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Molecular modeling and physicochemical properties of 1-alkyl-3-methylimidazolium-FeX₄ and -Fe₂X₇ (X = Cl and Br) magnetic ionic liquids

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Abstract

Magnetic Ionic Liquids (MILs) are room temperature ionic liquids composed of a metal-containing anion and an organic cation, which present paramagnetic properties that make them interesting materials for industrial applications. [Molecular modeling calculations of MILs](#) from the combinations of four 1-N-alkyl-3-methylimidazolium (NMIIm) cations and the anions: tetrachlorideferrate (III), tetrabromideferrate (III), heptachlorideferrate (III) and heptabromideferrate (III) have been carried out using DFT methods. The dependence of properties, such as energies, dipole moments and magnetic couplings, on the chain length has been studied and compared with similar non magnetic ionic liquids containing chloridealuminate anions. Density and viscosity were estimated using COSMO-RS obtaining good agreement with experimental data.

Keywords: Magnetic ionic liquids, DFT calculations, Molecular structure, Physicochemical properties, COSMO-RS method

1. Introduction

Magnetic Ionic Liquids (MILs) are room temperature ionic liquids (ILs) which present paramagnetic properties originated from the anion or cation or both of them.[1, 2] MILs are typically composed of a metal-containing anion and an organic cation. Their interest has increased since the discovery of the first MIL in 2004 by Hayashi and Hamaguchi [3]. MILs have aroused great interest in the scientific community during the last decades because of their interesting properties and possible future applications.[2, 4] Besides the properties that usually make common ILs attractive for industrial applications, MILs present an enormous advantage because of the possibility of tuning their physicochemical properties by applying magnetic fields.[4]

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MILs have a wide variety of applications in industrial chemistry. Some recent works have reported the possibility of using magnetic ionic liquids as potential contrast agents [5], or in processes such as extractive desulfuration of fuel oils [6], extractive separation of hydrocarbons [7], CO₂ separation using supported MILs membranes [8], DNA extraction [9], separation magnetic nanoparticles [10], and biodiesel production. [11] Studies in human cells were published concerning the understanding of the magnetic anion toxicity. [12, 13]

In the last years a huge amount of experimental work has been published in this field for MILs containing several metals such as Fe(III), Co(II), Mn(II), and also lanthanides as anions, which are known for their strong response to an applied external magnetic field [5, 6, 7, 8, 9, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31]. In some of them the behavior of physicochemical properties like viscosity with the application of external magnetic fields has been studied. Thus, Daniel et al. [19] reported the properties of a bunch of MILs containing Co, Mn and Fe. In all cases the application of a magnetic field significantly reduces the viscosity. De Pedro et al. [16] studied the long-ranged magnetic ordering of EMImFeCl₄. Daniel et al. [21] studied the response of tri-octylmethylammonium (Aliquat) chloride ([Aliquat][Cl]) and a mixture of [Aliquat][Cl] and small quantities of [Aliquat][FeCl₄] to the application of a magnetic field. They observed that the application of a magnetic field reduces the viscosity of the mixture while the viscosity of [Aliquat][Cl] remains constant. They also studied mixtures of [P₆₆₆₁₄][FeCl₄] with [P₆₆₆₁₄][Cl] observing that the viscosity decreased with the magnetic field strength and measured viscosities and densities of these MILs at different temperatures [22]. Yoshida and Saito [32] measured experimental densities at 293.15K and viscosities at 298.15K of 1-alkyl-3-methylimidazolium tetrahalogenoferrate (III), and Bwamrocket al. introduced a new technique to measure densities using magnetic levitation [33].

Despite the increasing interest on MILs, only a few theoretical works have been reported. [34, 35, 36, 37, 38, 39] Sitze et al. [34] calculated the infrared spectra for BMIm, FeCl₄, FeCl₃ and Fe₂Cl₇ mixtures at DFT level and compared the results with experimental data. Martínez-Magadán et al. [35] studied the desulfuration of natural gasoline by analyzing the interaction of BMImFeCl₄ and BMImFe₂Cl₇ with ethanethiol using DFT methods. Li et al. [38] applied DFT methods to investigate the structure of BMImFeCl₄ and its interaction with aromatic sulfur compounds. García-Saiz et al. [36] investigated the structure of EMImFeCl₄ at low temperature (4K) and applied DFT

methods to determine the magnetic coupling between magnetic centers.

The use of MILs is constantly growing due to their switchable properties in the presence of an external magnetic field in addition to the outstanding properties of ILs. Since their thermophysical properties depend to a large extent on the type and chemical structure of the cation and the anion, their properties can be tuned for specific applications by a suitable choice of the combination of anion / cation pairs. For this purpose, a predictive molecular modeling of the ions provides estimations of the thermophysical properties that can be useful for predicting the behavior of particular MILs under specific conditions. In this spirit, we present here a study on some relevant physicochemical properties of four families of MILs (1-alkyl-3-methylimidazolium- FeCl_4^- , -FeBr_4^- , $\text{-Fe}_2\text{Cl}_7^-$ and $\text{-Fe}_2\text{Br}_7^-$) using computational tools, aimed at establishing a link between their molecular structure and their macroscopic properties. We will use two computational tools to analyze the systems studied: i) DFT methods to compute equilibrium geometries of the ion pairs and the properties related to the molecular structure and the interactions within the ion pair. ii) a COSMO-RS approach to predict physicochemical properties (density and viscosity).

2. Computational details

Different systems with anions containing magnetic Fe atoms have been analyzed. The studied systems are four families of MILs formed by the combination of four 1-N-alkyl-3-methylimidazolium (NMIIm^+) cations (N=2,4,6,8), Ethyl-, Butyl-, Hexyl- and Octyl-, respectively and four anions: tetrachlorideferrate (III) (FeCl_4^-), tetrabromideferrate (III) (FeBr_4^-), heptachlorideferrate (III) (Fe_2Cl_7^-) and heptabromideferrate (III) (Fe_2Br_7^-). In order to determine the influence of magnetic centers in the molecular structures and properties, calculations of nonmagnetic ILs with tetrachloridealuminate (AlCl_4^-) and heptachloridealuminate (Al_2Cl_7^-) anions combined with the same cations have been carried out for comparison.

The molecular structure of ion pairs was characterized by analyzing geometries, interaction energies, dipole moments and bond critical points (BCPs). All the geometries of the ion pairs were obtained with M06-2X functional[40] in combination with 6-311+G** basis set using Gaussian 09 software[41]. This functional provides an accurate description of non-covalent interactions [42]. M06-2X functional in combination with Pople type basis sets has been shown to provide accurate results for calculations involving ILs [43, 44].

Given the complexity of the ions and the number of possible stable structures is quite high. The ions were optimized separately, then the optimized structures were put together and the ensemble was reoptimized. Since there are several conformers for each ion pair, the choice of the starting geometry for the optimization was based in previous optimizations with ion pairs containing long alkyl chains and different anions[45, 46, 47]. Energy minima have been confirmed by the absence of imaginary vibrational frequency calculations. LC-wPBE functional[48] was used for the calculation of dipole moments in order to reduce the effect of the self interaction error [45, 49, 44]. Atoms in Molecules (AIM) analysis was carried out using AIMAll package [50]. Figures for structures were prepared using GaussView5[51] and DAMQT[52].

The exchange coupling constant (J) is modeled by the Heisenberg–Dirac–van Vleck Hamiltonian:

$$H = -2JS_AS_B \quad (1)$$

where J is the exchange coupling parameter and S_A and S_B are local spin-operators for the interacting sites A and B, respectively. The magnetic coupling has been calculated using the Broken Symmetry method proposed by Noodleman [53], where the magnetic coupling is expressed as

$$J = -\frac{E_{HS} - E_{BS}}{s_{max}^2} \quad (2)$$

where E_{HS} and E_{BS} are the energies of the high-spin (HS) and broken symmetry (BS) determinants, respectively and s_{max} is the largest spin.

DFT calculations have also been successfully applied to the estimation of the exchange coupling constants, J , for a variety of transition-metal complexes. The J evaluations based on DFT calculations depend on the exchange-correlation functional and the chosen basis sets. Comparisons between the results of various functionals have been performed by different authors (Ref [54] and references therein). The magnetic coupling constants calculated using M06-2X functional, reduces the values of coupling compared to gradient corrected or hybrid functionals ([54]). In particular, the B3LYP functional presents a remarkable agreement with the experimental results, providing accurate values for Fe transition-metal complexes ([55, 56]). For this reason, J calculations were carried out at the B3LYP/6-311+G* level using ORCA software[57].

Density and viscosity of the families of MILs studied were estimated using the COnductor-like Screening MOdel for Real Solvents (COSMO-RS) method [58], which combines molecular cal-

culations on isolated ion pairs with COSMO methodology to estimate physicochemical properties using a statistical treatment with COSMOtherm program [59]. This approach provides a feasible nonexpensive method to estimate physicochemical properties of ILs [58]. Following COSMO's prescription, the input was prepared from a single point calculation at the BVP86/TZVP/DGA1 level, since this is the standard COSMO package level [60]. Theoretical results were compared to available experimental data.

3. Results and discussion

a) Molecular modelling

Geometry optimizations have been carried out for 24 structures of NMIm-FeBr₄, -FeCl₄, -AlCl₄, -Fe₂Br₇, -Fe₂Cl₇ and Al₂Cl₇ ion pairs and are depicted in Figures S1 and S2 in the Supporting Information (SI). Optimized geometries, containing the more relevant parameters of NMIm-YX₄ and -Y₂X₇, are sketched in Figures 1 and 2. In general, the relative positions of the cation and the anion remain unchanged as the the cation alkyl-chain is enlarged. Table 1 lists the distances between the metal and the Carbon A atom in the imidazolium ring (see Figure 1) for NMIm-YX₄ ion pairs. The distance between anion and cation does not change with the size of the cation, but is higher when the anion contains Br atoms than when it contains Cl atoms. This effect is clearly related with the steric size of the four halogen atoms in a tetrahedric anion. Two significant parameters will be considered in the discussion of geometries for the NMIm-Y₂X₇ ion pairs: the angle (α) formed by the atoms Y1, Y2 and CA and the distance (d) between the atoms X3 and NL (see Figure 2). The distance between ions of the ion pairs in NMIm-Y₂X₇ MILs is significantly shorter for EMIm than for the remaining cations. This difference is more noticeable in the case of NMIm-Fe₂Br₇ as shown in Table 2, showing a decrease of the distance from 4.03 to 3.59 Å. It is remarkable too that both parameters α and d are similar for the four NMIm-Al₂Cl₇ ILs treated here, with a distance between ions greater than in NMIm-Fe₂Cl₇ MILs, as it can be expected from the larger atomic radius of Al.

Interaction energies of the MILs studied in this work are reported in Table 3. These energies are defined as the energy of the ion pair minus the sum of energies of the isolated cation and anion. The computed values fall in the range of interaction energies for ILs reported in previous works [43, 45]. The length of the alkyl chain of cations does not significantly affect the magnitude of the interaction

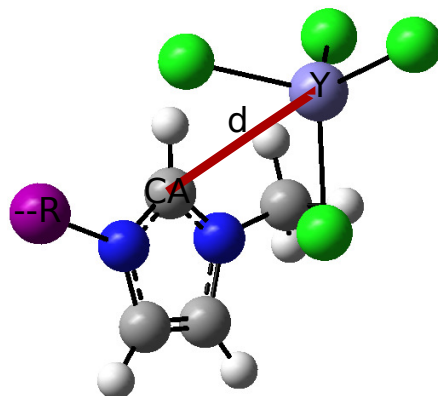


Figure 1: Geometry of BMImYX₄ ion pairs including the significant parameter between cation and anion, d in brown

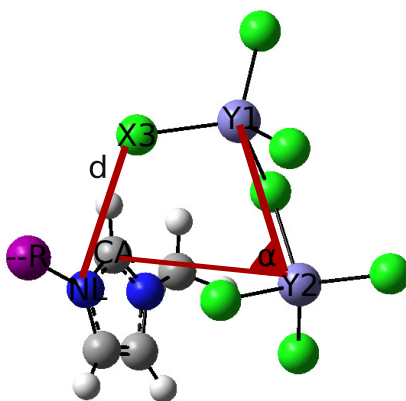


Figure 2: Geometry of BMImY₂X₇ ion pairs including the significant parameters between cation and anion, α and d in brown

Table 1: Distance between the metal (Al or Fe) and CA in the imidazolium ring (Å)

| | FeBr₄ | FeCl₄ | AlCl₄ |
|-------------|-------------------------|-------------------------|-------------------------|
| EMIm | 3.78 | 3.63 | 3.62 |
| BMIm | 3.80 | 3.65 | 3.64 |
| HMIm | 3.80 | 3.64 | 3.64 |
| OMIm | 3.79 | 3.65 | 3.64 |

Table 2: Significant geometrical parameters of NMImY₂X₇ ion pairs: α angle (degree) and distance d(X3-NL) (Å). Parameters are depicted in Figure 2

| | α | | | d | | |
|-------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| | Fe₂Br₇ | Fe₂Cl₇ | Al₂Cl₇ | Fe₂Br₇ | Fe₂Cl₇ | Al₂Cl₇ |
| EMIm | 57.4 | 65.1 | 59.6 | 3.59 | 3.68 | 4.29 |
| BMIm | 61.4 | 61.5 | 59.7 | 4.03 | 3.84 | 4.26 |
| HMIm | 61.7 | 62.2 | 61.4 | 4.03 | 3.86 | 4.29 |
| OMIm | 61.7 | 61.4 | 59.8 | 4.03 | 3.83 | 4.28 |

energy between ions. However, the interaction energy for EMImFe₂Br₇ ion pair is slightly smaller than those of ion pairs with longer alkyl chains, which is consistent with the remarkable difference in geometry. From Table 3, it can be observed that interaction energies are slightly higher for ion pairs containing Cl in the anion than those with Br. These results are consistent with the shorter distances between anion and cation in NMIm-FeCl₄ and NMIm-Fe₂Cl₇(see Table 1). BSSE is small for ion pairs containing Cl and very small (less than 1%) for ion pair containing Br, due to the employment of a large basis set (see Tables S1 and S2 in the SI).

Table 3: Interaction energies (kJ/mol) for NMImYX₄ and NMImY₂X₇ ion pairs.

| | FeBr₄ | FeCl₄ | AlCl₄ | Fe₂Br₇ | Fe₂Cl₇ | Al₂Cl₇ |
|-------------|-------------------------|-------------------------|-------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| EMIm | -326.0 | -332.8 | -333.2 | -290.8 | -303.1 | -306.1 |
| BMIm | -326.2 | -332.6 | -333.1 | -297.5 | -303.6 | -305.5 |
| HMIm | -325.0 | -331.4 | -331.6 | -296.5 | -302.9 | -303.8 |
| OMIm | -325.2 | -331.2 | -331.4 | -296.3 | -302.5 | -304.0 |

Dipole moments of the ion pairs were also calculated and are displayed in Figure 3. The growth of imidazolium cation allylic tail produces a smooth decrease of dipole moments for NMIm-YX₄. It is clear that the structure and size of the cation have a significant effect on this property. The NMIm-FeBr₄ MILs present higher values, around 0.5 D, with respect to NMIm-FeCl₄. These results agree with the computed geometries in which cation-anion distances of chloride derivatives are shorter than those of bromide MILs (see Figure 1 and Table 1). The dipole moments for NMIm-AlCl₄ ILs lie between the corresponding values of both MILs families, according to the size of Fe

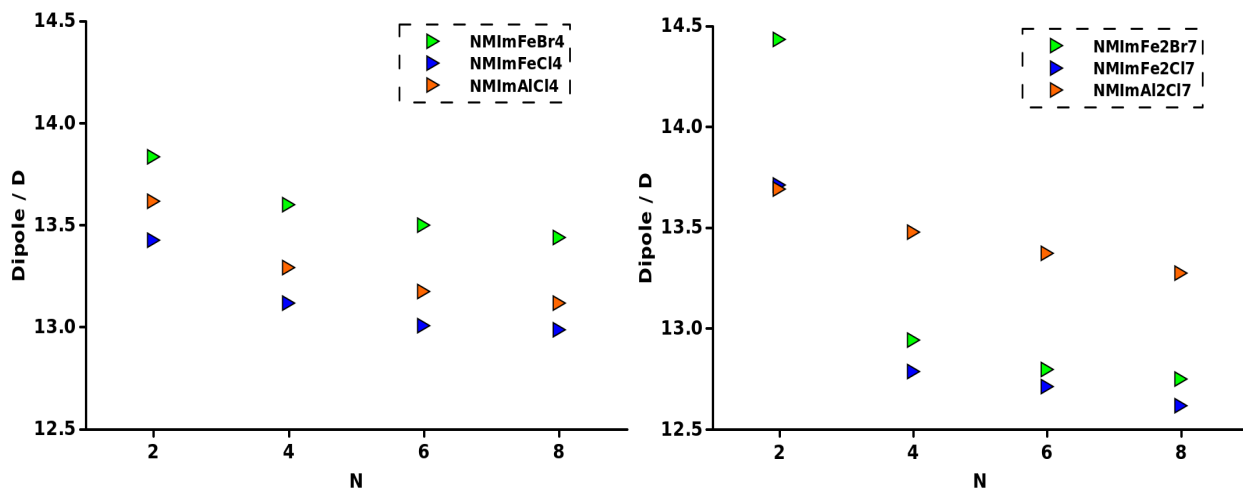


Figure 3: Dependence of the dipole moment on the length of the alkyl chain

and Al. In case of Y_2X_7 families, the trend is similar to that of ion pairs with YX_4 . Regarding the dependence of dipole moment with the side chain, it can be observed that its value decreases as the chain enlarges. This decrease is more marked for the first terms of the series, from EMIm ($\mu_{Fe_2Br_7} = 14.43D$ and $\mu_{Fe_2Cl_7} = 13.71D$) to BMIm ($\mu_{Fe_2Br_7} = 12.94D$ and $\mu_{Fe_2Cl_7} = 12.78D$), and smoother for the remaining ones. This different behavior is also found in the interaction energies of Fe_2Br_7 MILs (see Table 3) and it is also related with the equilibrium geometries as discussed above.

In order to get insight on the interactions between the ions, a study was carried out using AIM methodology which facilitates the comparison of interactions between ions for the different ILs. Table 4 contains the bond critical points (BCPs) calculated using the EMIm cation as a reference in combination with the three YX_4 anions. The label used for each atom is specified in Figure 4 for NMIm YX_4 ion pairs and in the Figure S3 of the SI for NMIm Y_2X_7 ion pairs. The number of BCPs found is similar in all cases and the values of electron density at the BCPs fall in the range 0.002-0.035 au which has been proposed as characteristic of hydrogen bonding [61].

Distances between atoms are smaller and BCP densities are slightly higher for ion pairs containing chloride than for the ion pairs containing bromide. This is consistent with the smaller interaction energies observed in $FeBr_4$.

AIM methodology also allows us to compare the interactions depending on the cation. Table S3 in the SI collects the BCPs found between atoms of the anion and the cation for all ion pairs

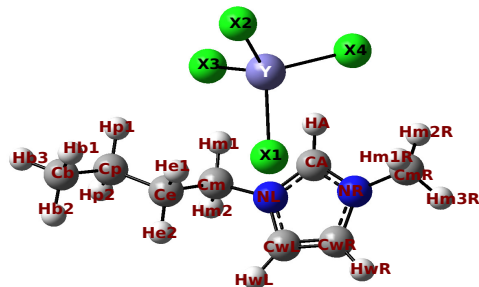


Figure 4: Schematic representation of the NMIImYX₄ ion pairs with the atom labels used for the AIM analysis

Table 4: BCPs found between anion and cation together with the density at the bond critical point and the distance between atoms At1 and At2 for EMImFeBr₄, EMImFeCl₄ and EMImAlCl₄.

| EMImFeBr ₄ | | | | EMImFeCl ₄ | | | | EMImAlCl ₄ | | | |
|-----------------------|------|---------------|-------|-----------------------|------|---------------|-------|-----------------------|------|---------------|-------|
| At1 | At2 | ρ (a.u.) | d (Å) | At1 | At2 | ρ (a.u.) | d (Å) | At1 | At2 | ρ (a.u.) | d (Å) |
| Br1 | CA | 0.0098 | 3.35 | Cl1 | CA | 0.0101 | 3.22 | Cl1 | CA | 0.0101 | 3.23 |
| | He1 | 0.0052 | 3.12 | | He1 | 0.0052 | 3.05 | | He1 | 0.0049 | 3.09 |
| Br3 | HA | 0.0054 | 3.20 | Cl3 | HA | 0.0067 | 2.99 | Cl3 | HA | 0.0068 | 2.99 |
| | Hm1 | 0.0097 | 2.85 | | Hm1 | 0.0104 | 2.71 | | Hm1 | 0.0106 | 2.71 |
| Br4 | He1 | 0.0075 | 3.02 | Cl4 | He1 | 0.0079 | 2.88 | Cl4 | He1 | 0.0078 | 2.89 |
| | HA | 0.0070 | 3.01 | | HA | 0.0074 | 2.90 | | HA | 0.0074 | 2.91 |
| | HmR2 | 0.0085 | 2.98 | | HmR2 | 0.0092 | 2.84 | | HmR2 | 0.0091 | 2.87 |

considering the NMIImFeCl₄ family. It can be seen that the same BCPs appear in all cases. Moreover, the density, ρ , and the distance between atoms are similar for the four ion pairs. Table S4 lists the BCPs between ions for the NMIImFe₂Cl₇ family. The number of BCPs increases when the number of carbons in the alkyl chain is augmented from 2 to 4, and it remains almost constant for chains with 6 and 8 carbon atoms. This is consistent with the differences found for dipoles and geometric parameters between EMImFe₂Br₇ and the ion pairs with longer alkyl chains.

The influence of Fe-Br-Fe and Fe-Cl-Fe angles in the magnetic coupling constants J has been studied. Last column of Table 4 shows the values of J , which are related to the ion pair geometry. The angles Fe-X-Fe are related to the distance between the magnetic centers that in turn affect the magnetic coupling constant. The distance, angle and magnetic coupling are listed in Table 5. It can be seen that the smaller the angle the lower the absolute value of J . In order to evaluate the influence of the cation on J values, the magnetic coupling has been calculated for the isolated anion and the anion within the ion pairs. In these ILs, the presence of the cation provokes a reduction of the value of J ca 7% by rapport to the isolated value. A decrease in the magnetic coupling caused by

the presence of the cation has been also reported previously [62].

A comparison of anion structures in the different Y_2X_7 ion pairs has been made paying special attention to the angle formed between the central atom (Cl or Br) and the two metals (Fe or Al), and to the distance between the two metals, as shown in Table 5. In the four NMIm- Al_2Cl_7 IIs, angles are very close to those of the optimized isolated anion $Al_2Cl_7^-$ (112.9 degrees), and Al-Al distances remain constant (see Figure S2) Angles Fe-Cl-Fe and distances Fe-Fe of the $Fe_2Cl_7^-$ anion in NMIm- Fe_2Cl_7 MILs are very similar to those obtained for $Al_2Cl_7^-$ ILs, except for the EMIm- Fe_2Cl_7 , whose angle and distance (106.0 degrees, 3.8 Å) are lower than in the other members of the NMIm- Fe_2Cl_7 series, ca. 112 degrees and 3.96 Å, respectively. The results for NMIm- Fe_2Br_7 ion pairs are very similar to those of NMIm- Fe_2Cl_7 , the Fe-Br-Fe angle and Fe-Fe distance in MILs with Emim cation being 4 degrees and 0.12 Å lower than in those with BMIm, HMIm and OMIm cations. The angles Fe-Cl-Fe and Fe-Br-Fe of the isolated anions (107.7 and 105.8 degrees) are closer to EMIm- Fe_2Cl_7 and EMIm- Fe_2Br_7 MILs, respectively (see Table 5). Geometries of EMIm- Fe_2Cl_7 and EMIm- Fe_2Br_7 are different from those of MILs with other cations, as illustrated in Table 2.

Two last columns of Table 5 show the values of magnetic coupling constants J for the isolated anions and ion pairs of NMIm- Fe_2X_7 MILs, respectively. Fe-Fe distances and consequently Fe-X-Fe angles in the anion of each ion pair rule the values of J , which are related to the distance between the magnetic centers. In Table 5, it can be seen that smaller angles are correlated to lower absolute value of J . The presence of the cation provokes a reduction of the value of magnetic coupling constants J ca 7% by rapport to the isolated anion value of these MILs. This trend of the decrease in the magnetic coupling caused by the presence of the cation has been also reported previously [62]. These values are related to optimized geometries and with dipole moments (see Figure 3). A change in both dipole moment and magnetic moment appears in the two sets of ion pairs (Fe_2Cl_7 and Fe_2Br_7) when passing from EMIm to BMIm and the values of both properties remain almost unchanged for BMIm, HMIm and OMIm. This different behavior for the smallest ion pairs, EMIm- Fe_2Cl_7 and - Fe_2Br_7 , is also related to the variation of the anion-cation distance d (X3-NL) (see Tables 2 and 3). We can conclude that the magnetic coupling constants of these ion pairs are influenced by the geometry of the anion, in particular by the distance between both active centers.

Table 5: Angle (degree) formed by Fe-Br-Fe, Fe-Cl-Fe and Al-Cl-Al in NMImY₂X₇ ion pairs, Fe-Fe and Al-Al distances (Å) and J (cm⁻¹) for the isolated anion (J_{ANION}) and the anion within the ion pair (J_{IP}).

| Fe₂Br₇ | Fe-Br-Fe angle | d(Fe···Fe) | J_{ANION} | J_{IP} |
|-------------------------------------|-----------------------|-------------------|--------------------------|-----------------------|
| EMIm | 106.8 | 4.08 | -9.53 | -8.97 |
| BMIm | 110.9 | 4.20 | -11.05 | -10.42 |
| HMIm | 110.7 | 4.20 | -11.08 | -10.46 |
| OMIm | 110.6 | 4.19 | -11.02 | -10.42 |
| Fe₂Cl₇ | Fe-Cl-Fe angle | d(Fe···Fe) | J_{ANION} | J_{IP} |
| EMIm | 106.0 | 3.82 | -7.89 | -7.47 |
| BMIm | 112.2 | 3.97 | -10.49 | -9.86 |
| HMIm | 111.0 | 3.95 | -9.96 | -9.37 |
| OMIm | 112.1 | 3.97 | -10.36 | -9.76 |
| Al₂Cl₇ | Al-Cl-Al angle | d(Al···Al) | | |
| EMIm | 113.7 | 3.86 | | |
| BMIm | 113.8 | 3.87 | | |
| HMIm | 113.6 | 3.86 | | |
| OMIm | 114.7 | 3.89 | | |

b) Physicochemical properties

Density and viscosity are two important physical properties for the industrial application of ILs and the scale-up from the laboratory to the industrial level of a desired process, and thus, an accurate knowledge of these properties is desirable. Density ρ is easy to measure experimentally and has a clear relationship with the size and structure of the ion pairs. Viscosity η , which is larger in ILs than in most common organic solvents, is directly related with the relative diffusion of ionic species, depends on the nature and combinations of cation and anion and is difficult to measure in these systems. Densities and viscosities of NMIm-YX₄ and NMIm-Y₂X₇ ILs have been computed using the COSMO-RS method [63] at 298.15K, using the optimized geometries of each ion pair reported in the above subsection. COSMO method takes as starting point the structure of the isolated molecule (ion pair) and uses it to build a cavity around the molecule. The cavity surface is discretized and a polarization charge is assigned to each segment of the surface. From this assignment, the σ -profile is constructed, from which a statistic treatment yields estimations of physicochemical properties. The Figure 5 shows the charge densities and the σ -profile for BMImFe₂Cl₇. Blue color illustrates positively charge segments (anion) while red color illustrates negatively charged segments (cation). The surfaces and σ -profiles for all the other compounds can be found in the Figures S4 and S5 in the SI.

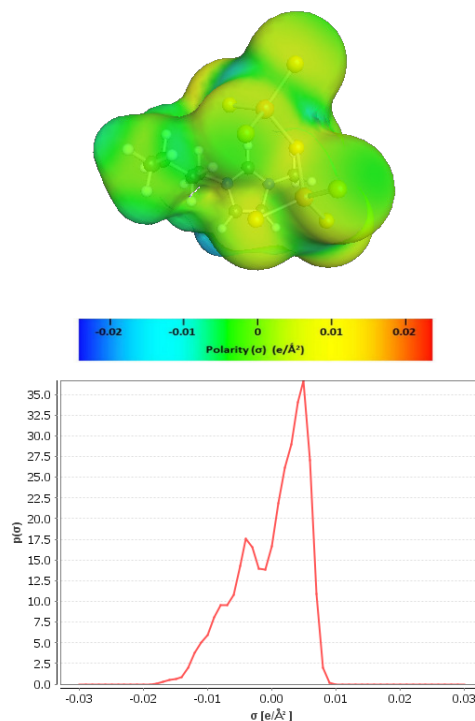


Figure 5: Charge density and σ -profile for BMImFe₂Cl₇

As it can be seen in figure 6, densities decrease with the length of the alkyl chain for the six series of ILs, and the behavior is similar to that of ion pairs containing Cl⁻ as anion, reported in a previous work [46]. In MILs series (NMIm-FeCl₄ and NMIm-FeBr₄), densities of Br derivatives are between 0.5 and 1.0 g/cm³ higher than those of the corresponding Cl-MILs. Theoretical densities for NMIm-FeCl₄ and NMIm-AlCl₄ have similar values, as it can be expected, since this property largely depends on the molecular size. The curves of densities for NMIm-Y₂X₇, depicted in the right plate of Figure 6, run parallel to those of NMIm-YX₄ ILs. However, in these series of compounds densities of Br-MILs are ca. 20 % higher than those of Cl-MILs.

Viscosities of ILs, computed with COSMO-RS, are displayed in Figure 7. It can be observed that their values increase with the chain length for the six sets of ion pairs. Nevertheless, viscosities of NMIm-YX₄ and NMIm-Y₂X₇ ILs lie in the ranges from 25 to 165 cP (left size of Fig. 7), and 45 to 600 cP (right size of Fig.7), respectively. On the other hand, values obtained for NMIm-YCl₄ ILs are almost equal in all cases, and slight differences are observed in NMIm-Y₂Cl₇ ILs. Viscosities are always higher for Br-MILs than for Cl-MILs, in both series of ion pairs NMImFe₂X₇ and NMIm-FeX₄. This behavior is due to the higher polarizability of Br⁻ with respect to Cl⁻ MILs.

Table 6: Estimated density (g/cm^3) and viscosity (cP) in comparison to experimental data for NMIm-FeBr₄ and NMIm-FeCl₄ a (Ref. [32]), b (Ref. [33]), c (Ref. [25]) and d (Ref.[66]).

| | Density | | Viscosity | |
|-----------------------------|---|------------|-----------------------------------|------------|
| | Exp. | Calculated | Exp. ^a | Calculated |
| EMImFeCl₄ | 1.42 ^a | 1.55 | 18 ^a | 27 |
| BMImFeCl₄ | 1.38 ^a , 1.39 ^b 1.37 ^c | 1.46 | 34 ^a , 30 ^d | 38 |
| HMImFeCl₄ | 1.33 ^a | 1.39 | 45 ^a | 61 |
| OMImFeCl₄ | 1.28 ^a | 1.32 | 77 ^a | 104 |
| EMImFeBr₄ | | 2.26 | | 45 |
| BMImFeBr₄ | 1.98 ^a | 2.09 | 62 ^a | 60 |
| HMImFeBr₄ | 1.86 ^a | 1.94 | 95 ^a | 99 |
| OMImFeBr₄ | 1.74 ^a | 1.83 | 121 ^a | 163 |

This increase of polarization in the anion produces stronger cohesive forces and polar molecular interactions. This fact determines the viscosity η , which increases in general with both anion and cation sizes.

Theoretical densities and viscosities estimated using COSMO-RS methodology have been compared to the available experimental data of NMIm-FeCl₄ and NMIm-FeBr₄ MILs (except for EMIm-FeBr₄), reported by Yoshida and Saito [32]. All values reported by these authors are collected in Table 6 besides other experimental data for BMImFeCl₄. Experimental densities decrease as the alkyl chain grows in fairly good agreement with our theoretical calculations (see Figure 6), which show a slight overestimation, in general lower than 5% for OMIm-ILs. The situation is very different in case of viscosity, where experimental references are not as sound as in case of density, because of the great dispersion in the values reported in the literature [64, 65]. These discrepancies can be attributed to the differences in experimental procedures and to the high influence of sample impurities (mostly water) in the results. It has been previously reported that the viscosities predicted using COSMO-RS are usually highly overestimated [46]. However, in the present work the reported values are, in general, closer to experiments than usual (same order of magnitude) with a slight overestimation. The values for both OMIm-FeX₄ MILs exhibit higher absolute errors than in the remainder MILs. The overall good agreement between theoretical densities and viscosities computed for NMIm-YX₄ MILs in this work using COSMO-RS with experimental data suggests that this method can be a suitable starting point for the estimation of these properties in NMIm-Y₂X₇ MLIs when experimental values are lacking or not reliable.

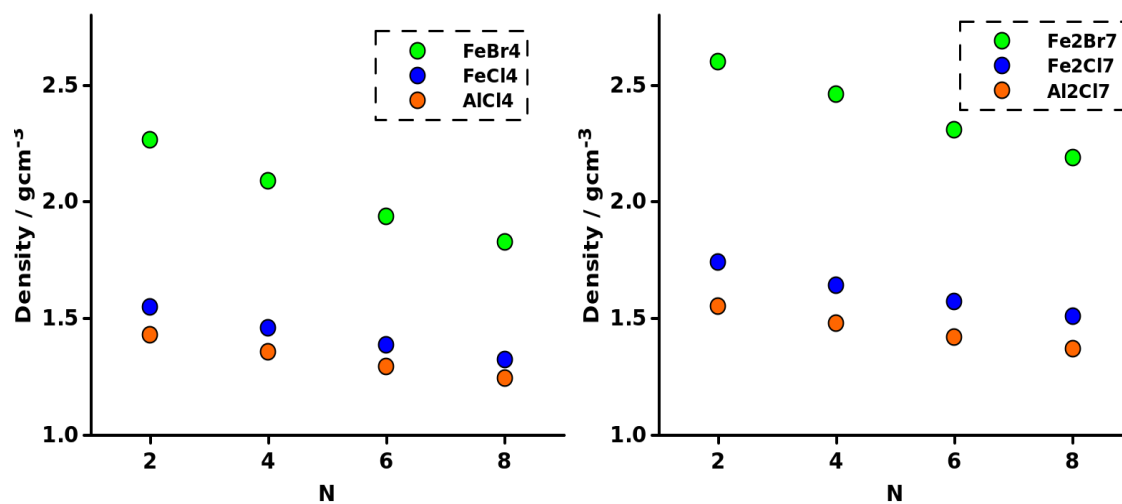


Figure 6: Density estimated with COSMO-RS method for NMIImYX₄ and NMIImY₂X₇ ion pairs

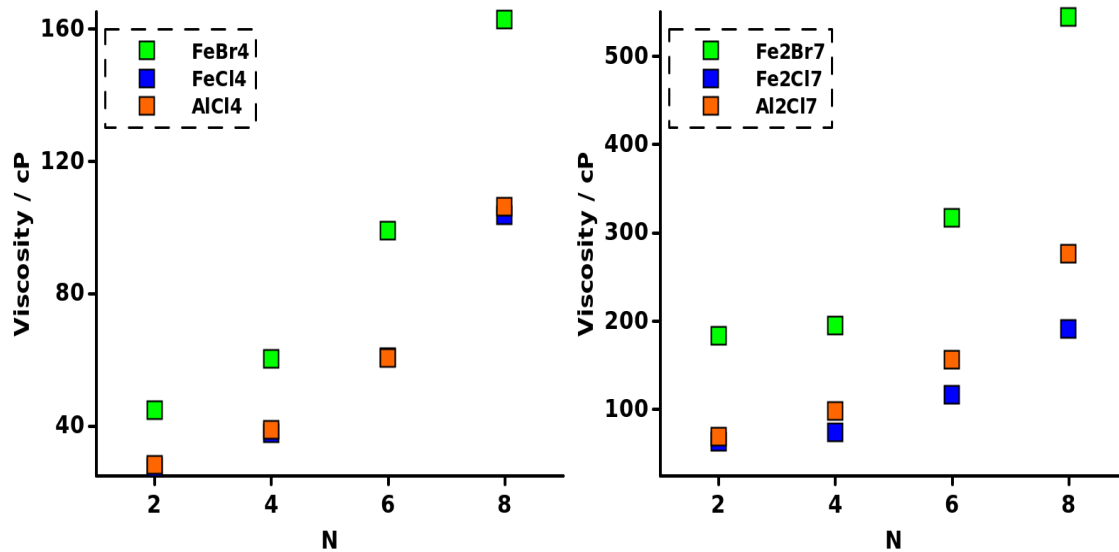


Figure 7: Viscosity estimated with COSMO-RS method for NMIImYX₄ and NMIImY₂X₇ ion pairs

4. Conclusions

DFT calculations have been carried for 24 MILs which result from the combination of 1-N-alkyl-3-methylimidazolium (NMI) cations with FeCl_4 , FeBr_4 , Fe_2Cl_7 and Fe_2Br_7 anions. The dependence of properties such as energies or dipole moments, on the chain length has been analyzed taking into account the molecular structures and the size of the cation for optimized ion pairs. Comparisons with two similar non-magnetic families of ILs containing Al (AlCl_4 and Al_2Cl_7) have been carried out. The interaction between the Fe atoms for Fe_2X_7 MILs show changes on ion pairs geometries and, consequently, modifies the interaction energies and the dipole moments of the smaller ion pairs. Magnetic coupling constants have been calculated and related with the geometries of the $-\text{Y}_2\text{X}_7$ ion pairs.

Some physical properties were systematically analyzed in the framework of the COSMO-RS approach, in particular densities and viscosities, which showed good agreement with the experimental values. It has been observed that enlargement of chain increases viscosity and decreases density. The reduction in fluidity which manifests itself in an increase of viscosity, greater for $-\text{Y}_2\text{X}_7$ ILs than $-\text{YX}_4$, can be attributed to the interaction between the chains and, to a larger extent, to the size of the halogen (Br vs Cl). On the other hand, the dependence of this property with the size of the metal (Al vs Fe) in the anions is less marked, and the presence of magnetic centers in the ILs has no significant influence.

Supporting Information

Optimized structures, interaction energies without BSSE correction, additional AIM parameters and COSMO surfaces and σ -profiles for all ion pairs are available in Supporting Information.

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