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Review

Paramagnetic ionic liquids for advanced applications: A review

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ABSTRACT

Magnetic ionic liquids (MILs) incorporated with inorganic or organic paramagnetic ions are a new type of ionic materials having high ionic conductivity, magnetic responsiveness and sometimes integrated with luminescence activity. This material has gained considerable research attention in the past few decades due to its many amazing properties. The MILs overcome many disadvantages faced by traditional magnetic fluids. In this review, we have outlined the important properties, scopes and attributes of this novel class of ionic liquids in various fields such as catalysis, nanomaterial synthesis, extraction process, cellulose dissolution, magnetic separation, gas adsorption, density measurements and environmental remediation.

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1. Introduction

Ionic liquids (ILs) are a centre of attraction of materials research since the 21st century. The various applications of ILs in liquid–liquid extraction processes, as green aprotic solvents in organometallic reactions, in biocatalysis, environmental remediation, catalytic cracking of polyethylene and radical polymerization using different kinds of organic cationic and anionic combinations are being widely reported [1]. Many properties like photo-induced electron transfer (PET) and electrochemically conductive nature of many of these materials have already been successfully established and functional [2]. Among the new generation ionic liquids, magnetic ionic liquids (MILs) which can be derived from room temperature ionic liquids (RTILs) by the incorporation of transition metals like Iron, Cobalt, Manganese, and Copper or different rare-earth ions like Neodymium, Gadolinium, and Dysprosium in it are a recent attraction [3–7]. Ionic liquids incorporated with metal atoms possess certain magnetic susceptibility. This can be done either by introducing a metal-ligating group as the anion or cation or by the direct addition of metal atom into either ion [8].

MILs possess magnetic properties by itself without any need for the addition of magnetic nanoparticles to ILs. Their paramagnetic properties originate either from the anion or cation or from both of them. This new class of magnetic fluids has been synthesized as a result of attempts to develop magnetic property incorporated ionic liquids and has progressively contributed to the research field of 'magnetism in liquids'. These single-component ionic liquids are magnetic nanoparticle-free unlike ferrofluids, but usually consist of complexes of magnetic ions with high magnetic moment. For example, $[C_6mim]_{5-x}[Dy(SCN)_{8-x}(H_2O)_x]$ ($x = 0$–2, C_6mim = 1-hexyl-3-methylimidazolium) [6].

A major advantage of these magnetic liquids over other conventional magnetic fluids such as ferrofluids and magnetorheological fluids is their optical transparency, small-line width and high color purity, which makes them appropriate for many potential optical applications [9]. Usually, MILs, due to their high thermal stability, low vapor pressure and mainly because of the possibility of magnetic separation and recycling, can be considered as comparatively greener than the conventional type of ionic liquids. However, sufficient studies on the toxic effects and cell biocompatibility of these materials are lacking. Incorporating different types of magnetic metal anions in MILs cause its strong sensitivity to magnetic field which creates in them an additional advantage of its recoverability and reuse [10]. Most of the applications of MILs exploit their inherent magnetic responsivity. A detailed review on the synthesis, characterization, physico-chemical properties such as density, viscosity, decomposition temperature, magnetic properties, toxicity, electro-chemical luminescence of some important MILs was given by Santos et al. [11].

In this review, we explore the current trends in the research directions towards the MILs. As discussed earlier, the magnetic entity in MILs is generally the transition and inner-transition metal containing complex anions [3–6]. However, there are reports on the synthesis of MILs from chiral amino acids, metal-free paramagnetic ions and also dicationic heteroanions with task-specificity [4,12]. Other applications of MILs include their use in the transport and separation of materials, as an absorbent for benzene emissions, for sulfide extraction in gasoline and as CO_2or SO_2 gas absorbent [13–15].

This review also gives an insight into the intermolecular and structural arrangements observed in MILs and the unique properties arising from it. In these materials, three different modes of interaction between an anion and a cation–Π system can be seen: (i) hydrogen bonding between the hydrogens of the positively charged organic cation and the highly electronegative atoms present in the anions, (ii) strong noncovalent anion-Π interactions, in which the anion is located above the center of the aromatic ring, (iii) weak noncovalent anion-Π interactions, where the anion will be present outside the periphery of the Π-system. The strength of all these interactions varies in different types of MILs depending on the nature of the atoms and aromatic ring systems present in them.

In this section, we first discuss the metal halide anion based MILs which are among the most widely studied ones. These MILs find applications as catalyst, reaction media, as magnetic fluids, for magnetic transport, density measurements, etc. They consist of anions with the general formulae $[Fe^{III}X_4]^-$ where X = Cl or Br and are the most commonly investigated ones. MILs with anions containing transition metals other than Fe and that also with inner-transition metals have also been synthesized and reported which are discussed in the following sections. Other than these, magnetic metal atoms can be incorporated inside the organic cationic part of the IL also such as in the case of metallocenium based MIL (detailed in Section 3).

2. Paramagnetic ionic liquids containing inorganic anions

Briefing on the historical background, the magnetic properties of 1-ethyl-3-methylimidazolium tetrachloroferrate ($[C_2mim][FeCl_4]$) was initially pointed out by Saito et al. [16]. Followed by this, Hayashi and Hamaguchi investigated the magnetic properties of 1-butyl-3-methylimidazolium tetrachloroferrate, ($bmim[FeCl_4]$) [17]. The qualities of these MILs like manipulation of non-magnetic objects and magnetic recovery from binary mixture of $bmim[FeCl_4]$ and water visibly attracted the attention of many researchers [18]. However, until Freeman and Angell independently investigated the physical properties of $[C_4mim][FeCl_4]$, not much attention was given to this unique material. Ever since then, various types of MILs based on imidazolium salts of tetrahalogenoferrate(III) anion, ammonium, and phosphonium cations with Co(III), Cr(III), Mn(II) and Fe(III) containing anions have been developed [3]. So far, many paramagnetic ILs consisting of magneto-active metal complex anions, some of them being $Fe^{III}X_4^-$ (X: Cl, Br),$Mn^{II}X_4{}^{2-}$ (X: Cl, Br), $Co^{II}X_4^{2-}$ $(X: Cl, NCS, N(CN)_2)$, $Gd^{III}Cl_6^{3-}$, and $Dy^{III}(SCN)_{8-x}$ $(H\ _2O)x(5-x)-$ (x: 02) anions in combination with conventional ionic liquid organic cations have been synthesized [3,5,7,6,4,19].

2.1. MILs with transition metal complex anions

Mostly, these MILs are prepared by the simple mixing of the halide salts and neutral metal complexes; for example, alkylimidazolium tetrachloroferrate $[C_nMI][FeCl_4]$ can be obtained by mixing exactly equimolar crystalline $[C_nMI]Cl$ and $FeCl_3$ under inert atmosphere at room temperature. Alternatively, the synthesis of MILs consisting tetrahaloferrate anions can be made possible by a two step reaction. Initially, ionic halide salts are prepared from an equimolecular mixture of alkyl halide and heterocyclic hydrocarbon at low temperatures (80 °C) which gives the cationic part in MIL. Then, the ionic halide salt of the heterocyclic alkane can be mixed with equimolecular amount of iron halide under N_2 atmosphere at about 50 °C. 1-Butyl-3-methylimidazolium tetrachloroferrate ($bmim[FeCl_4]$), 1-butyl-1-methylpyrrolidium tetrachloroferrate ($bmP[FeCl_4]$) and N-butylpyridium tetrachloroferrate ($bPy[FeCl_4]$) have been prepared by this method (shown in Fig. 1) [19]. This simple procedure doesn't create the need for any solvents as the reaction medium or the use of an ion exchange process.

The presence of tetrahalogenoferrate anions which are primarily based on high-spin d^5 iron(III) in combination with various counter cations are the source of many peculiar properties like superexchange magnetic interactions between the molecular lattice planes observed in these MILs. Most of these MILs evidenced a paramagnetic temperature dependent magnetic susceptibility exhibiting only small deviations from the Curie law at low temperatures. The strong magnetic response in them is evident from their high effective magnetic moments (μ_{eff}) in the range of 5.66–5.89 μ_B, which is close to the spin-only value (5.92 μ_B) for paramagnetic high-spin Fe(III) ions.