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ARTICLE

Magnetic Ionic Liquids: Synthesis, properties and applications

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Magnetic Ionic liquids are room temperature ionic liquids, which have paramagnetic properties by itself without the need of adding magnetic particles. These paramagnetic properties are set from the anion, the cation or both of them. Most common paramagnetic ionic liquids are those which contain transition metal or lanthanide complexes in their anion structure. These tuneable fluids present unique physicochemical properties, resulting in responsive materials to an external magnetic field. The reported studies on the synthesis and applications of magnetic ionic liquids have increased in recent years. Therefore, this review attempts to highlight the achievements and current status concerning the synthesis, properties and main applications of magnetic ionic liquids, providing insights into this research frontier.

1. Introduction

Room temperature ionic liquids (RTILs) are defined as salts with a melting point below 373 K typically comprised of bulky organic cations (i.e. imidazolium, phosphonium, ammonium or pyridinium) and organic or inorganic anions (i.e. BF₄⁻, PF₆⁻, Cl⁻ or Br⁻)¹. They exhibit very interesting physicochemical properties including negligible vapour pressure, non-flammability, high thermal and chemical stability, high conductivity and widely tuneable properties by the appropriate selection of the cation or anion in their structure². RTILs have received increasing interest in the fields of catalysis^{3,4}, electrochemistry^{5,6} or separation processes^{7,8}.

Lately, considerable attention has been focused on Magnetic Ionic Liquids (MILs). Metal-containing ionic liquids can combine the general properties of RTILs with those associated with the incorporation of a metal ion in their structure such as a strong response to an external magnetic field, photophysical/optical or catalytic properties. Among the first examples were those studied by Hayashi and Hamaguchi in 2004^{9,10}. Although the MIL 1-butyl-3-methylimidazolium tetrachloroferrate, [Bmim][FeCl₄], has been known for a while¹¹, they reported for the first time the magnetic properties and potential application of [Bmim][FeCl₄] and 1-butyl-3-methylimidazolium tetrachloroferrate, [Nbmim][FeCl₄], under the application of a neodymium, Nd, magnet (0.55 Tesla). Yoshida et al.¹²⁻¹³ explored the magnetic properties of tetrachloroferrate, [FeCl₄], and tetrabromoferrate [FeBr₄] anion-based MILs. The discovery of these MILs with these magnetic properties opened up a new research area of interest. Del Sesto et

al.^{14,15} described a larger variety of MILs with iron, Fe(III), cobalt, Co(II), manganese, Mn(II) and gadolinium, Gd(III)-containing anions. Afterwards, MILs based on the transition metal coordination complexes Fe(III)⁹⁻¹⁶, Co(II)¹⁴⁻¹⁹ and Mn(II)¹⁷, have been reported in the literature by different authors. Recently, lanthanide complexes (i.e. Gd, Nd or dysprosium, Dy)^{16,20,21} have been also explored due to their strong response to an external magnetic field and, in some cases, luminescence properties. The MILs all showed simple paramagnetic behavior over a temperature range of 300 K resulting in new materials with potential applications for magnetic and electrochromic switching. Finally, the first examples of magnetic chiral ionic liquids derived from amino acids which simultaneously contain chiral and magnetic properties have been reported by Li et al. in 2009²².

MILs may show applications in both process and product engineering as an expanding field full of opportunities to create devices, processes and products. The overall objective of this review is to offer an overview of the state of art of the synthesis, properties and main applications of MILs.

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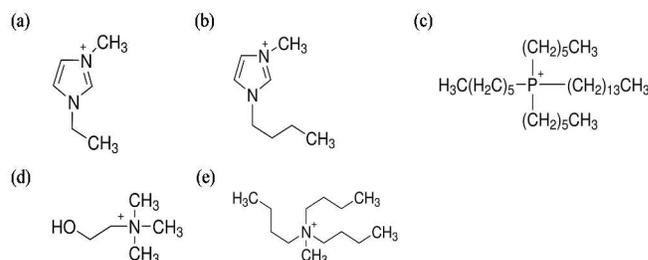


Fig. 1. Common cations in MILs: (a) [Emim], (b) [Bmim], (c) [P_{6,6,6,14}], (d) [choline] and (e) [aliquat].

2. Synthesis and characterization of MILs

Nowadays, the preparation and structure of MILs based on several different cations and anions containing metal-transition complexes can be found in the literature. Fig. 1 shows the common cations used in the synthesis of MILs. Apart from the widely employed 1-ethyl-3-methylimidazolium, [Emim], and 1-butyl-3-methylimidazolium, [Bmim], cations in the recent literature²³⁻⁴² and MILs based in higher alkyl chain length of imidazole cations^{10, 20, 33-34, 36}, the most preferred salts used are those with trihexyl(tetradecyl)phosphonium, [P_{6,6,6,14}]^{15-17, 38, 43}, choline^{35, 36} or aliquat^{29, 44}, which is a RTIL itself. These cations are widely employed due to their easy availability at a reasonable price. The elongation of alkyl chain results in the increased ion size and interionic van der Waals interactions, both of which modify the ion diffusivity in the unfavourable direction⁴⁵. One significant disadvantage to the imidazolium cation is that the 2-position of the imidazolium ring has a relatively acidic proton, making the cation a fairly strong hydrogen bond donor, yielding extended network structures of cations and anions and discouraging formation of MILs, as observed in the [Bmim][MnBr₄] salt synthesized from the aqueous-phase reaction of [Bmim][Br] with [MnBr₂]¹⁴.

There is now also an increasing interest in cations with functionalized groups, for example pyrimidin, ammonium, pyrrolidinium or surfactants chains^{31, 33, 36, 39, 46-48} which are often optimized for given applications. Dual functionalities, namely the paramagnetism and chiral discrimination ability, were recently realized by the combination with the chiral protonated L-amino acid methyl esters^{22, 48}. However, the physical properties of this new generation of MILs are still not completely explored although they are considered to play an important role for the development of new applications in the near future.

Among the anions, much work have focused initially on salts based on [FeCl₄] due to the abundance and low cost of iron materials^{9, 14}. The synthesis of the first MIL studied, [Bmim][FeCl₄], was reported

by Sitze¹¹ and Hayashi and Hamaguchi⁹ by mixing crystal powder of [Bmim][Cl] with two ferric chlorides, anhydrous FeCl₃ and FeCl₃·6H₂O. The higher magnetic moments of other elements, however, can result in fluids with stronger magnetic properties. Recently, Albo et al.⁴³ reported the preparation of MILs based on Fe, Co, Mn or Gd paired with [P_{6,6,6,14}] cation. The procedure basically consisted on the addition of cobalt chloride, iron chloride hexahydrate, manganese chloride or gadolinium chloride hexahydrate to a solution of [P_{6,6,6,14}] in dichloromethane. The solution was stirred at room temperature, the organic phase was dried over magnesium sulphate, MgSO₄, and the solvent was removed under vacuum at 60 °C overnight. As a result [P_{6,6,6,14}][FeCl₄], [P_{6,6,6,14}][CoCl₄], [P_{6,6,6,14}][MnCl₄] and [P_{6,6,6,14}][GdCl₆] were obtained as a viscous oils at yields from 94 to 98%. Del Sesto et al.¹⁵ previously prepared a series of paramagnetic MILs having tetraalkylphosphonium or alkylmethylimidazolium cations combined with transition metal halide anions (i.e. Fe, Co, Mn and Gd) following similar preparation procedure. The reaction was performed with the addition of small volumes of water or chloroform to ensure efficient mixing. Fig. 2 shows the structure of common anions used in the synthesis of MILs. Lately, MILs based on rare earths (i.e. Y, La, Pr, Nd, Sm, Eu, Tb, Ho, Er, Yb and Dy)^{20, 21} have been prepared, showing in some cases stronger magnetic response and other particular characteristics. The compounds were synthesized by a metathesis procedure starting from stoichiometric amounts of lanthanide (III) perchlorate, ammonium thiocyanate, and a thiocyanate RTIL with the corresponding imidazolium cation. [C₆mim]_{5-x}[Dy(SCN)_{8-x}(H₂O)_x]; x= 0-2 compounds were obtained by mixing [C₆mim]SCN, KSCN and [Dy(ClO₄)₃·6H₂O] resulting in valuable materials for various applications that can be manipulated by external magnetic fields and at the same time can be monitored by its luminescence²⁰.

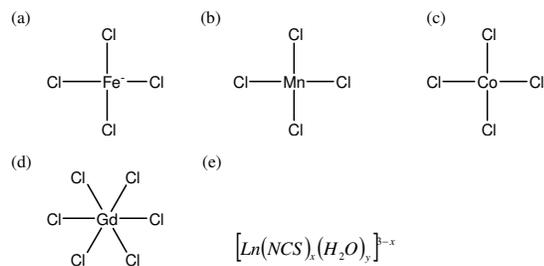


Fig. 2. Common anions in MILs: (a) $[\text{FeCl}_4]$, (b) $[\text{MnCl}_4]$, (c) $[\text{CoCl}_4]$, (d) $[\text{GdCl}_6]$, and (e) $[\text{Ln}(\text{NCS})_x(\text{H}_2\text{O})_y]^{3-x-}$ ($x= 6-8$; $y= 0-2$; $\text{Ln}= \text{Y, La-Yb}$).

MILs are normally prepared by dispersing and stirring metal components in a carrier fluid. In a similar manner, magnetic nanoparticles can be added to a non-magnetic RTIL to create fluids with magnetic response⁴⁵. The ion structure of RTILs has been pointed out to work well for the stabilization of metal nanoparticles in general⁴⁹. This is the case of positively charged Pt nanoparticles dispersed in 1-butyl-3-methylimidazolium tetrafluoroborate, $[\text{Bmim}][\text{BF}_4]$, and 1-butyl-3-methylimidazolium hexafluorophosphate, $[\text{Bmim}][\text{PF}_6]$ ⁵⁰, dispersion of pure iron, iron oxides, silica-coated iron particles or cobalt in 1-ethyl-3-methylimidazolium ethyl sulphate, $[\text{Emim}][\text{EtSO}_4]$, and 1-ethyl-3-methylimidazolium diethylphosphate, $[\text{Emim}][\text{Et}_2\text{PO}_4]$ ⁵¹, and the suspensions of either micron-or nanosized magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) particles in eight different RTILs^{52,53}. In any case, for a proper implementation and commercialization of MILs and magnetic nanoparticle-based RTILs a more applied study of these fluids is still required. It is important to notice that some companies offer in the market different RTIL-based magnetic smart materials, including MILs. In the following subsections the characteristics of MILs reported in the literature are analysed.

2.1. Physico-chemical properties

Initial research on the properties of MILs has concentrated on developing and understanding the relationship between the nature and structure of the cation-anion and the physical properties.

2.1.1. Densities

The density of the $[\text{FeCl}_4]$ anion-based MILs has been evaluated by different authors^{13, 16, 38, 54-55}. Yoshida and Saito¹³ reported the density of $[\text{Bmim}][\text{FeCl}_4]$, 1-hexyl-3-methylimidazolium tetrachloroferrate, $[\text{Hxmim}][\text{FeCl}_4]$, and 1-octyl-3-methylimidazolium tetrachloroferrate, $[\text{Omim}][\text{FeCl}_4]$, with values ranging from 1.3-1.38 $\text{g}\cdot\text{cm}^{-3}$. Moreover, Palomar et al.⁵⁴ used COSMO-RS, a thermodynamic model based on quantum chemistry calculations, to estimate the specific density of the $[\text{FeCl}_4]$ anion in combination with 1-methyl-3-methylimidazolium, $[\text{Mmim}]$, $[\text{Emim}]$, $[\text{Bmim}]$, $[\text{Hxmim}]$ and $[\text{Omim}]$ cations. Predicted densities at 298 K were in the range of 1.28-1.57 $\text{g}\cdot\text{cm}^{-3}$ being in very good agreement with the experimental values (less than 3% deviation)¹³. Furthermore, Cruz et al.³⁸ reported the density of $[\text{Bmim}][\text{FeCl}_4]$ between 293 and 363 K (1.37 to 1.31 $\text{g}\cdot\text{cm}^{-3}$) and $[\text{P}_{6,6,6,14}][\text{FeCl}_4]$

(0.99 and 0.94 $\text{g}\cdot\text{cm}^{-3}$). Zhuravlev et al.⁵⁵ studied the densities of tetrachloroferrates of 1, 3-disubstituted imidazolium derivatives varying from 1.39-1.58 $\text{g}\cdot\text{cm}^{-3}$. Additionally, Nockemann et al.²¹ reported the density of different lanthanide complexes $[\text{Bmim}]_x\text{[Ln(NCS)}_x(\text{H}_2\text{O})_y]$ ($x= 6-8$; $y= 0-2$;) where $\text{Ln}= \text{La, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, and Yb}$ at 294 K ranging from 1.29-1.53 $\text{g}\cdot\text{cm}^{-3}$. Finally, it has been reported¹⁶ the density of $[\text{P}_{6,6,6,14}][\text{CoCl}_4]$, $[\text{P}_{6,6,6,14}][\text{FeCl}_4]$, $[\text{P}_{6,6,6,14}][\text{MnCl}_4]$ and $[\text{P}_{6,6,6,14}][\text{GdCl}_6]$ in a temperature range from 293.15 to 303.15 K, obtaining values from 1.012 to 0.943 $\text{g}\cdot\text{cm}^{-3}$. In general, the majority of known MILs are denser than water.

2.1.2. Viscosities

Most RTILs are viscous liquids, with viscosities more comparable to oils, that is two to three orders of magnitude greater than those for conventional organic solvents. Deng et al.⁵⁶ reported a viscosity value of 0.914 Pa·s for $[\text{P}_{6,6,6,14}][\text{FeCl}_4]$ at room temperature. The experimental viscosity at 278 and 373 K was reported by Cruz et al.³⁸ being 103 and 6.3 m·Pas for $[\text{Bmim}][\text{FeCl}_4]$ and 4,145 and 40.7 mPa·s for $[\text{P}_{6,6,6,14}][\text{FeCl}_4]$ respectively. It has been reported the viscosity of $[\text{P}_{6,6,6,14}][\text{CoCl}_4]$, $[\text{P}_{6,6,6,14}][\text{FeCl}_4]$, $[\text{P}_{6,6,6,14}][\text{MnCl}_4]$ and $[\text{P}_{6,6,6,14}][\text{GdCl}_6]$ in a temperature range from 293 to 373 K obtaining values between 44 and 123,500 m·Pas¹⁶. Moreover, a group contribution method based on the Orrick-Erbar equation was developed by Daniel et al.⁵⁷ for the same four MILs at different temperatures by evaluating cation/anion influence in the viscosity in a group contribution methodology. The modelling estimations showed a good agreement with the experimental results (7.64% of mean percentage deviation (MPD) and $R^2= 0.98$) which confirmed the interest of this model for the estimation of MIL viscosity at increasing temperatures.

2.1.3. Decomposition temperatures

Different authors reported the thermal stability and thermal decomposition behavior of MILs, as measured by thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC). The results showed a high thermal stability with decomposition temperatures in the range 623-658K for $[\text{FeCl}_4]$ ^{16,24,34,46,56,58}, 573-633K for $[\text{Fe}_2\text{OCl}_6]$ ⁵⁹, 619K $[\text{MnCl}_4]$ ¹⁶, 646K for $[\text{CoCl}_4]$ ¹⁶, 625K for $[\text{GdCl}_6]$ ¹⁶ and 557-622K for $[\text{Bmim}]_x\text{[Ln(NCS)}_x(\text{H}_2\text{O})_y]$ ($x= 6-8$; $y= 0-2$;) where $\text{Ln}= \text{La, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, and Yb}$ ²¹.

2.2. Magnetic properties

MILs usually show a paramagnetic behavior under the application of an external magnetic field. Paramagnetic materials do not retain any magnetization in the absence of an externally applied magnetic field, because thermal motion causes the spins to become randomly oriented without it, as measured by a SQUID magnetometer. Hayashi and Hamaguchi⁹ reported a magnetic mass susceptibility of $40.6 \times 10^{-6} \text{ emu}\cdot\text{g}^{-1}$ for $[\text{Bmim}][\text{FeCl}_4]$ corresponding to a molar susceptibility of $\chi_{mT}= 4.11 \text{ emu K}\cdot\text{mol}^{-1}$. Hence, they extended the study to another MIL, $[\text{Nbmim}][\text{FeCl}_4]$, by replacing the butyl group

of the [Bmim] cation with the butyronitrile group¹⁰. The effective magnetic moment of $\chi_{\text{eff}} = 5.8 \chi_{\text{B}}$ was in accordance with a high-spin $S=5/2$ state (spin only value = $5.92 \chi_{\text{B}}$) for Fe(III). Lately, De Pedro et al.²³ found a long-range antiferromagnetic ordering (permanent magnetic moment in the absence of an external field) of the MIL [Emim][FeCl₄], when it was frozen. RTILs whose magnetic properties extend far beyond that of the existing ones may be those with the pronounced response to the external stimuli and with the pronounced magnetic interactions including long-range magnetic ordering, which is interesting in view of new technological applications such as chemical switches, molecular sensors, or new devices for separation processes. The magnetic susceptibilities of

other MILs containing Co (2.06-2.48 emu K⁻¹mol⁻¹), Mn (4.22-4.23 emu K⁻¹mol⁻¹) or Gd (6.51-7.72 emu K⁻¹mol⁻¹) have been also reported in literature^{15, 16}. Furthermore, the incorporation of lanthanide ions into MILs offers the advantage of a metal ion that has a considerably higher effective magnetic moment than any known transition metal. The size of the magnetic moment on a lanthanide atom can be quite large as it can carry up to seven unpaired electrons. In this context, Mallick et al.²⁰ synthesized dysprosium-based MILs with an effective magnetic moment of $\chi_{\text{eff}} = 10.48 \chi_{\text{B}}$ which approximately doubled the value of Fe(III). The magnetic susceptibilities reported on the literature up to date are summarized in Table 1.

Table 1. Magnetic susceptibility of the MILs.

Anion	Cation	Magnetic Susceptibility/ χ_{mT} (emu K ⁻¹ mol ⁻¹)	Reference
[CoCl ₄]	[P _{6,6,6,14}]	2.10/2.48	Santos et al. 2014 ¹⁶ /Del Sesto et al. 2008 ¹⁵
[Co(NCS) ₄]	[P _{6,6,6,14}]	2.06	Del Sesto et al. 2008 ¹⁵
[MnCl ₄]	[P _{6,6,6,14}]	4.23/4.22	Santos et al. 2014 ¹⁶ /Del Sesto et al. 2008 ¹⁵
	[P _{6,6,6,14}]	4.29/4.34/4.05	Santos et al. 2014 ¹⁶ /Del Sesto et al. 2008 ¹⁵ /Deng et al. 2011 ⁵⁶
	[Emim]	4.03	De Pedro et al., 2010 ²³
	[Bmim]	4.11	Hayashi et al. 2006 ⁹
[FeCl ₄]	[C ₁₀ mim]	4.01	Del Sesto et al. 2008 ¹⁵
	[Nbmim]	4.34	Hayashi et al. 2006 ⁹
	[Bpy]	4.31	Zhu et al. 2013 ⁴⁶
	[Pyrr ₁₄]	4.47	Krieger et al. 2010 ⁴⁸
	[N ₁₄₄₄]	4.42	Krieger et al. 2010 ⁴⁸
	[N ₄₄₄₄]	4.27	Krieger et al. 2010 ⁴⁸
[FeCl ₄] _{0.75} [Cl] _{0.27}	[A336]	3.2	Kogelnig et al. 2010 ⁴⁷
[Fe ₂ OCl ₆]	3a-3g	1.26-2.88	Chang et al. 2010 ⁵⁹
[FeCl ₃ EtSO ₄]	[Emim]	5.17	Takagi et al. 2012 ³⁰
[GdCl ₆]	[P _{6,6,6,14}]	6.51/7.72	Santos et al. 2014 ¹⁶ /Del Sesto et al.

			2008 ¹⁵
$[\text{C}_6\text{mim}]_{5-x}[\text{Dy}(\text{SCN})_{8-x}(\text{H}_2\text{O})_x]$ ($x=0-2$)	$[\text{C}_6\text{mim}]$	13.41-14.00	Mallick et al. 2008 ²⁰

2.3. Electrochemical luminescence

Lanthanide compounds have gained widespread attention as potential materials in photochemistry and spectroscopy^{21, 60-65} due to the fact that they displayed luminescence. Tang et al.⁶⁵ studied europium, Eu(III), containing RTILs with improved luminescence performance as well as enhanced photochemical stability (i.e. high lifetimes at high Eu(III) concentration, small linewidth and high color purity). This new luminescent soft materials show advantages in fabricating optical devices⁶⁶⁻⁶⁷. Luminescent ionogels prepared from lanthanide-containing RTILs have also been reported⁶⁸⁻⁷⁷. The ability to easily shape the ionogels provides an attractive versatility to prepare coatings, rods or pellets, making it possible to implement optical devices. Particularly these ionic conductor materials are excellent candidates for the design of electroluminescent devices. Lunstroot et al.⁶⁸ reported luminescent ionogels prepared by doping an Eu(III) tetrakis β -diketonate complex into an imidazolium RTIL, followed by immobilization of the RTIL by confinement in a silica network. The hybrid material showed a very intense red photoluminescence under ultraviolet irradiation with a very high coloric purity as shown in Fig. 3.

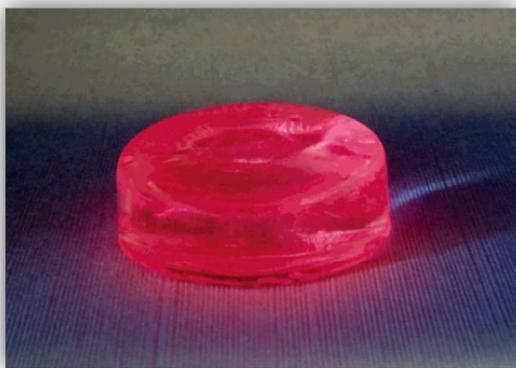


Fig.3. Luminescence of Eu(III)-doped ionogel under ultraviolet irradiation⁶⁸.

Mudring and co-workers²⁰ focused on a dysprosium-based system as the magnetic moment of Dy (III) is twice the size of that of Fe(III). Interestingly, the Dy-containing RTIL also displayed luminescence, a behaviour already known for lanthanide ions dissolved in water-free ionic liquids⁷⁸⁻⁷⁹.

2.4. Toxicity

The increasing use of MILs entails the need to consider the human health and environmental effects that their release may cause. Their negligible vapour pressure and non-flammability reduces or eliminates the risk of air emissions⁵⁵. Nevertheless, some of them are soluble in water⁸⁰⁻⁸² so they may pose environmental risks to aquatic ecosystems that have to be assessed, where the biodegradability has also significance. Luis et al.⁸³ studied the ecotoxicity of some MILs using the bioluminescent bacteria (EC50, *Vibrio fischeri*). A QSAR (Quantitative Structure-Activity Relationship) based on a group contribution method was applied to describe the influence of the molecular structure of MILs in ecotoxicity. The presence of iron in the molecular structure of imidazolium based RTILs produced an increase in the ecotoxicity. In the case of ammonium and phosphonium-based RTILs, this conclusion was not so obvious since the comparison was made among cations with different substitutions (i.e. carbon chains); thus, other influences, like the length of the carbon chain, was strongly involved. Lately, Alvarez-Guerra and Irabien⁸⁴ studied a new approach for estimating the ecotoxicity of RTILs, by the application of Partial Least Squares-Discriminant Analysis (PLS-DA); the $[\text{FeCl}_4]$ anion included in the analysis had the most severe influence on the PLS-DA model as positive discriminator (more toxic than toluene taken as volatile solvent reference). Tricaprylmethylammonium tetrachloroferrate, $[\text{A336}][\text{FeCl}_4]$, a hydrophobic quaternary ammonium RTIL based on the aliquat® 336 cation, was toxicologically investigated on human colon cancerous cells by Frade et al.⁸⁵. More recently, the same group reported several toxicological results of $[\text{C}_8\text{mim}]$ and $[\text{Choline-Cn}]$ cations in combination with $[\text{FeCl}_4]$, $[\text{MnCl}_4]$, $[\text{CoCl}_4]$ and $[\text{GdCl}_6]$ anions³⁵. In vitro studies were developed in two cell models: human colorectal adenocarcinoma (CaCo-2) and human normal skin fibroblasts (CRL-1502). Their results suggested that $[\text{FeCl}_4]$ and $[\text{GdCl}_6]$ were the anions inducing lower toxicity whereas $[\text{CoCl}_4]$ and $[\text{MnCl}_4]$ were likely the most toxic.

3. Applications

MILs have found applications in a variety of research areas both in process and product engineering.

3.1. Process applications

3.1.1. Fluid-fluid separations

MILs are starting to attract a wide interest in the field of separation processes. Jiang et al.⁸⁶ showed a benzene solubility increase in the paramagnetic MIL $[\text{Bmim}][\text{FeCl}_4]$ when applying a rotational

magnetic field. Okuno et al.⁸⁷ demonstrated the possibility of magnetic transport of a gas in MILs, illustrated by the change in N₂ bubbles trajectory in the presence of a magnetic field as shown in Fig. 4.

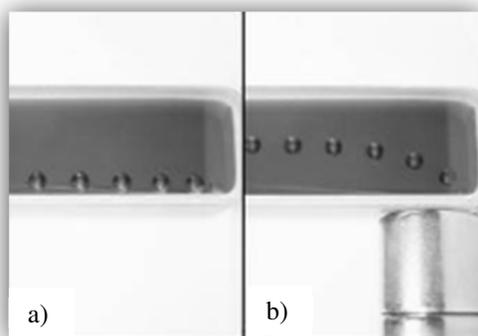


Fig. 4. Change in the N₂ bubbles trajectory, (a) in absence and; (b) in the presence of an external magnetic field⁸⁷.

In addition, Lee et al.⁸⁸ as well as Wang et al.⁸⁹ investigated the recovery of [Bmim][FeCl₄] from its mixture with water. Recently^{42, 90}, it has been prepared a new class of supported liquid membranes based on MILs: Supported Magnetic Ionic Liquids Membranes (SMILMs) for CO₂ separation. The influence of the application of an external magnetic field on CO₂/N₂ and CO₂/air permeability through SMILMs in the range of 0-1.5 Tesla was evaluated using the experimental setup described in Fig. 5 composed of an electromagnet, a polyvinylidene fluoride (PVDF) permeation cell and two pressure transducers to follow the pressure change in both compartments. An increase in the gas permeability (3.27% per unit of χ_{mT}) was observed due to MILs viscosity decrease depending on the magnetic field applied. Experimental results confirmed the supported liquid membranes gas permeability modulation by tuning the magnetic field intensity.

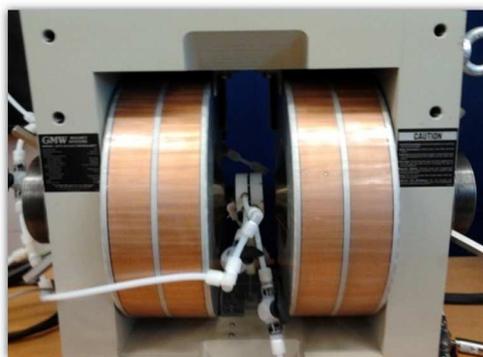


Fig. 5. Experimental setup for the gas separation performance in the presence of an external magnetic field⁹⁰.

Traditional solvent extraction employs a partitioning of a solute between two immiscible phases, typically an organic solvent and an aqueous solution. However, the organic solvents used in traditional solvent extraction systems are usually volatile, toxic and flammable. MILs are proposed as alternative solvents to remove the extraction solvent in the presence of an external magnetic field. The magnetic extraction overcomes the formation of emulsions typically present in conventional extraction processes. Deng et al.⁵⁶ studied the use of [P_{6,6,6,14}][FeCl₄] as an extraction solvent for the separation of phenolic compounds from aqueous solution in the presence of a Nd magnet. A significantly higher extraction efficiency of pentachlorophenol, a major component in the contaminated soil sample, was achieved for [P_{6,6,6,14}][FeCl₄] when comparing with selected traditional non-magnetic RTILs. Moreover, Wang et al.⁹¹ investigated the use of [BPy][FeCl₄] as an effective extractant for asphaltene fractions from coal direct liquefaction residues (CDLR). The results show that pyridine based MILs are an effective extractant for asphaltenes from CDLR among the three magnetic ILs studied. Moreover, the extracts might be good precursors for preparing high-value-added carbon materials because of their higher carbon content, lower H/C and ash content. Deep desulfurization (DDS) of fuel oils, such as gasoline and diesel, has attracted increasing interest because of the enforcing regulation on the environmental pollution caused by exhaust gases, such as SO_x and NO_x to the atmosphere. Ko et al.⁹² reported the use of Fe-containing RTILs, as effective extractants for the desulfurization of a model oil containing dibenzothiophene (DBT).

Additionally, Jiang et al.⁹³ investigated the MIL 1-n-butyric acid-3-methylimidazolium chloride/iron chloride, [C₃H₆COOHmim][Cl]-FeCl₃, for the extraction and catalytic oxidative desulfurization of a model oil under mild conditions. The removal of benzothiophene, which has been regarded as a refractory aromatic sulphur compound, could be achieved at up to 100% in 10 min. After reaction, the MIL could be easily separated from the model oil by applying an external magnetic field, due to its paramagnetic properties.

Furthermore, magnetic surfactants are starting to receive great attention. Brown et al.³¹ reported, for the first time, RTILs surfactants that are magneto-responsive, thus offering the potential to perturb liquid emulsions simply by the application of an external magnetic field. Additionally, Klee et al.³³ proposed microemulsions with magnetic properties formed by employing a MIL as polar phase, cyclohexane as oil, and an appropriate mixture of ionic surfactant and decanol as a cosurfactant. Fig. 6 shows the displacement of the MIL at different magnetic field intensities.

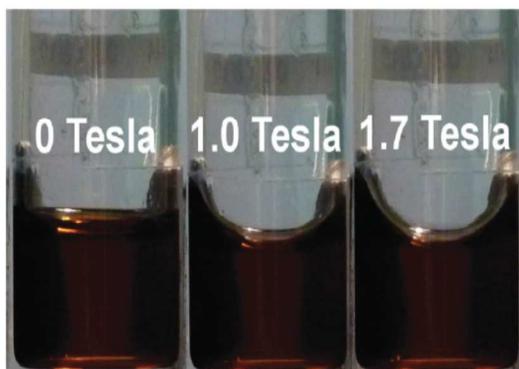


Fig. 6. Response of the MIL containing microemulsion to the field gradient of an electromagnet³³. The sample shown consists of 31.2 wt% D12-cyclohexane, 46.1 wt% [Bmim][FeCl₄], 11.8 wt% [C₁₆mim][Cl] and 10.9 wt% decanol.

3.1.2. Chemical reactions

One of the main applications of MILs is in the field of the catalytic reactions. The toxic and/or hazardous properties of many solvents, notably chlorinated hydrocarbons, make necessary the development of novel reaction media. Their purely ionic character of RTILs makes them excellent solubilizers for a wide range of inorganic, organic, as well as organometallic substrates, thus substituting polar aprotic solvents. Other important attributes of RTILs include negligible vapor pressure, recyclability and easy separation of products from the reaction mixture. Since iron is one of the most inexpensive metals, the scope for iron-catalyzed organic reactions is of great interest and constantly growing. All of these features open a new frontier of reinventing organic reactions practiced in chemical industry leading to improved process performance. MILs have been used in chemical reactions as catalyst, solvent or reaction medium.

- Catalysts:

Valkenberg et al.⁹⁴ investigated the use of iron chloride-based RTILs in the Friedel-Crafts acylation of aromatic compounds as an alternative to existing homogeneous catalysts. High conversions and very high selectivities were obtained in a variety of reactions. Experiments in liquid and gas phases were performed and possible reasons for the deactivation of the catalyst were discussed. Tilve et al.⁹⁵ developed a new method for the synthesis of 2, 3-unsaturated glycopyranosides by the glycosidation of 3, 4, 6-tri-*O*-acetyl-d-glucal with various alcohols using [Bmim][Cl]-1.5FeCl₃. This MIL has proved to be an efficient reaction medium, playing a dual role of a catalyst as well as of a solvent. Bica and Gaertner⁹⁶ established a successful approach to iron-catalyzed hydroxymethylation of various β -keto esters using [Bmim][FeCl₄]. Nguyen et al.⁹⁷ investigated the use of imidazolium-based Fe-containing catalysts [Bmim][FeCl₄], [Bmim][Fe₂Cl₇], and [Bmim][FeCl₄] for the selective dimerization of bicyclo-[2.2.1]hepta-2,5-diene (2,5-norbornadiene, NBD) to produce hexacyclic endo–endo NBD dimer, Hnn, in high yield. Wang et al.⁹⁸ studied the use of [Bmim][FeCl₄] in the catalysis of depolymerization of PET in ethylene glycol. The proposed

mechanism indicates that the high catalytic activity of the MIL is attributed to the synergic effect of its cation and anion which makes the attack of oxygen in ethylene glycol on the carbon cation of the ester group much easier. Therefore, [Bmim][FeCl₄] might have the potential to substitute traditional compounds to catalyze the depolymerization of PET in industrial production. Misuk et al.²⁶ reported, for the first time, the combination of both, the magnetic and catalytic behaviour of imidazolium based MILs to establish a so-called liquid fixed-bed (LFB) in a micro/meso-structured reactor. Furthermore, Godajdar et al.⁹⁹ reported the synthesis of 1, 2-azidoalcohols via regioselective ring opening of their epoxides using the magnetic imidazolium based dicationic RTIL, [pbmim][FeCl₄], as an efficient magnetic phase transfer catalyst in water. Zhu et al.⁴⁶ explored the use of N-butylpyridinium tetrachloroferrate [BPy][FeCl₄] as catalyst into oxidative desulfurization, which presents feature of liquid-liquid ECODS system at 40 °C. Besides, [BPy][FeCl₄] exhibits a strong response to a magnet and can be easily separated from model oil by applying an external magnetic field, achieving five times recycling without significant decrease in activity described in Fig. 7. Liquid-liquid extractive and catalytic oxidation mechanism was researched and validated by GC-MS. Finally, Khalafi-Nezhad and Mohammadi¹⁰⁰ proposed a general method for the synthesis of 1- and 5-substituted 1H-tetrazoles from nitriles and amines using chitosan supported magnetic ionic liquid nanoparticles (CSMIL) as a novel heterogeneous catalyst which can be applied for different organic functional group transformations in green processes.

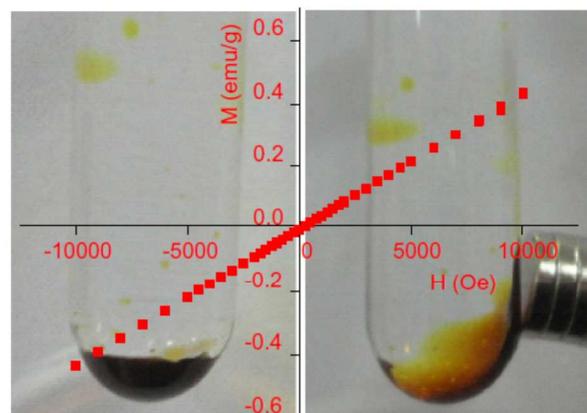


Fig.7. Magnetization of [BPy][FeCl₄] as a function of the applied magnetic field⁴⁶.

- Solvent:

The tetrahalogenidoferrate (III) anions show high solubility in polar solvents, especially in water due to hydrogen bonding interactions, causing solubility of the substances in water and alcohol. Tang et al.¹⁰¹ studied the solubility of [VRIM][FeCl_mBr_{4-m}] (R= n-butyl, m= 2, 3, 4; R= n-pentyl, m= 3, 4; R= nhexyl, m= 3,4) compounds in polar and nonpolar solvents. [VRIM][FeCl_mBr_{4-m}] was soluble in water and alcohol, slightly soluble in ethyl acetate and benzene, and

insoluble in diethyl ether. The solubility of tri(1-ethyl-3-methylimidazolium) hexachlorogadolinium, [Emim][GdCl₆], di(tetramethylammonium) tetrachloromanganese, [TMA][MnCl₄], tri(1-butyl-3-methylimidazolium) hexachlorogadolinium, [Bmim][GdCl₆], and cholinium tetrachloroferrate, [Choline][FeCl₄], in water, ethanol, 1-propanol and 1-butanol was studied by Zakrzewska et al.³⁶ The relative affinity of the studied solutes to ethanol and 1-propanol follows the order: [Choline][FeCl₄] > [Emim][GdCl₆] > [TMA][MnCl₄] > [Bmim][GdCl₆]. It can also be observed that the solubility of all solutes decreased with increasing alcohol chain length. Diferrate dicationic salts exhibited good solubility in polar solvent such as water, methanol, acetonitrile and dimethylsulfoxide. However, they cannot be dissolved in methanol, acetone, ethyl acetate, and ethyl ether⁵⁵.

- Reaction medium

MILs have attracted attention as potential pretreatment agents in cellulosic biomass processing. Muraoka et al.³⁹ firstly reported an effective MIL for dissolving crystalline cellulose and for the magnetically recovery after cellulose dissolution. The esterification of oleic acid to biodiesel in the presence of [Bmim][FeCl₄] at reaction temperature of 65 °C has been investigated by Fauzi et al.⁴² in a batch reactor process. Artificial neural network-genetic algorithm (ANN-GA) was used to simultaneously optimized methyl oleate yield and oleic acid conversion for the reaction. Both, predicted yield and conversion were 83.4% at optimum conditions. Thus, [Bmim][FeCl₄] is a promising new type of catalyst for conversion of high free fatty acid (FFA) feeds to biodiesel. Sahiner et al.¹⁰² produced different metal nanoparticles (Co, Ni, Cu, and Fe) within cationic microgels (shown in Fig. 8), and investigate their catalytic properties for hydrogen production from the hydrolysis of NaBH₄ and NH₃BH₃ as an alternative to fossil fuel based energy storage systems. The cationic microgels absorbed metal salts from alcohol media via electrostatic interaction between metal chloride salts dissolved in molecular form and cationic hydrogels and later reduced to their corresponding metal nanoparticle. Therefore, these metal nanoparticle-embedded RTIL colloids can also be used as catalyst media for various reactions.

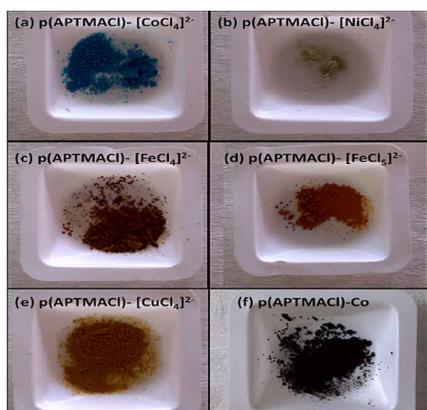


Fig. 8. Metal nanocomposites based on (3-Acrylamidopropyl)-trimethylammonium chloride, p(APTMACI), cation¹⁰².

3.2. Product applications

3.2.1. Polymer chemistry

There is an increased drive towards the fabrication of nanostructured and reduced dimensionality materials (i.e. thin films, tubes, wires or particles) which can exhibit markedly different properties from those of the bulk conducting polymeric materials. Conducting polymers, such as polyaniline, polypyrrole, polythiophene and their derivatives have been recently investigated because of their interesting electrical and optical properties, leading to applications in the fields of electromagnetic interference shielding, organic conductors, etc. MILs as electrolytes and solvents can be used in the polymerization of conducting polymers. Specifically, the MIL [Bmim][FeCl₄] is known to self-organize in a way that is adaptable to the fabrication of microstructures/nanostructures of conducting polymers and inorganic materials. The goal is to produce a new composite material that has distinct properties that were not observed in the individual components. Li et al.¹⁰³ synthesized poly(3,4-ethylenedioxythiophene) nanospheres with their size ranging around 60 nm by simply adding monomers into [Bmim][FeCl₄]. The polymers produced in this MIL system are compared to those synthesized in conventional solution and emulsion polymerizations. Poly(3-methyl thiophene) nanospheres with their size ranging around 50-60 nm have been synthesized into [Bmim][FeCl₄] by Shang et al.¹⁰⁴ Lately, Wei et al.¹⁰⁵ synthesized polypyrrole (PPy)/AgCl nanocomposites with their size ranging around 70-100 nm using [Bmim][FeCl₄] as the oxidant in the interface polymerization system. Nanostructured conducting polypyrrole and poly(N-methylpyrrole) were successfully synthesized by simply adding monomers into the same MIL by Kim et al.¹⁰⁶ The shape of polypyrrole nanoparticles synthesized at room temperature was almost spherical with their size ranging around 60 nm with a relatively narrow size distribution. Moreover, porous PPy films were synthesized by Shen et al.⁴⁰ by facile interfacial polymerization using again [Bmim][FeCl₄] as oxidant. The effect of the concentrations on the morphology and electrochemical performance of PPys has been investigated. Electrochemical performances showed its potential application as supercapacitor materials. Finally, polyaniline/AgCl nanocomposites with their size ranging around 50-80 nm at the water/MIL interface were reported by Zhang et al.²⁷ Polyaniline/AgCl nanocomposites on a glassy carbon electrode showed strong electrocatalytic activity for hydrogen peroxide, H₂O₂, and could be used to construct a H₂O₂ biosensor.

3.2.2. Electrochemical and medical devices

MILs have been investigated as new electrochromic materials for the manufacturing of different electronic devices such as information displays, anti-glare rear view of automobiles, smart windows, etc. taking profit from the MILs unique magnetic, photophysical/optical or catalytic properties that originate from the metal incorporated in the complex anion properties. Branco et al.²⁸ proposed MILs capable of behaving not only as electrolytes but also as an electrochromic component by the appropriate combination of electrochromic and magnetic anions. They proposed anions or

cations capable of reversible oxidation/reduction processes involving strong changes in colour, and or their magnetic properties. Akitsu and Einaga¹⁰⁷ reported a new photo-controllable supramolecular system containing [Bmim][FeCl₄] and azobenzene as a new photofunctional magnetic material with application for memory devices. Furthermore, MILs could be also used in flow battery systems¹⁰⁸⁻¹⁰⁹.

MILs with poor color contrast upon switching can find applications as contrast agents in Magnetic resonance Image (MRI) for medical diagnostics although this application is limited due to the MILs toxicity^{83-85,110}. The development of novel MRI contrast agents remains an active area of research, with many new agents currently in preclinical development or in clinical trials¹¹¹. Gd-based contrast agents are the most commonly used in clinical MRI. There have been significant efforts to design and develop novel Gd(III) contrast agents with high relaxivity, low toxicity, and specific tumor binding. Despite the inherent toxicity of the Gd ion and the relative youth of Gd-based contrast agents, there has been remarkable uniformity in both efficiency and safety of these compounds, making them simple to use, relatively innocuous, and essentially interchangeable. Recently, Zhou and Lou¹¹² reviewed the design and development, physicochemical properties, and in vivo properties of several classes of Gd(III)-based MR contrast agent tumor imaging.

3.2.3. Magnetic fluids

Other products in the field of MILs are the Magnetic Fluids (MFs). MFs are generally composed of stable dispersions of magnetic nanoparticles (MNPs) in an ionic liquid acting as solvent or carrier¹¹³. These suspensions are usually classified into magnetorheological fluids (MRF) and ferrofluids (FF). MRF find applications as lubricants in semi-active shock absorbers (automotive industry), dampers for seismic damage controls (civil engineering), seals, valves, robotics, microelectronic devices, etc. whereas FF can be applied in fields such as mechanical engineering, aerospace, medicine and optics¹¹³. Guerrero-Sánchez et al.⁵² prepared RTIL-based MRF consisting in the dispersion of micron or nanosized magnetite particles in different RTILs. The most stable MRF was obtained for a composition of 10 vol% of magnetite microparticles suspended in [Bmim][PF₆]. Colloidal stability was achieved without the addition of any stabilizing agents due to the physical adsorption of the RTIL ions on magnetite surface (for which they had strong affinity) that gave rise to steric repulsion between the dispersed particles. Furthermore, the influence of temperature on the RTIL-MRF behavior has been also studied¹¹⁴. Additionally, stable dispersions of Fe₃O₄ MNPs in 1-ethyl-3-methylimidazolium ethylsulfate, [Emim][EtSO₄], were obtained by Rodríguez-Arco et al.¹¹⁵⁻¹¹⁶. Stable dispersions of magnetic maghemite (γ -Fe₂O₃) and cobalt ferrite (CoFe₂O₄) MNPs in [Bmim][BF₄] were prepared by Oliveira et al.⁵³. However, the obtained MIL was unstable in the presence of water ([Bmim][BF₄] is highly hydrophilic), and stable dispersions could not be achieved with either [Bmim][PF₆], or 1-n-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [Bmim][NTf₂]. Jain et al.¹¹⁷ also attempted to synthesize RTIL-based FFs using maghemite nanoparticles. Medeiros et al.¹¹⁸

reported stable dispersions of surface modified γ -Fe₂O₃, Fe₃O₄, and CoFe₂O₄ magnetic nanoparticles in the hydrophobic RTIL [Bmim][NTf₂]. Silica-coated Fe₃O₄ magnetic nanoparticles supported dual Brønsted acid ionic liquid 1-(propyl-3-sulfonate)imidazolium hydrogen sulfate [SO₃H-(CH₂)₃-HIM]-[HSO₄] was prepared by Wu et al.¹¹⁹. The magnetic nanoparticle was successfully introduced into silica matrix, and the Brønsted acidic ionic liquid was immobilized on the surface of nanoparticle via coupling reagent. The synthesized catalyst RTIL-Fe₃O₄@SiO₂ showed good performance in the synthesis of biodiesel with oleic acid and ethanol. Moreover, Zhang et al.²⁹ prepared RTIL-stabilized iron oxide (Fe₂O₃) nanoparticles by the ultrasonic decomposition of iron carbonyl precursors in [Emim][BF₄] without any stabilizing or capping agents. The resulting Fe₂O₃-[Emim][BF₄] can be directly used to prepare millimeter-sized MIL marble by coating with hydrophobic and unreactive polytetrafluoroethylene (PTFE) which can be easily transported with applied magnetic field. Finally, Pei et al.¹²⁰ prepared a magnetically responsive nanomaterial by covalent attachment of [Bmim][FeCl₄] to single-walled carbon nanotubes. They reported for the first time the hybrid magnetic material by combining MIL and carbon nanotubes. This material and other similar MIL-based carbon nanotubes can be engineered as coating materials, antistatic materials, novel electronic devices and so on, applicable in various fields of biomedical and bionanoengineering.

Conclusions

In this review, the main results related to the synthesis, characterization and applications of magnetic fluids have been discussed. MILs containing the [FeCl₄] anion were the first to be synthesized and they are widely disseminated. Recently, MILs based on the transition metals Co and Mn and the lanthanide complexes Gd or Dy have been also studied. MILs show particular optical or luminescence properties leading to new interesting applications in both process and product engineering. Regarding process engineering, MILs may be applied in fluid-fluid separations and in chemical reactions acting either as catalyst, solvent or reaction medium. Taking in mind the product engineering, MILs find applications in polymer chemistry, the development of electrochemical and medical devices and as magnetic fluids. Overall, the use of MILs is in constant growth taking advantage of their switchable properties in the presence of an external magnetic field, together with the interesting properties of ionic liquids.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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