated aqueous effluents towards the *Vibrio fischeri* bacteria. It was possible to identify the main compounds produced upon Fenton oxidation in the final aqueous effluents (acetic, oxalic and formic acids) and the results seem to suggest that the Fenton oxidation is a good degradation methodology for most of the ILs tested, achieving TOC conversions in the range of 40-80% and 30-40% for aromatic and aliphatic ILs, respectively. Furthermore, non-toxic effluents were obtained at the end of the treatment for all the ILs investigated with the exception of the cyano-based ones due to the release of highly toxic cyanide species to the aqueous medium.

Keywords: Ionic liquid; Fenton oxidation; degradation; toxicity; anion; cation.

1. Introduction

The synthesis of ILs often takes place in aqueous media, and their industrial application also involves aqueous effluents [1, 2]. It can thus be expected the presence of ILs in aqueous industrial effluents related with their manufacture and use. Various authors reported successful studies on the IL's recovery and recyclability after some specific processes for several consecutive cycles [3-5] being the main criteria for the choice of the IL recovery process, the IL concentration [6, 7]. However, their recyclability may be limited to a certain number of cycles by the accumulation of the contaminant/impurities which concentration may become too high rendering them unusable [6]. Moreover the IL recovery may not be practical when dealing with dilute solutions [6]. In this context, the development of efficient chemical treatments for the degradation of such persistent, non-biodegradable and/or high toxic compounds has been the focus of considerable research efforts in the last few years [8], principally for water streams with low amounts of IL. Advanced oxidation processes (AOPs), based on the action of hydroxyl radicals at near ambient temperature and pressure, have been proposed as an interesting alternative by several authors [9-16]. Included in the AOPs, Fenton oxidation represents the most realistic approach for the degradation of ILs in water, due to its simplicity and cost-efficiency [17]. So far, the few works reported dealing with the treatment of ILs by Fenton oxidation have been focused on the degradation of imidazolium-based ILs at ambient and mild conditions [18-20]. Although the viability of the process has been demonstrated, since the complete conversion of the IL ($[\text{C}_2\text{mim}]\text{Cl}$) within 90 min of exposure was achieved ($[\text{IL}]_0 = 1 \text{ mM}$; $[\text{Fe}^{3+}]_0 = 1 \text{ mM}$; $[\text{H}_2\text{O}_2]_0 = 400 \text{ mM}$), high excess of H_2O_2 was used, and information about the evolution of total organic carbon (TOC) or toxicity, which is crucial for the potential application of Fenton oxidation, was not provided [20]. In a recent contribution, we applied the Fenton process to degrade four ILs' families ($[\text{IL}]_0 = 1000 \text{ mg L}^{-1}$), viz. imidazolium, pyridinium, ammonium and phosphonium, at different operating conditions, establishing that 70°C , the stoichiometric amount of H_2O_2 and a Fe^{3+} dose of 50 mg L^{-1} allowed the complete conversion of ILs with more than 60% TOC reduction, giving rise to non-toxic effluents within 4 hours of reaction time [21]). In the same line, we also demonstrated the efficiency of this

process working at those operating conditions for the degradation of imidazolium-based ILs taking into account their structure characteristics, represented by the length of the alkyl chain (C_2 to C_{16}) and the nature of the counter anion (Cl^- , $[CH_3SO_3]^-$, $[CH_3SO_4]^-$, $[CH_3CO_2]^-$) [22]. However, the potential application of the Fenton process to the treatment of IL-based wastewaters still remains an open question due to the wide range of anions and cations that need to be tested. For instance, the degradation of aliphatic cations such as cholinium and quaternary ammonium structures as well as complex anions such as tosylate or cyano-containing ones has not been yet studied. In this context, the aim of this work is to analyze the capability of the Fenton process for the degradation of a wide variety of ILs, considering the influence of the chemical structure of anion and cation, on their reactivity towards Fenton oxidation under the operating conditions previously reported [21, 22] and the ecotoxicity of the non-treated and treated effluent. The evolution of the chemical oxygen demand (COD), Total Organic Carbon (TOC), the type of acids formed and the toxicity of the Fenton oxidation effluents towards the *Vibrio fischeri* marine luminescent bacteria, upon oxidation were evaluated.

2. Materials and methods

2.1. Chemicals

All chemicals were analytical grade reagents and were used without further purification. The molecular structure of the eleven ILs studied is provided in Fig. 1. These ILs are: 1-ethyl-3-methylimidazolium chloride, $[C_2mim]Cl$ (98% of purity); 1-butyl-4-methylpyridinium chloride, $[C_4mpyr]Cl$ (98% of purity); 1-ethyl-3-methylimidazolium tetracyanoborate, $[C_2mim][B(CN)_4]$ (98% of purity); 1-ethyl-3-methylimidazolium dicyanamide, $[C_2mim][N(CN)_2]$ (>98% of purity); 1-ethyl-3-methylimidazolium tricyanomethanide, $[C_2mim][C(CN)_3]$ (>98% of purity); 1-ethyl-3-methylimidazolium thiocyanate, $[C_2mim][SCN]$ (98% of purity); 1-ethyl-3-methylimidazolium dimethylphosphate, $[C_2mim][DMP]$ (98% of purity); 1-ethyl-3-methylimidazolium tosylate, $[C_2mim][TOS]$ (99% of purity); tetrabutylammonium chloride, $[N_{4,4,4,4}]Cl$ (97% of purity); tetrabutylphosphonium chloride, $[P_{4,4,4,4}]Cl$

(98% of purity); and cholinium chloride, [Chol]Cl (98% of purity), all purchased at Iolitec – Ionic Liquids Technologies, Fluka, Sigma-Aldrich[®], or kindly offered by Cytec (phosphonium-based IL). Hydrogen peroxide solution (30 wt.-%) in a stable form and nitric acid (65%) were purchased from Sigma-Aldrich[®]. Iron (III) nitrate nonahydrate (purity of 98%) was acquired at Panreac.

2.2. Fenton experiments

The oxidation runs were carried out in 100 mL stirred glass bottles placed in a constant-temperature bath at an equivalent stirring velocity of 200 rpm. The reaction volume was 50 mL, and the reactants were added simultaneously at the beginning of each oxidation run. Briefly, the IL solution (48 mL, 1000 mg L⁻¹) at pH = 3 (HNO₃) was placed in the reactor and heated to 70 °C. When the temperature was at steady state, 1 mL of an H₂O₂ solution at the appropriate concentration (the theoretical stoichiometric amount necessary for the complete mineralization of the IL), and 1 mL of the Fe(NO₃)₃ aqueous solution (50 mg L⁻¹ Fe³⁺ in the reactor) were injected. After 4 hours of reaction, the heating was switched-off and the samples were diluted and immediately analyzed. The toxicity of the effluents was measured once the reactor was cooled to room temperature and the residual hydrogen peroxide was removed with sodium bisulfite (<10% of the initial hydrogen peroxide concentration in all experiments realized). The experiments were performed in triplicate, being the standard deviation obtained always less than 5%.

2.3. Analytical methods

The progress of the reaction was followed by measuring TOC, COD, the toxicity of the effluents obtained after the Fenton oxidation, and the concentration of short-chain organic acids produced. The TOC parameter was measured with a TOC analyzer (Shimadzu TOC V_{SCH}). COD measurements were performed by the Moore method [23]. Short-chain organic acids were analyzed by ion chromatography

with chemical suppression (Metrohm 790 IC) using a conductivity detector. A Metrosep A supp 5-250 column (25 cm length, 4 mm internal diameter) was used as the stationary phase and an aqueous solution of Na_2CO_3 (3.2 mM) as the mobile phase. The hydrogen peroxide concentration was determined by colorimetric titration with an UV 2100 Shimadzu UV-VIS spectrophotometer [24].

2.4. *Microtox*[®] acute toxicity assays

The toxicity of the IL solutions and the corresponding Fenton oxidation effluents was determined by a standard toxicity test conducted with the luminescent bacteria *Vibrio fischeri*, strain NRRL B-11177 (*Microtox*[®]; Azur Environmental 1998). This test was performed using a range of diluted aqueous solutions (from 0 to 100%) of each pure IL or Fenton sample. The experiments were conducted at 15 °C, with osmotic pressure adjusted to values closer to 2% NaCl and pH between 6 and 8. The EC_{50} is defined as the effective nominal concentration (mM) that reduces the intensity of light emission by 50% after 15 minutes of contact time between each sample and the bacteria. For complex samples, like the Fenton oxidation effluents, IC_{50} is used, and it is defined as the reciprocal of the dilution percentage giving rise to 50% reduction of light emission. The toxicity units (TU) were calculated and are inversely proportional to the biological toxicity expressed as IC_{50} values.

3. Results and discussion

3.1. Fenton oxidation of ILs

Table 1 collects the results obtained upon Fenton oxidation of all ILs investigated. In general, ILs were effectively oxidized by the Fenton process, which is demonstrated by the high reduction values of COD and TOC. Moreover, the COD/TOC ratio, which indicates the extent of the overall reaction [25], was also significantly reduced during the treatment. Aromatic ILs, such as imidazolium and pyridinium

families showed in general higher mineralization degrees than the aliphatic ones, in particular cholinium, quaternary ammonium and phosphonium cations. This can be explained by the presence of double bonds in the aromatic ILs. These results are in good agreement with previous works dealing with the oxidation of aliphatic compounds by Fenton treatment, in which it was observed that unsaturated compounds were more prone to oxidation by hydroxyl radicals because of their electron-rich double bonds [26-28]. Actually, the IL containing both aromatic cation and anion, the [C₂mim][TOS], showed the highest conversion values of TOC and COD.

It is well-known that the final products obtained upon Fenton oxidation of organic compounds are non-toxic short-chain organic acids [29, 30]. Table 2 shows the concentration of those compounds present in the final Fenton effluents of the eleven ILs tested in this work. As observed, acetic, oxalic and formic acids were more abundantly present in the effluents originated in the Fenton oxidation, since they present high resistance to further oxidation, whereas fumaric, maleic and malonic acids are firstly formed and then degraded upon the treatment [31-33]. With the exception of the ILs based in cyano-anions ([B(CN)₄], [N(CN)₂], [C(CN)₃], [SCN]) and [chol]Cl), short-chain organic acids represented the main products obtained from the ILs' Fenton oxidation, being the proportion of carbon in the form of short-chain organic acids around 40-60% of the residual TOC. In the particular case of the cyano-based ILs, it has to be considered the presence of cyanide species (C≡N⁻), released during the treatment, highly refractory to the •OH radicals attack. The contribution of those species to the initial TOC for [C₂mim][B(CN)₄], [C₂mim][C(CN)₃], [C₂mim][N(CN)₂], and [C₂mim][SCN] are 46, 40, 30 and 15%, respectively, which explains the lower contribution of short-chain organic acids in these cases as well as the differences obtained among them.

3.2. Evaluation of toxicity of pure ILs and effluents generated during the Fenton oxidation

Table 3 reports the toxicity values obtained from the Microtox[®] acute toxicity test for the Fenton oxidation effluents of the ILs studied and also for the IL solutions as starting contaminants (1000 mg

L⁻¹). The first observation is that the values of toxicity reported for the IL solutions are quite different from those previously reported in literature [34] for example in the case of [chol]Cl, due to the maintenance of the osmotic pressure and pH. In this context, no comparisons between these ILs results of toxicity and literature will be carried out. The Microtox[®] treatment was here adopted as an easy method to directly compare the toxicity of the pre and post oxidation IL effluent samples. As observed in the results reported in Table 3, most of the effluents were non-toxic or showed negligible toxicity values, which is particularly important in the case of pyridinium, quaternary ammonium and phosphonium families, since they presented significant toxicity values before the treatment (TU_{[C4m_{pyr}]Cl} = 3.4, TU_{[N4,4,4,4]Cl} = 2.1, TU_{[P4,4,4,4]Cl} = 5.8). However, it has to be highlighted a dramatic increase of toxicity when cyano-based ILs were treated ([C₂mim][B(CN)₄], [C₂mim][C(CN)₃] and [C₂mim][SCN]). As previously mentioned, it can be directly related to the degradation of the anion and subsequent release of highly toxic cyanide species. Interestingly, [C₂mim][N(CN)₂] was the only cyano-based IL which did not show any toxicity increase upon the Fenton oxidation. This fact can be explained by the higher resistance of the N-C≡N bond of the anion towards ·OH radicals, which prevents the release of toxic cyanide species.

Summing up, in this work, it was demonstrated the capacity of Fenton oxidation to degrade ILs with a variety of cations and anions. However, it is notorious, from the present results and others previously reported in literature [6], that the best approach for dealing with an ionic liquid requires a simultaneous attention to the cation and the anion. Cyano-based ILs are good examples of problematic anions, where compounds more toxic than the original ions may result from the oxidation reaction. These results emphasize the need to make an adequate choice of the degradation or recovery method to be applied to each particular IL contaminated effluent.

4. Conclusions

The treatment of a wide variety of ILs in water including aliphatic cations *viz.* cholinium and quaternary ammonium structures as well as complex anions *viz.* tosylate or cyano-based, by Fenton oxidation has been studied, showing that this process is an efficient technique for the degradation of most of them. In general, aromatic ILs are more readily oxidized than the aliphatic ones, due to the presence of unsaturated bonds, showing the IL containing both aromatic cation and anion ([C₂mim][TOS]), the highest oxidation ($X_{\text{COD}}=80\%$) and mineralization ($X_{\text{TOC}}=78\%$).

Except for the ILs based in anions with cyano groups, short-chain organic acids represented the main oxidation products obtained after the Fenton treatment, originating non-toxic effluents or showing negligible toxicity values, which is particularly important in the case of pyridinium, quaternary ammonium and phosphonium families, since, before the treatment, they presented significant toxicities. Special attention has to be paid to the nature of IL since a dramatic increase of toxicity has been observed for cyano-based ILs treated by Fenton oxidation, as consequence of the anion degradation and the subsequent release of highly toxic cyanide to the aqueous medium. Therefore, it is important to make a correct choice of the degradation or recovery method to be applied in each IL contaminated effluent.

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Figure and Tables

Figure 1. Chemical structure of the ILs studied in this work, and respective abbreviation.

Table 1. Results obtained after the Fenton oxidation of ILs ($[\text{IL}]_0 = 1000 \text{ mg L}^{-1}$; $[\text{Fe}^{3+}]_0 = 50 \text{ mg L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = \text{stoichiometric amount}$; $T = 70 \text{ }^\circ\text{C}$; $\text{pH}_0 = 3$).

Table 2. Short-chain organic acids obtained upon the Fenton oxidation of all ILs.

Table 3. Toxicity parameters, EC_{50} in mM and TU at 15 min of exposure time for the 1000 mg L^{-1} IL solutions and the Fenton oxidation effluents originated after 4 hours of Fenton reaction.

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Table 1

Table 1. Results obtained after the Fenton oxidation of ILs ($[\text{IL}]_0 = 1000 \text{ mg L}^{-1}$; $[\text{Fe}^{3+}]_0 = 50 \text{ mg L}^{-1}$; $[\text{H}_2\text{O}_2]_0$ = stoichiometric amount; $T = 70 \text{ }^\circ\text{C}$; $\text{pH}_0 = 3$).

Ionic Liquid	TOC₀ (mg L⁻¹)	COD₀ (mg L⁻¹)	X_{TOC} (%)	X_{COD} (%)	COD₀/TOC₀	COD_f/TOC_f
[C ₂ mim][B(CN) ₄]	531	1168	49.9	71.1	2.2	1.3
[C ₂ mim][N(CN) ₂]	542	1264	56.3	68.3	2.3	1.7
[C ₂ mim][C(CN) ₃]	640	1563	40.7	73.6	2.4	1.1
[C ₂ mim][SCN]	496	1418	67.3	72.7	2.9	2.4
[C ₂ mim][DMP]	508	1456	44.1	47.2	2.9	2.7
[C ₂ mim][TOS]	553	1643	77.8	80.2	3.0	2.7
[C ₂ mim]Cl	516	1751	65.3	77.4	3.4	2.0
[C ₄ mpyr]Cl	656	2210	43.7	61.2	3.3	2.3
[chol]Cl	430	1662	36.1	45.7	3.9	3.3
[N _{4,4,4,4}]Cl	652	2275	38.2	63.1	3.5	2.1
[P _{4,4,4,4}]Cl	681	2459	28.2	49.6	3.6	2.5

Table 2

Table 2. Short-chain organic acids obtained upon the Fenton oxidation of all ILs.

Ionic liquid	Maleic	Fumaric	Malonic	Acetic	Oxalic	Formic	$\sum C_{\text{organic}}$
	(mg L ⁻¹)						acids/TOC (%)
[C ₂ mim][B(CN) ₄]	0.0	0.0	0.6	15.9	12.8	1.1	11.2
[C ₂ mim][N(CN) ₂]	0.0	0.0	0.0	28.6	2.8	17.6	21.2
[C ₂ mim][C(CN) ₃]	0.0	0.0	0.0	12.5	0.3	29.5	11.8
[C ₂ mim][SCN]	0.0	0.0	0.0	30.6	15.5	5.2	27.7
[C ₂ mim][DMP]	0.0	0.0	0.0	29.8	0.0	42.1	32.9
[C ₂ mim][TOS]	0.0	0.0	0.0	39.1	16.7	3.1	54.8
[C ₂ mim]Cl	0.0	9.4	5.5	46.5	130.2	107.9	47.6
[C ₄ mpyr]Cl	3.2	19.8	31.7	227.7	184.4	146.8	53.2
[chol]Cl	0.0	0.0	5.5	0.0	0.4	3.8	3.8
[N _{4,4,4,4}]Cl	0.0	3.5	36.0	221.8	73.0	89.4	59.0
[P _{4,4,4,4}]Cl	0.0	0.0	46.3	219.9	54.6	118.2	44.1

Table 3

Table 3. Toxicity parameters, EC₅₀ in mM and TU at 15 min of exposure time for the 1000 mg L⁻¹ IL solutions and the Fenton oxidation effluents originated after 4 hours of Fenton reaction.

Ionic liquid	EC ₅₀ (mM)	TU at 15 min	Fenton effluent (TU at 15 min)
[C ₂ mim][B(CN) ₄]	4.1	1.1	4.1
[C ₂ mim][N(CN) ₂]	23.5	0.2	non-toxic*
[C ₂ mim][C(CN) ₃]	3.6	1.4	18.0
[C ₂ mim][SCN]	28.1	0.2	11.0
[C ₂ mim][DMP]	30.3	0.1	1.5
[C ₂ mim][TOS]	70.8	0.1	non-toxic*
[C ₂ mim]Cl	27.1	0.3	non-toxic*
[C ₄ mpyr]Cl	1.6	3.4	0.1
[chol]Cl	--	non-toxic*	1.7
[N _{4,4,4,4}]Cl	1.7	2.1	non-toxic*
[P _{4,4,4,4}]Cl	0.6	5.8	0.2
non-toxic* <0.01 TU			

Figure 1

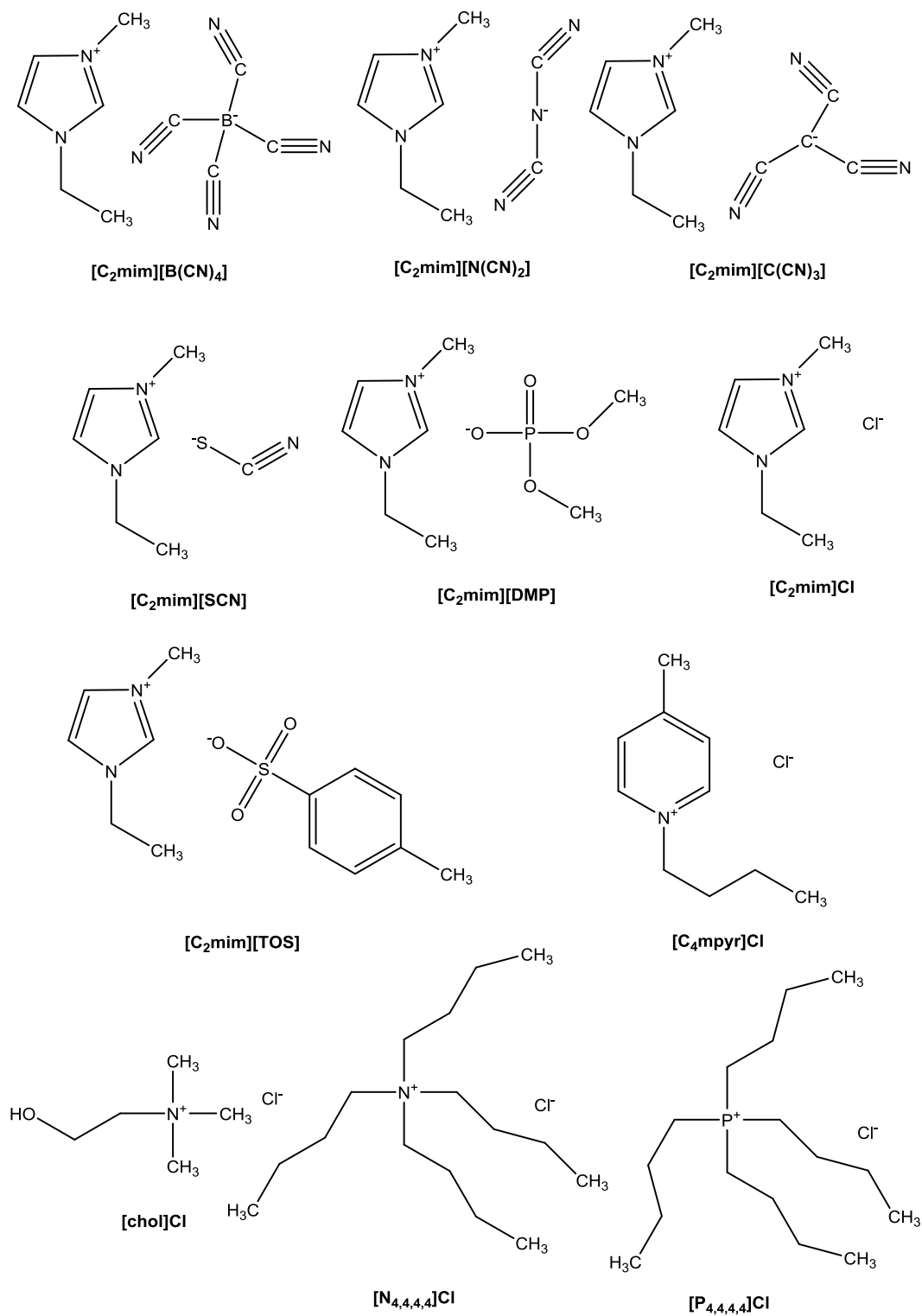


Figure 1. Chemical structure of the ILs studied in this work, and respective abbreviation.

