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PERSPECTIVE

## Interface properties of ionic liquids containing metal ions: features and potentialities

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Interfaces and surfaces are the regions where important events happen: catalysis, molecular recognition, charge transfer, polymerization, and many other critical processes take place at the boundary between one medium and another. In this article we discuss the interface (liquid/air) properties of ionic liquids (ILs) containing dissolved metal ions with the aim to show the possibility to use metal salts to transform ILs and their surfaces into engineered liquid supports to apply in material sciences, separation procedures or to use as optical devices.

Room-temperature ionic liquids (ILs) are a relatively recent class of liquids composed purely of ions with many potentialities for applications such as synthesis, (bio)catalysis, separation processes, electrochemistry as well as in material sciences and for the development of new electrical and electrochemical devices.<sup>1</sup> ILs are normally composed of an organic cation and a monoatomic or polyatomic anion. They are characterized by very low vapor pressure, high thermal and electrochemical stability, good electrical and ionic conductivity. The practically infinite possibilities to modify the anion and the cation, also introducing specific function groups on both ions, make them widely tuneable. In this article, we examine the properties and the possible applications of metal containing ionic liquids with a special attention to their surface properties.

### Metal containing ILs

ILs with optimized properties may be designed for specific applications. The physico-chemical properties (density, viscosity, conductivity, hydrophobicity or hydrophilicity, Lewis or Brønsted acidity or basicity and so on) and the biological properties can be modified and modulated through the choice of the respective cation and anion and the ion combination.<sup>2</sup> Metal-containing ILs represent a promising sub-class of charged liquids which combine the properties of ILs with magnetic, photophysical/optical or catalytic properties of the incorporated metal salts. ILs that contain palladium, ruthenium, platinum, gold, aluminium (but also iron, nickel, zinc or copper) have been used with success in catalysis.<sup>3</sup> Solutions of f-element compounds in ILs are also considered promising as soft luminescent materials for use in photochemistry and spectroscopy, besides the fact that

their Lewis acidity makes them potential catalysts to apply in synthesis.<sup>4</sup> A further promising possibility is to use ILs that contain metals to prepare new electrical dispositives or sensors. Finally, metals can be electrodeposited from mixtures of metal salts in ILs to obtain new materials having specific characteristics (thin films, nanostructures and others).<sup>5,6</sup>

Both IL components (anion and cation) can act as complexing agents for the metal in different oxidation states; often generating new chemical species. The complexation ability of positively charged species of the metal ( $M^{+n}$ ) by IL cations normally requires the presence of specific functional groups (such as, CN, CH=CH<sub>2</sub>, OH, OR) which interact with the metal cation in a way not very different from that of analogously functionalized molecular solvents. On the other hand, the coordination ability of some anions (chloride, bromide, thiocyanates and so on) is able to transform the metal cations in new “stable” negatively charged species.

Consequently, the structure of ionic liquids affects the solubility of the metal salts and their “availability”, hence determining their chemical behavior. In acidic 1-butyl-3-imidazolium chloroaluminates ([bmim][AlCl<sub>4</sub>] + [bmim][Al<sub>2</sub>Cl<sub>7</sub>]), obtained by addition an excess of AlCl<sub>3</sub> to ([bmim]Cl), the reduction of Ni<sup>2+</sup> occurs easily, whereas under basic conditions (*i.e.* in the presence of an excess of chloride ions) Ni<sup>2+</sup> forms a chlorocomplex ([NiCl<sub>4</sub>]<sup>2-</sup>) which cannot be reduced within the electrochemical potential window.<sup>7</sup>

ILs bearing a nitrile group on the cation alkyl chain(s) are able to facilitate the solubilization of Pd<sup>2+</sup> salts, *via* coordination of the metal cation with the nitrile group. However, when the IL counteranion is chloride, Pd<sup>2+</sup> forms a chlorocomplex, [PdCl<sub>4</sub>]<sup>2-</sup>, which is less catalytically active or, more probably, less prone to give the real catalytic active species, *i.e.* palladium nanoparticles.<sup>8</sup>

It is to note that IL structure is able to affect not only the solubility and chemical behavior of the added metal salt but it can affect also the structural features of the solid materials obtained by chemical transformation of the dissolved salts. The highly structured anions and cations networks, characterizing

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most of the ILs,<sup>9</sup> may induce a structural directionality (IL effect) in the new materials generated in these organized environments.<sup>10</sup> Moreover, the high degree of self-organisation characterizing the liquid state of these media may be an “entropic driver” able to favour a spontaneous, well defined and extended ordering of nanoscale structures. The large and flexible organic ions, usually bearing delocalized electrostatic charges and with nonpolar side chains, determine a high degree of structural and dynamic heterogeneity that characterizes both the liquid bulk and the interfaces (IL/solid, IL/air, IL/other liquids). The highly cohesive charged groups tend to segregate from the side chains if these are sufficiently long, resulting in liquids with a heterogeneous structure at the nanometre scale that offer both ionic and non-polar environments inside the IL and at the surface.

Recently, it has shown that the preferential solubility of the nanomaterials precursors in the polar or non-polar domains characterizing ILs may affect nanomaterials features.<sup>11</sup> One approach to control size and shape of the product is consequently the ability to modulate the volumes of the polar/non-polar domains in the ionic liquid.

## IL surfaces

The surface properties of ionic liquids, such as surface tension, water absorption ability, mass transport characteristic and surface reactivity, are strongly dependent upon the near surface region composition. The presence of different ions is a situation that can strongly affect surface composition. In the case of metal containing ILs, both ions that compose the IL and the metal ions dissolved in it are responsible of locally unbalanced electrical forces and may cause the chemical composition of the near-surface region and the molecular arrangement at the surface to be very different than those of the bulk.

These phenomena are important in order to fully understand the properties of ILs at the molecular level and exploit the mixtures of transition metals and ionic liquids. Therefore, the accurate chemical and structural characterization of the surface plays a key role in explaining their macroscopic properties.

### Surface characterization of ILs

Investigating IL surface properties presents peculiar challenges and opportunities. It is well known that, in order to obtain a high surface sensitivity, surface probes usually use charged particles, such as ions or electrons. The propagation of an ion or electron beam requires high vacuum conditions, also needed to maintain solid surfaces clean from atmospheric contaminants. The need of ultra high vacuum (UHV) environments precludes the study of most liquids which, normally, would simply evaporate in vacuum. But most ILs do not present this problem since their vapour pressure is negligible at room temperature. Therefore, UHV-based techniques can be profitably employed for studying their surface chemical structure and properties as evidenced by Steinrück's work.<sup>12</sup> As a consequence, during the past few years a number of surface science techniques have been applied to study ILs, such as X-ray photoelectron spectroscopy (XPS),<sup>13–16</sup> UV photoelectron spectroscopy (UPS),<sup>17,18</sup> direct recoil spectroscopy (DRS),<sup>19,20</sup> inverse photoelectron spectroscopy (IPES),<sup>21</sup> X-ray absorption spectroscopy (NEXAFS)<sup>22</sup> and time-of-flight secondary ions mass spectroscopy (TOF-SIMS).<sup>23</sup>

Since the species present in ionic liquids are highly mobile in comparison to solid ionic compounds, the surfaces show phenomena such as surface segregation, preferential orientation, and others in much larger extent than crystalline or amorphous solids. An example was provided by one of the first studies about the surface properties of a commercially available ionic liquid. The ILs examined proved to be contaminated by silicon that was probably originated by silicon containing grease or a silicon cork used to seal the glassware used for the sample preparation. The level of bulk Si-contamination was in the range of ppm or below, since it could not be detected by means of bulk analysis. Nevertheless, the XPS signal due to Si core level transitions was clearly detectable, evidencing strong surface segregation effects.<sup>24</sup> Furthermore, since ions in an IL are relatively free to move in and out from the surface, the conventional cleaning procedure such as argon sputtering does not permanently remove contaminants which are present in the bulk, as recently demonstrated by Kolbeck *et al.*<sup>25</sup> Apart from these difficulties, the possibilities opened by the investigation of physico-chemical properties of ILs are remarkably interesting. An idea of these possibilities can be found in the review works of Lovelock *et al.*<sup>26</sup> and Torimoto *et al.*<sup>27</sup>

If the surface of pure ILs presents such peculiar characteristics, it is reasonable to expect that great care and effort should be dedicated to the study of systems constituted by metal ions dissolved in ionic liquids. Because of the larger number of chemical species present in such ionic mixtures, the chemical and structural differences between bulk and surface can be subtle and, perhaps, tunable to some extent. The presence of complexation equilibria may lead to the simultaneous presence of several chemical species; either ionic or neutral. These species would present different affinity toward the liquid/gas interface. It is to be expected that slight variations in the mixture chemical composition as well as different ionic liquids/metal ratios would change the chemical species present as well as their molar ratio. Both these effects will dramatically result in changes in surface composition and properties.

Therefore, the atomic scale investigation of surface properties plays a key role in understanding the properties of such complex chemical systems.

This type of studies is still in its infancy and just a few preliminary investigations have been carried out. Nevertheless, X-ray photoelectron spectroscopy (XPS), also denoted as electron spectroscopy for chemical analysis (ESCA), proved to be particularly suited for this type of investigation.

Since the core binding energies are sensitive to the chemical state (*e.g.*, oxidation state) of the atoms, the evaluation of the so-called “chemical shift” generates information on the charge state of the chemical species present in the sample surface region. Normally, the binding energies of atoms in non-equivalent chemical environments (*e.g.* Fe<sup>2+</sup> and Fe<sup>3+</sup> species) are large enough to allow peak separation by deconvolution and the quantification of the atomic ratio of the two non-equivalent species. Not surprisingly, the surface ratio can be very different than it is in the bulk. In such a way, surface segregation phenomena can be easily evidenced providing invaluable information for new and very interesting applicative purposes such as multiphase catalysis.

Since XPS surface sensitivity comes from the low inelastic mean free path of the photo-generated electrons, assuming

that the surface is flat, it is possible to vary the analyzed depth from a few nm to include almost exclusively the topmost atomic layer (depending also on the electron energy and the density of the ionic liquid). This technique is called angle resolved XPS (AR-XPS) and it has been used to detect contaminants in pure ILs<sup>14,25</sup> or to disclose the surface orientation of asymmetric ILs.<sup>28,29</sup> Recently, the technique has been applied to copper ions/ILs solution systems obtained dissolving metal salts in ILs<sup>30</sup> or generating ions “*in situ*” via electrooxidation.<sup>31</sup> Chiappe *et al.*<sup>32</sup> observe the XPS signal of metal ions dissolved in ILs, providing information about the nature of metal ion coordination sphere. A large, very stable coordination sphere keeps the metal ion far away from the surface region, decreasing the probability that the electrons photo-generated by these ions can escape from the liquid phase, especially for high take off angles (grazing angle). On the contrary, metal ions with small or no coordination sphere are not affected by the shielding and are physically present in the topmost layer of the surface region. As a consequence, in this case the XPS signal result is relatively unaffected by the take off angle. Since it is reasonable to think that differently charged ions would be characterised by different coordination spheres, AR-XPS would be useful in providing information about such behaviour.

Another future direction to get an atomic scale overview of the surface of metal ions–ILs mixtures can be based on particle scattering based techniques. Examples of these methods are Metastable Impact Electron Spectroscopy (MEIS), Rutherford backscattering (RB) and Low Energy Ion Scattering (LEIS). All these techniques are based on the detection of neutral or electrically charged particles bouncing back after impacting on the liquid/vacuum interface. The low probability for the probe particles to scatter from atoms lying beneath the surface determines the inherent surface sensitivity of the method. Even though these techniques are well known and largely applied to the study of solid surfaces, few studies have been performed on pure ILs (RBS,<sup>33</sup> MIES<sup>13,34</sup> and LEIS<sup>35</sup>) and none on metal ions-bearing ILs. Nevertheless, the use of such techniques would provide profitable information about the nature of the atoms present in the topmost layer except their chemical status.

### Air/ionic liquid interface properties of metal containing ILs and development of advanced technologies

Starting from the fact that the composition of ionic mixtures arising from dissolution of metal salts in ILs can be significantly different in bulk and at the surface, the interface properties of these systems, which are always tunable on changing IL structure, can be used to develop new technologies to apply in catalysis, separation processes or materials science.

Molecular layering, orientation and enrichment at the IL/air (gas) surface play an important role (together with other bulk and solid phase/IL surface properties) in the ILs chemistry on supported materials (supported IL phase, SILP).<sup>36–38</sup> Solid catalysts containing metal salts with an ionic liquid layer (SCILL),<sup>39</sup> which combine the advantages of ILs media with

solid support matrices, enable the application of fixed-bed technologies for in continuous-flow gas-phase reactions of volatile reagents, or of non-volatile reagents using proper media as mobile phase, such as supercritical CO<sub>2</sub>.<sup>40</sup>

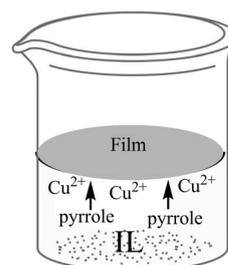
Analogously, the same interfacial properties probably affect the performance of separation processes when ILs are used as membranes in gas-separation processes,<sup>41</sup> or as surface-bonded stationary phases in chromatography separations.<sup>42</sup> Related to the specific case of the use of metal containing ILs in gas separation processes, for example, it has been recently shown that when ILs are doped with metals CO<sub>2</sub> sorption can be increased; metal containing ILs might find important applications in this field.<sup>43</sup>

Nevertheless, plasma–IL interfaces are important for the creation of various kinds of metal nanoparticles by the reduction of metal salts dissolved in the ionic media.<sup>44</sup>

In materials science, recently the air/ionic liquid interface properties of an IL (1-ethyl-3-methylimidazolium tetrafluoroborate, [emim][BF<sub>4</sub>]) containing CuCl<sub>2</sub> as a source of Cu<sup>+2</sup> have been used<sup>45</sup> for the one-pot fabrication of a uniform, large-area polypyrrole film with controlled thickness through an oxypolymerization. In this process, the addition of BriJ-35 is able to increase film uniformity, decreasing the IL surface tension, whereas the metal catalyst concentration determines the smoothness degree of the two polymer faces. Although the side facing air was always smooth, the opposite side, the one facing the solution, showed a roughness that was found to depend on the copper concentration (Fig. 1).

Unfortunately, in this study only one IL ([emim][BF<sub>4</sub>]) has been examined as ionic medium, with the added disadvantage that it is prone to rapid decomposition into the toxic hydrofluoride.<sup>46</sup> Furthermore, in this study the copper concentration at the surface has been modified by changing the concentration of the dissolved salt (CuCl<sub>2</sub>), without any consideration of surface enrichment phenomena. However, it is possible to hypothesize that the important parameters affecting this process (*i.e.* medium viscosity, surface tension, the catalyst concentration at air/IL surface and pyrrole concentration at the surface) may be modified also by changing the IL cation and anion and consequently the ionic composition at the surface.

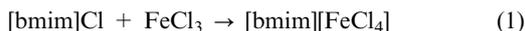
Design of proper metal containing ILs may represent a versatile pool of customizable surfaces for the fabrication of free-standing conducting polymers, nanomaterials as well as composites<sup>47</sup> containing conducting polymers (polypyrrole) and inorganic nanoparticles.



**Fig. 1** Use of the IL/air interface to prepare uniform, large-area films with controlled thickness.

## Air/ionic liquid interface properties of paramagnetic metal ions in ionic liquids

Among metal containing ILs, those including paramagnetic ions are an intriguing class of ionic fluids which add a magnetic moment to the remarkable physical and chemical properties of the ionic media. The first example of a paramagnetic IL reported in the literature<sup>48</sup> is 1-butyl-1-methylimidazolium tetrachloroferrate, [bmim][FeCl<sub>4</sub>], which has been prepared by addition of an equimolar amount of FeCl<sub>3</sub> to [bmim]Cl, eqn (1):



This IL is characterized by a magnetic mass susceptibility  $\chi_g$  of  $40.6 \times 10^{-6} \text{ emu g}^{-1}$  corresponding to a molar susceptibility  $\chi_{\text{mol}}$  of  $0.0137(7) \text{ emu mol}^{-1}$ . The effective magnetic moment of  $\mu_{\text{eff}} = 5.8 \mu_B$  is in accordance with a high-spin  $S = 5/2$  state.

1-Ethyl-3-methylimidazolium tetrachloroferrate, [emim][FeCl<sub>4</sub>], has been also shown<sup>49</sup> to be a superparamagnet with a global spin freezing temperature of 3.8 K. Below this temperature, [emim][FeCl<sub>4</sub>] is a ferromagnet approximant, meaning that a large part of the spins order, although some spin clusters are present.

Starting from 2004, several other Fe-containing ILs have been prepared and characterized:<sup>50</sup> all present similar magnetic moments and show a strong response to external magnetic fields.

Certainly, tetrachloroferrate based-ILs show some of the fundamental features of a paramagnetic ionic liquid:

- Fe(III) is a d<sup>5</sup> ion, the maximum possible number of unpaired electrons for a d transition metal.
- the chloride is a low field ligand leading to a high spin complex.
- the charge of the resulting coordination complex is one. The complex formation practically requires an equimolar amount of ionic liquid and FeCl<sub>3</sub>. The anion molar fraction, and thus of the paramagnetic center, is 0.5.
- the anion of the starting ionic liquid and the anion of the added salt coincide leading to a pure ionic liquid rather than a more complex mixture.

Nevertheless, if we are interested in exploiting the magnetic properties of these ionic liquids, it is imperative to try to maximize the volumetric magnetic moment  $M$ . This quantity is proportional to the numerical density of paramagnetic centers times the effective magnetic moment,  $\mu_{\text{eff}}$ , of the paramagnetic center.  $\mu_{\text{eff}}$  is in a first approximation proportional to the number of unpaired electrons (this approximation does not hold for lanthanides that show also a contribution from orbital angular momentum).<sup>51</sup> However, all these parameters are affected by the structural features summarized in the first three points of the above reported list. Halides lie on the left side of the ligand spectrochemical series along with thiocyanate and sulfur; these ligands have to be preferred. Ions with a high number of unpaired electrons can be found in the right part of the d and f transition series. Some possible metals and oxidation states<sup>52</sup> with  $n \geq 5$  are listed in Table 1 (we exclude unstable oxidation states). Finally, considering that most of the IL cations bear a unit charge, the metal containing anion should have a unitary negative charge.

Certainly, these concepts are valid in the absence of chemical constraints; the necessity to use metals having specific

**Table 1** Some possible paramagnetic ion complexes

M(N)	Electronic state	Coordination number	Example anion
Mn(II)	d <sup>5</sup>	2, 4, 5	[MnCl <sub>4</sub> ] <sup>2-</sup>
Fe(III)	d <sup>5</sup>	3, 4, 5, 6	[FeCl <sub>4</sub> ] <sup>-</sup>
Ru(III), Os(III)	d <sup>5</sup>	4, 6	[RuCl <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>-</sup>
Rh(IV), Ir(IV)	d <sup>5</sup>	6	[IrCl <sub>6</sub> ] <sup>2-</sup>
Pt(V)	d <sup>5</sup>	6	[PtF <sub>6</sub> ] <sup>-</sup>
Eu(III)	f <sup>6</sup>	6	[EuCl <sub>6</sub> ] <sup>3-</sup>
Gd(III)	f <sup>7</sup>	6	[GdCl <sub>6</sub> ] <sup>3-</sup>

catalytic properties may require the use of different ligands and the formation of complexes bearing a non-unitary charge. Nevertheless, on the basis of the requirements listed above, Fe(III), present in the anion of the first synthesized paramagnetic IL, shows nearly optimal properties. Furthermore, Fe(III) salts are non-toxic, non-expensive and easily to use (air and water stable). The alternative of using lanthanides<sup>53</sup> to obtain paramagnetic ILs may have a limit in the triple negative charge characterizing these complexes. In any case, however, it is the chemical nature of cations and ligands that determines the density and other physical and chemical properties of the resulting ionic liquids. Thus, a rational design of paramagnetic ILs, which is only slightly more constrained than that of a common IL, may overcome some problems and limits arising from the choice of a specific metal or ligand.

In an actual test, dysprosium ILs ([C<sub>6</sub>mim]<sub>3</sub>[Dy(SCN)<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub>], [C<sub>6</sub>mim]<sub>4</sub>[Dy(SCN)<sub>7</sub>(H<sub>2</sub>O)<sub>2</sub>], [C<sub>6</sub>mim]<sub>5</sub>[Dy(SCN)<sub>8</sub>]) with strong luminescence and response to magnetic fields ( $\mu_{\text{eff}} = 10.48 \mu_B$ ) were synthesized<sup>54</sup> from [C<sub>6</sub>mim]SCN, KSCN and Dy(ClO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O, whereas [C<sub>12</sub>mim]<sub>3</sub>[DyBr<sub>6</sub>], with an effective magnetic moment of  $\mu_{\text{eff}} = 9.6 \mu_B$ , was prepared<sup>55</sup> by addition of DyBr<sub>3</sub> to [C<sub>12</sub>mim]Br. In these systems, the high  $\mu_{\text{eff}}$  of dysprosium compensates the low molar fraction of the paramagnetic center due to the multiple charged anions.

It is to note that the paramagnetic chloroferrate ionic liquids prepared accordingly to eqn (1) (*i.e.* by addition of an equimolar amount of inorganic chloride to the proper chloride based IL) can exhibit a residue solvation capacity towards the inorganic salt generating ILs characterized by a different anion speciation.

A series of FeCl<sub>3</sub>/[bmim]Cl ILs have been recently prepared<sup>56</sup> by adding different amounts of FeCl<sub>3</sub> to the pure ionic liquids. Information on their physico-chemical properties, at the macro- and microscopic level, have been obtained combining IR, Raman, freeze-fracture transmission electron spray microscopy (FF-TEM) with thermodynamic properties. These measurements have shown that when FeCl<sub>3</sub> is in excess, [Fe<sub>2</sub>Cl<sub>7</sub>]<sup>-</sup> begins to appear (eqn (2));



Nevertheless, nanostructures have been detected in these systems using biological imaging. In particular, it has been shown that these nanostructures show a thermal variability and a dependence on the mole ratio of FeCl<sub>3</sub>/[bmim]Cl: probably, they are affected by the IL composition which determines the strength of the inter-ionic interactions. In FeCl<sub>3</sub>/[bmim]Cl ILs the inter-ionic interactions follows the order  $1/1.5 > 1/1 < 1.5/1$  as a consequence of the formation of [FeCl<sub>4</sub>]<sup>-</sup> and [Fe<sub>2</sub>Cl<sub>7</sub>]<sup>-</sup>. Unfortunately, the properties of “overloaded” paramagnetic ILs have not been yet studied in

detail and only few data have been reported<sup>57</sup> about the surface features of [FeCl<sub>4</sub>]-based ILs.

The physical properties of magnetic liquids are the subject of an interesting book *Ferrohydrodynamics* by Ronald E. Rosensweig.<sup>58</sup> The book, which has been written before the “ionic liquids age”, takes into account only two kinds of magnetic liquids: ferrofluids and paramagnetic salts. The first class is represented by multi-phase liquids; normally, colloidal dispersions of small paramagnetic or ferromagnetic particles in organic solvents. The magnetic moments for unit of volume of these materials are of some degrees of magnitude larger than the values obtainable with paramagnetic ILs. However, they are subjected to the classical problems of colloids. In particular, there are limits to the strength of the magnetic field that can be applied without affecting the colloidal equilibrium. This issue does not affect paramagnetic ILs. The other category of magnetic liquids is represented<sup>59</sup> by paramagnetic aqueous or alcoholic solutions of rare earth salts. The solubility of these salts in these media is limited and the atomic concentration of paramagnetic centers cannot reach the value of 1 : 1 solvent–paramagnetic salt. Thus, paramagnetic ILs can have properties which do not overlap with previously existing magnetic liquids, so extending the potentialities of these systems.

The force that acts on a volume  $V$  of a paramagnetic liquid embedded in a magnetic field is:

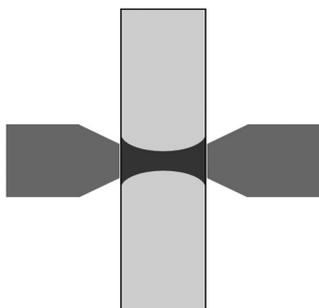
$$\mathbf{F} = \mu_0 V (\mathbf{M} \times \nabla) \mathbf{H}_0$$

where  $\mathbf{M}$  is the magnetization vector and  $\mu_0 \mathbf{M}$  represents the magnetic moment for the volume unit. When a magnetic field is applied to a paramagnetic IL or to another magnetic liquid, the shape of the paramagnetic IL changes until it reaches the equilibrium.

A similar effect may be obtained also applying to any liquid a centrifugal force (*e.g.* rotating the container). A simple example, reported in the Rosensweig book,<sup>58</sup> is illustrated in Fig. 2.

Magnets of different strength and shape can be therefore used to modulate the shape of paramagnetic IL surfaces and the surface/volume ratio (*e.g.* for obtain thin meniscus of paramagnetic ILs) with possible applications in membranes based on the use of ILs.

On the other hand, droplets of paramagnetic ILs in immiscible diamagnetic liquids can be manipulated by strong permanent magnets like Nd–Fe–B magnets<sup>60</sup> or electromagnets. Considering that some of these systems present also Lewis acidity, paramagnetic



**Fig. 2** Approximate shape of a magnetic liquid droplet in a capillary under the field of two pencil tip shaped magnets. Adapted from ref. 58.

IL droplets can be used as solvents/catalysts for reactions occurring inside the droplets or on their surface with the advantage that, at the end of the process, the droplets can always be recovered using an appropriate magnet. These features may be used for the development of in-continuous processes and could be applied for emerging technologies, such as microreactors.

Paramagnetic ILs (1-alkyl-3-methylimidazolium tetrachloroferrate, [Rmim][FeCl<sub>4</sub>]) and their bulk properties have been already used to synthesize nanostructured conducting polymers starting from pyrrole and methylpyrrole;<sup>61</sup> the alkyl side chain length and/or the application of an external magnetic field are able to affect the nanostructure of the resulting polymer, modifying the local structure of the IL that serves as a template for highly organized polymers. Nevertheless, more recently, a polypyrrole/AgCl nanocomposite has been successfully synthesized in [bmim][FeCl<sub>4</sub>] using the redox reaction of the IL and pyrrole monomer in the presence of AgNO<sub>3</sub> at the interface between water and IL.<sup>47</sup> Probably, in this case the reaction between Cl<sup>−</sup> of [FeCl<sub>4</sub>]<sup>−</sup> (present in the IL phase) with Ag<sup>+</sup> of AgNO<sub>3</sub> (present in the aqueous phase) has determined the controlled formation of AgCl at the interface favoring the synthesis of nanocomposites. In the previously discussed examples, instead, a determining role to favor the formation of organized nanopolymers has been played by the bulk self-assembled (in the absence of magnetic field) or induced (in the presence of magnetic field) local structures of the IL. However, we cannot exclude that also surface properties and organization could be used to obtain polymer nanostructures or nanocomposites having special features.

Ferrofluids show also other peculiarities in the presence of strong magnetic fields, in particular they are characterized by instabilities which could be used to develop new technologies and devices. A spectacular example is the so-called spike instability.<sup>62,63</sup> If a drop of a ferrofluid is placed on a horizontal surface, such as glass, and a magnetic field is applied in the vertical direction (*e.g.* placing a Nd–Fe–B magnet under the drop on the other side of the glass) the shape of the drop changes and the drop begins to develop spikes and other complex shapes. The physical origin of this kind of instability is related to the fact that a portion of liquid tends to assume the shape that will minimize energy. Gravity, surface tension, and, in this case, magnetic field interplay to determine the shape. The applied magnetic field tends to align the magnetic dipoles inside the magnetic liquid leading to a repulsive interaction between them. This repulsive force works against gravity and surface tension leading to a complex shape.

However, although these phenomena are nice to see and impressive videos can be easily found, for application in chemistry probably another kind of instability is more useful: it is the so-called “labyrinthine instability”.<sup>64,65</sup> When a magnetic liquid is placed together with an immiscible liquid between two vertical glasses, to form a thin layer, the two liquids stratify as shown in Fig. 3, left.

The application of a strong magnetic field, orthogonal to the thin layer of liquids, modifies the separation surface: it assumes a chaotic shape and the two liquids assume a maze-like shape. The amount of the two liquids involved in the maze and the thickness and average length of the maze walls depend on the nature of the liquid and on the strength of the magnetic field.



**Fig. 3** Variation of the separation surface between a paramagnetic liquid (black) and an immiscible diamagnetic liquid (white). The field is normal to the plane of the paper and increases from left to right. The density of the black liquid is greater than those of the white one. Adapted from ref. 58.

The possibility to produce this kind of phenomena using paramagnetic ILs and, eventually the magnitude of the magnetic field that should be applied, has not been yet investigated. However, if possible these phenomena could find application in catalysis, separation procedures and to develop optical devices.

## Conclusions

Ionic Liquids (ILs) which contain metal salts represent a fascinating field that opens up new possibilities in areas such as catalysis and material science. This paper has examined some of their properties with a special view on the behavior of their surfaces and their magnetic properties. It turns out that metal-containing IL surfaces are unique under many respects. In general, ILs are the sole room temperature liquids known to be stable in vacuum. That allows, among other things, the possibility of using a lot of investigation techniques that, so far, could only be used to study solid surfaces. With the knowledge that comes from these studies, it may be possible to use metal salts in order to customize surfaces to be used as membranes for separation procedures, liquid matrices to design proper (nano)materials or as catalytic surfaces. For these applications, ILs have the advantage that the liquid nature of the bulk generates their continuous renewal, unlike the case of conventional heterogeneous materials which are easily poisoned during the catalytic process. Furthermore, it is becoming apparent that the use of paramagnetic metal salts can generate magnetic ionic liquids whose surface behavior is still to be investigated but that could provide new materials for applications in areas such as optical and optoelectronic devices. The Ionic Liquid revolution is just starting.

## Notes and references

- N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123.
- P. Wasserscheid and T. Welton, *Ionic liquids in Synthesis*, Wiley-VCH, Weinheim, 2nd edn, 2008; C. Chiappe and D. Pieraccini, *J. Phys. Org. Chem.*, 2005, **18**, 275.
- T. Welton, *Coord. Chem. Rev.*, 2004, **248**, 2459; J. P. Hallett and T. Welton, *Chem. Rev.*, 2011, **111**, 3508.
- K. Driesen, P. Nockemann and K. Binnemans, *Chem. Phys. Lett.*, 2004, **395**, 306; K. Binnemans, *Chem. Rev.*, 2007, **107**, 2592.
- F. Endres, A. P. Abbott and D. R. MacFarlane, *Electrodeposition from Ionic Liquids*, Wiley-VCH, Weinheim, 2008.
- F. Endres and S. Z. El Abedin, *Phys. Chem. Chem. Phys.*, 2006, **8**, 2101.
- R. J. Gale, B. Gilbert and R. A. Osteryoung, *Inorg. Chem.*, 1979, **18**, 2487.
- Z. Fei, D. Zhao, D. Pieraccini, W. H. Ang, T. J. Geldbach, R. Scopelliti, C. Chiappe and P. J. Dyson, *Organometallics*, 2007, **26**, 1588.

- C. Chiappe, *Monatsh. Chem.*, 2007, **138**, 1035; R. Bini, O. Bortolini, C. Chiappe, D. Pieraccini and T. Siciliano, *J. Phys. Chem. B*, 2007, **111**, 598.
- L. Leclercq and A. Schmitzer, *Supramol. Chem.*, 2009, **21**, 245.
- J. N. A. Canongia Lopes and A. A. H. Padua, *J. Phys. Chem. B*, 2006, **110**, 3330; A. Triolo, O. Russina, H. J. Bleif and E. Di Cola, *J. Phys. Chem. B*, 2007, **111**, 4641; T. Gutel, C. C. Santini, K. Philippot, A. A. H. Padua, K. Pelzer, B. Chaudret, Y. Chauvin and J. M. Basset, *J. Mater. Chem.*, 2009, **19**, 3624; A. S. Pensado and A. A. H. Padua, *Angew. Chem., Int. Ed.*, 2011, **50**, 8683.
- H. P. Steinrück, *Surf. Sci.*, 2010, **604**, 481.
- S. Krischok, M. Eremtchenko, M. Himmerlich, P. Lorenz, J. Uhlig, A. Neumann, R. Otting, W. J. D. Beenken, O. Hoff, S. Bahr, V. Kempter and J. A. Schaefer, *J. Phys. Chem. B*, 2007, **111**, 4801.
- J. M. Gottfried, F. Maier, J. Rossa, D. Gerhard, P. S. Schulz, P. Wasserscheid and H. P. Steinrück, *Z. Phys. Chem.*, 2006, **220**, 1439.
- V. Lockett, R. Sedev, C. Bassell and J. Ralston, *Phys. Chem. Chem. Phys.*, 2008, **10**, 1330.
- N. Paape, W. Wei, A. Bosmann, C. Kolbeck, F. Maier, H. P. Steinrück, P. Wasserscheid and P. S. Schulz, *Chem. Commun.*, 2008, 3867.
- D. Yoshimura, T. Yokoyama, T. Nishi, H. Ishii, R. Ozawa, H. Hamaguchi and K. Seki, *J. Electron Spectrosc. Relat. Phenom.*, 2005, **319**, 144.
- K. Kanai, T. Nishi, T. Iwahashi, Y. Ouchi, K. Seki, Y. Harada and S. Shin, *J. Electron Spectrosc. Relat. Phenom.*, 2009, **174**, 110.
- T. J. Gannon, G. Law, P. R. Watson, A. J. Carmichael and K. R. Seddon, *Langmuir*, 1999, **15**, 8429.
- G. Law, P. R. Watson, A. J. Carmichael and K. R. Seddon, *Phys. Chem. Chem. Phys.*, 2001, **3**, 2879.
- K. Kanai, T. Nishi, T. Iwahashi, Y. Ouchi, K. Seki, Y. Harada and S. Shin, *J. Chem. Phys.*, 2008, **129**, 224507.
- T. Nishi, T. Iwahashi, H. Yamane, Y. Ouchi, K. Kanai and K. Seki, *Chem. Phys. Lett.*, 2008, **455**, 213.
- A. Tolstogouzov, U. Bardi, O. Nishikawa and M. Taniguchi, *Surf. Interface Anal.*, 2008, **40**, 1614.
- E. F. Smith, I. J. Villar-Garcia, D. Briggs and P. Licence, *Chem. Commun.*, 2005, 5633.
- C. Kolbeck, M. Killian, F. Maier, N. Paape, P. Wasserscheid and H. P. Steinrück, *Langmuir*, 2008, **24**, 9500.
- K. R. J. Lovelock, I. J. Villar-Garcia, F. Maier, H. P. Steinrück and P. Licence, *Chem. Rev.*, 2010, **110**, 5158.
- T. Torimoto, T. Tsuda, K. I. Okazaki and S. Kuwabata, *Adv. Mater.*, 2010, **22**, 1196.
- K. R. J. Lovelock, C. Kolbeck, T. Cremer, N. Paape, P. S. Schulz, P. Wasserscheid, F. Maier and H. P. Steinrück, *J. Phys. Chem. B*, 2009, **113**, 2854.
- T. Cremer, M. Killian, J. M. Gottfried, N. Paape, P. Wasserscheid, F. Maier and H. P. Steinrück, *ChemPhysChem*, 2008, **9**, 2185.
- S. Caporali, C. Chiappe, T. Ghilardi, C. S. Pomelli and C. Pinzino, *ChemPhysChem*, DOI: 10.1002/cphc.201100876.
- F. Qiu, A. W. Taylor, S. Men, I. J. Villar-Garcia and P. Licence, *Phys. Chem. Chem. Phys.*, 2010, **12**, 1982.
- C. Chiappe, M. Malvaldi, B. Melai, S. Fantini, S. Caporali and U. Bardi, *Green Chem.*, 2010, **12**, 77.
- K. Nakajima, A. Ohno, M. Suzuki and K. Kimura, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2009, **267**, 605.
- O. Höfft, S. Bahr, M. Himmerlich, S. Krischok, J. A. Schaefer and V. Kempter, *Langmuir*, 2006, **22**, 7120.
- S. Caporali, U. Bardi and A. Lavacchi, *J. Electron Spectrosc. Relat. Phenom.*, 2006, **151**, 4.
- J. Huang, T. Jiang, H. X. Gao, B. X. Han, Z. M. Liu, W. Z. Wu, Y. H. Chang and G. Y. Zhao, *Angew. Chem., Int. Ed.*, 2004, **43**, 1397; A. Riisager, R. Fehrmann, M. Haumann and P. Wasserscheid, *Eur. J. Inorg. Chem.*, 2006, 695.
- M. Ruta, G. Laurency, P. J. Dyson and L. Kiwi-Minsker, *J. Phys. Chem. C*, 2008, **112**, 17814.
- U. Kernchen, B. Etzold, W. Korth and A. Jess, *Chem. Eng. Technol.*, 2007, **30**, 985; H. P. Steinrück, J. Libuda, P. Wasserscheid, T. Cremer, C. Kolbeck, M. Laurin, F. Maier, M. Sobota, P. S. Schulz and M. Stark, *Adv. Mater.*, 2011, **23**, 2571.
- M. Sobota, M. Happel, M. Amende, N. Paape, P. Wasserscheid, M. Laurin and J. Libuda, *Adv. Mater.*, 2011, **23**, 2617.

- 40 C. P. Mehnert, R. A. Cook, N. C. Dispenziere and M. Afeworki, *J. Am. Chem. Soc.*, 2002, **124**, 12932.
- 41 R. D. Noble and D. L. Gin, *J. Membr. Sci.*, 2011, **369**, 1.
- 42 D. Han and K. H. Row, *Molecules*, 2010, **15**, 2405.
- 43 A. E. Rosamilia, *COIL-4, Washington, Abstract 167*, Patent Application WO 2011/011830, 2011.
- 44 T. Kanebo, K. Baba and R. Hatakeyama, *Plasma Phys. Controlled Fusion*, 2009, **51**, 124011; N. Kulbe, O. Höfft, A. Ulbrich, S. Z. El Abedin, S. Krischok, J. Janek, M. Pölleth and F. Endres, *Plasma Processes Polym.*, 2011, **8**, 32.
- 45 D. Wang, Y. X. Li, Z. Shi, H.-L. Qin, L. Wang, X.-F. Pei and J. Jin, *Langmuir*, 2010, **26**, 14405.
- 46 M. G. Freire, C. M. S. S. Neves, I. M. Marrucho, J. A. P. Coutinho and A. M. Fernandes, *J. Phys. Chem. A*, 2010, **114**, 3744.
- 47 Y. Wei, Y. Zhao, L. Li, X. Yang, X. Yu and G. Yan, *Polym. Adv. Technol.*, 2010, **21**, 742.
- 48 S. Hayashi and H. Hamaguchi, *Chem. Lett.*, 2004, 1590.
- 49 T. Bäcker, O. Breunig, M. Valldor, K. Merz, V. Vasylyeva and A. V. Mudring, *Cryst. Growth Des.*, 2011, **11**, 2564.
- 50 S. Hayashi and H. Hamaguchi, *IEEE Trans. Magn.*, 2006, **42**, 12; S. H. Lee and S. H. Ha, *J. Appl. Phys.*, 2007, **101**, 113709; K. F. Wang, L. Zhang, R. R. Zhuang and F. F. Jian, *Transition Met. Chem.*, 2011, **36**, 785.
- 51 S. G. Vulfson, *Molecular Magnetochemistry*, Gordon & Breach, Amsterdam, 1998.
- 52 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, John Wiley & Son, New York, 5th edn, 1988.
- 53 R. E. Del Sesto, T. M. McCleskey, A. K. Burrell, G. A. Baker, J. D. Thompson, B. L. Scott, J. S. Wilkes and P. Williams, *Chem. Commun.*, 2008, 447.
- 54 B. Mallick, B. Balke, C. Felser and A. V. Mudring, *Angew. Chem., Int. Ed.*, 2008, **47**, 7635.
- 55 A. Gentis, B. Balke, C. Felser and A. V. Mudring, *Cryst. Growth Des.*, 2009, **9**, 4429.
- 56 J. G. Li, Y. F. Hu, S. F. S. Sun, S. Ling and J. Z. Zhang, *J. Phys. Chem. A*, DOI: 10.1021/jp206819h.
- 57 A. W. Taylor, F. L. Qiu, I. J. Villar-Garcia and P. Licence, *Chem. Commun.*, 2009, 5817.
- 58 R. E. Rosensweig, *Ferrohydrodynamics*, Dover, NY, 1985.
- 59 U. Ts. Andres, *Mater. Sci. Eng.*, 1976, **26**, 269.
- 60 D. Brown, B. M. Ma and Z. Chen, *J. Magn. Magn. Mater.*, 2002, **248**, 432.
- 61 J. Y. Kim, J. Y. Kim, E. A. Song, Y. K. Min and H.-o. Hamaguchi, *Macromolecules*, 2008, **41**, 2886; E. A. Song, W. G. Jung, D. W. Ihm and J. Y. Kim, *Bull. Korean Chem. Soc.*, 2009, **30**, 1009.
- 62 S. Odenbach, *Magnetoviscous Effects in Ferrofluids*, Springer, Berlin, 2002.
- 63 C. Gollwitzer, A. N. Spyropoulos, A. G. Papathanasiou, A. G. Boudouvis and R. Richter, *New J. Phys.*, 2009, **11**, 053016.
- 64 L. B. Lubomyr, M. M. G. Slusarczuk and D. A. Thompson, *IEEE Trans. Magn.*, 1975, **11**, 26.
- 65 J. Richardi, D. Ingert and M. P. Pileni, *J. Phys. Chem. B*, 2002, **106**, 1521.