

Account/Revue

Use of ionic liquids in sol-gel; ionogels and applications

André Vioux^{a,*}, Lydie Viau^a, Sabrina Volland^a, Jean Le Bideau^b

^a UMR 5253 CNRS – UM2 – ENSCM – UM1, institut Charles-Gerhardt de Montpellier, sciences et techniques du Languedoc, université Montpellier 2, cc 1701, place Eugène-Bataillon, 34095 Montpellier cedex 5, France

^b Institut des matériaux Jean-Rouxel, université de Nantes, 2, rue de la Houssinière, BP 32229, 44322 Nantes, France

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Abstract

The current strong interest in ionic liquids is motivated by their unique combination of properties such as negligible vapour pressure, thermal stability, non-flammability, high ionic conductivity and wide electrochemical stability window. The first part of this short review deals with all the specific aspects of sol-gel in the presence of ionic liquid, which can act as drying control chemical additive, catalyst, porogenous agent and solvent or co-solvent. The second part is devoted to the properties of the gels in which the ionic liquid is kept confined (ionogels) and their applications as electrolyte membranes, optical devices, catalysts and sensors. **To cite this article:** A. Vioux et al., C. R. Chimie 13 (2010).

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Résumé

Le fort intérêt que connaissent actuellement les liquides ioniques est motivé par la combinaison unique de propriétés comme la non volatilité, la stabilité thermique et l'inflammabilité, ainsi qu'une conductivité ionique élevée et une large fenêtre de stabilité électrochimique. Dans une première partie, cette courte revue aborde les aspects spécifiques du sol-gel en présence de liquide ionique, qui peut agir comme additif pour le contrôle du séchage, catalyseur, agent porogène ou solvant. La seconde partie est consacrée aux gels dans lesquels le liquide ionique est maintenu confiné (ionogels) et à leurs applications comme électrolytes, dispositifs optiques, catalyseurs et capteurs. **Pour citer cet article :** A. Vioux et al., C. R. Chimie 13 (2010).

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1. Introduction

Salts (generally salts of organic cations: ammoniums, phosphoniums, imidazoliums, pyridiniums, etc.) which have melting points lower than 370 K are called

ionic liquids (ILs). Interestingly, a large family of them are air and water stable, as well as thermally stable at temperatures higher than 570 K [1]. Actually, most attractiveness of ionic liquids relies on the possibility to tune their properties by the choice of the anion-cation combination. Moreover, the properties of imidazolium salts, a widely used class of ILs, may be adjusted by the nature of side-chains (substitution at the 1- and 3-positions on the ring): long carbon-chains may induce

* Corresponding author.

E-mail address: vioux@univ-montp2.fr (A. Vioux).

anisotropy [2,3], whereas functional carbon chains lead to task-specific ionic liquids designed for one selected application [4].

Ionic liquids have attracted the attention of electrochemists for a long time, as a result of their high ionic conductivity and their wide electrochemical potential window (up to 6 V) [5]. More recently, ionic liquids, which are able to solubilise both organic and inorganic species, have been widely used as reaction media for synthesis, catalysis and biocatalysis, being claimed as “green” solvents, in relation to their negligible vapour pressure, chemical stability and non flammability, combined with their ability to be recycled in liquid-liquid processes [6]. Nevertheless, to what extent ionic liquids are actually benign and environment friendly is in debate nowadays [7], even though some ionic liquids have been recently synthesized from biomolecules (amino acids, betaines, choline, etc.) [8–10]. Anyway, considerable developments have been carried out in organic chemistry, especially in the field of homogeneous catalysis by organometallic complexes, as in many cases ionic liquids bring about some improvement of the efficiency and selectivity of the catalysts and permit easy separation of products [11]. On the other hand, the interest of ionic liquids in inorganic chemistry is just emerging, particularly in metal electrodeposition [12], “ionothermal” syntheses [13] and sol-gel. In the latter, ionic liquids (usually imidazolium salts) have been shown to be able to act as drying control chemical additives, catalysts, structure directing agents and even as solvents (or cosolvents).

Moreover, numerous applications of ionic liquids properties in such fields as optics, sensors and separation have received much attention, as they have opened wide prospects in materials science. Thus, there is currently a marked interest in using ionic liquids in electrochemical devices, such as actuators, lithium batteries, electric double-layer capacitors, dye-sensitized solar cells and fuel cells [14]. The immobilization of ionic liquids within organic or inorganic matrices makes it possible to take advantage of their unique properties in the solid state, thus circumventing some drawbacks related to shaping and risk of leakage. Accordingly, many works have been devoted to immobilizing ionic liquids within polymer matrices, used as free standing tractable electrolyte membranes, which typically exhibit high proton transport at temperatures ranging from 370 to 450 K [15]. The superiority of these electrolyte membranes, over the classical water-swollen membranes, lies on the non-volatility of ionic liquids. Different routes to “supported liquid” membranes have been reported, as polymerization of monomers in ionic

liquids, solvent casting, wetting or swelling of polymers [16]. However, the use of such systems generally remains limited by the loss of mechanical resistance on increasing the ionic liquid loading. The polymerization of ionic liquid monomers offers an interesting alternative, even though this approach refers more to the concept of polyelectrolyte, and does not remove the intrinsic limitation related to the weak thermal stability of organic matrices [17].

In this context, the sol-gel approach is currently attracting a growing interest. A gel is defined as a solid interconnected network spreading throughout a liquid phase. In classical sol-gel processing the liquid phase is removed, the targeted material being the porous solid obtained after drying (xerogel or aerogel). However the use of ionic liquids, endowed with negligible vapour pressure, permits one to regard the gel itself as a material. This stable solid-liquid system is called ionogel, in the same way as names “aquogel” and “alcoogel” refer to water and alcohol solvents. Ionogels combine the physical properties of the two networks (oxide and ionic liquid) intermingled at nanometer scale. In fact, the immobilization of ionic liquids in gels is of interest for applications as temperature-resistant electrolyte membranes in electrochemistry devices. Moreover, the encapsulation of functional molecules (catalysts, sensing molecules, fluorescent metal complexes) in ionogels opens a new way to functionalize nanostructured oxide materials. Nevertheless, to date a few researches are devoted to ionogels, in which the ionic liquid is kept confined in the oxide network. On the other hand, most works aim at obtaining nanostructured gels after removal of the ionic liquid, which actually acts as a templating agent, as mentioned above. The scope of this short review encompasses both all the specific aspects of sol-gel in the presence of ionic liquid and the properties and miscellaneous applications of ionogels.

2. Ionic liquids in sol-gel chemistry

2.1. Specific properties of imidazolium ionic liquids

Most works involving sol-gel processing in ionic liquids were performed in imidazolium salts, widely used as solvents in organic chemistry, organometallic catalysis, electrochemistry and separation processes [18]. Many of their typical features arise from the acidic character of the ring proton in C2 position (C2H), located between two electronegative nitrogen atoms [19]. Thus, the interactions between C2H and anions that are disclosed in crystalline structures play a key

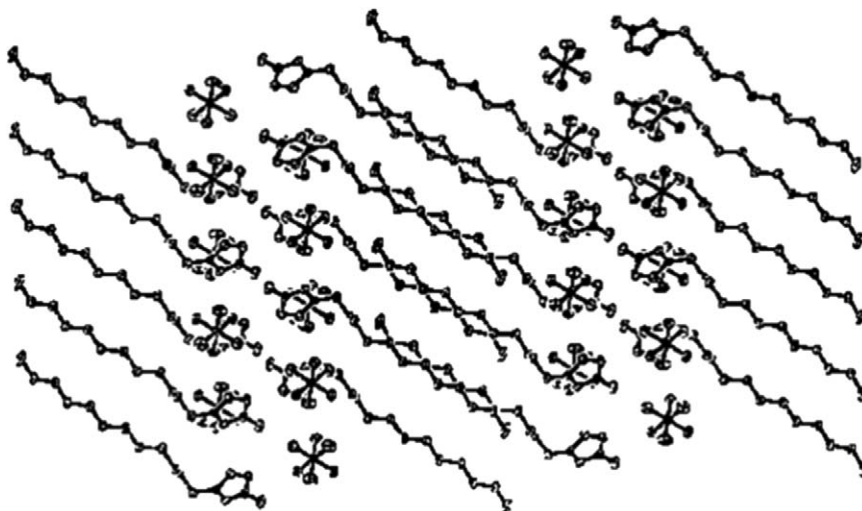


Fig. 1. Crystal structure of $[\text{C}_{12}\text{mim}][\text{PF}_6]$.

role in the structure of liquid phases through extended hydrogen bonded networks resulting in supramolecular ions aggregates [20,21]. This contributes to distinguish them from other ionic liquids which generally form ion pairs. With long-chain imidazolium salts, the crystal packing results in alternate polar and non polar layers as in the typical structure of 1-dodecyl-3-methylimidazolium hexafluorophosphate (Fig. 1) [3].

For a longer carbon-chain, this layered structure is maintained in the liquid state as a smectic phase. Thus, in hexadecylmethylimidazolium hexafluorophosphate a liquid crystal domain exists in the range of temperature between about 70 and 120 °C [3]. Surprisingly, there is no more smectic phase when the anion is change to bis(trifluoromethylsulfonyl)imide $[\text{NTf}_2]$, which well illustrated the key role of anion-cation interaction [22]. However, even “isotropic” room-temperature ionic liquids are structured on a nanometer-scale [23]. Computer simulation predicted that pure ionic liquids of the 1-alkyl-3-methylimidazolium family show structuring of their liquid phases in a manner that is analogous to microphase separation between polar and nonpolar domains (Fig. 2) [24]. It was observed that the polar domain has the structure of a tridimensional network of ionic channels, whereas the nonpolar domain is arranged as a dispersed microphase for ethylmethylimidazolium ILs and as a continuous one for longer side-chains, such as hexyl, octyl or dodecyl. The butyl side-chain would mark the onset of the transition from one type of structure to the other. As a result, ionic liquids can accommodate both ionic and molecular solutes.

Recent studies evidenced that the dissolution of some surfactants in imidazolium ILs depressed the surface tension in a manner analogous to aqueous solutions [25]. This phenomenon indicates that there are solvophobic interactions with the hydrocarbon moieties of the surfactants [26]. Accordingly, ILs (both

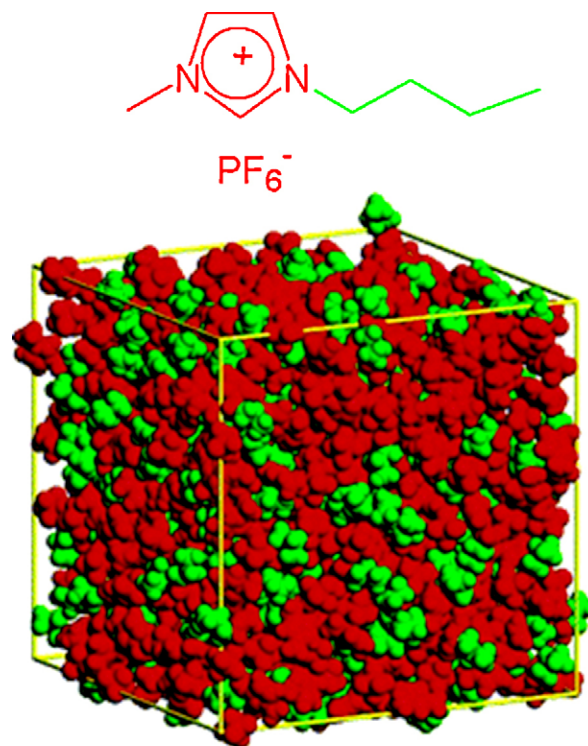


Fig. 2. Simulation snapshot of $[\text{BMIm}][\text{PF}_6]$.

protic and aprotic) support amphiphile self-assembly, in relation to their cohesive energy density (measured by the Gordon parameter) [27]. What is important in sol-gel synthesis is that imidazolium ILs may be regarded both as structured and structuring media, their nanostructural organization acting as “entropic driver” for spontaneous extended ordering of oxide-based structures.

2.2. Gels by impregnation of silica particles

Among a number of studies on nanoparticles, a striking stabilization in ILs has been reported, even in the absence of any stabilizers, as surfactants and polymers [28]. Nevertheless, bare silica colloids were shown to be unstable in ILs, leading to the formation of an interconnected particulate network. In fact, the addition of only 2 to 3 wt % of silica nanoparticles made 1-ethyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide ($[\text{C}_2\text{Mim}][\text{NTf}_2]$) dispersions gelled (Fig. 3) [29].

It has been postulated that charged colloidal particles should easily approach each other, due to the charge screening effect, as far as particles do not have any other repulsive force. Actually, the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, which readily explained the qualitative feature of colloidal stability in terms of the interplay between the London-van der Waals attraction and electrostatic repulsion, suggested that in IL-colloid systems the electrostatic repulsive force hardly stabilizes bare silica particles because of the high

ionic strength of ILs, even though the particles are assumed to be highly charged [30].

A specific nanostructure of ionic liquids is likely induced at the surface of nanoparticles, which should influence aggregation processes. Thus, the structure of the IL/ SiO_2 interface was recently investigated by sum-frequency vibrational spectroscopy (SFVS) for a series of hydrophobic ILs composed of 1-alkyl-3-methylimidazolium (C_nMim , $n = 6, 8$ and 10) and bis(trifluoromethylsulfonyl)imide (NTf_2) or bis(trifluoroethylsulfonyl)imide (BETI) anion. SFVS disclosed the orientation of the cation as well as the structure of water at the IL/ SiO_2 interface [31,32]. The alkyl chain of the imidazolium cation was determined to be nearly normal to the surface. The water at the surface associated with the IL was determined to be hydrogen-bonded either singly or doubly to the anions at the SiO_2 interface. In addition, the nature of the hydrogen-bonding was found to be dependent on the amount of bulk water contained in the IL. However, the surface modification of silica particles can afford the complete stabilization of dispersions in ILs, as recently shown with polymer-grafted silica particles [29]. Note that emulsions of ionic liquids (both ionic liquid-in-water and ionic liquid-in-oil types) were reported, which were stabilized using fumed silica nanoparticles coated to different extents with hydrophobic methyl groups [33].

The gelation of ionic liquid silica mixtures was shown to take place over a range of ionic liquid content,

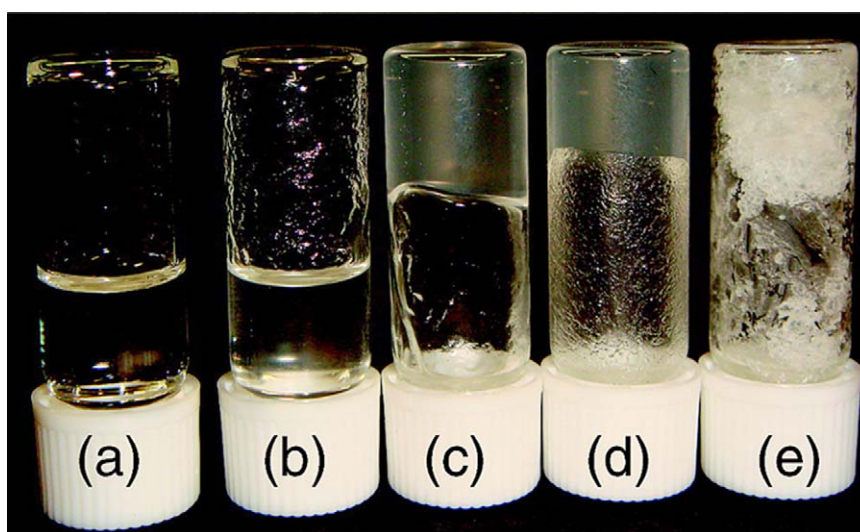


Fig. 3. Dispersions of silica nanoparticles in $[\text{C}_2\text{Mim}][\text{NTf}_2]$ with different particle concentrations: a: neat $[\text{C}_2\text{mim}][\text{NTf}_2]$; b: 1 wt (%); c: 3 wt (%); d: 5 wt (%); e: 15 wt (%).

which depends on the particle size of the silica used as the solidifying agent. Thus, with a particle size of 70 nm, powders turned into gels near 30 wt % of IL, before turning to viscous above 40 to 50 wt % of IL. Ionogels containing more than 90 wt % of IL could be obtained with particle size of 7 nm; however with only 80 wt % of IL they became viscous as early as 120 °C [34]. Quasi-solid electrolytes with liquid-like mobilities could be prepared by simple mechanical mixing process, which were successfully used in high-performance dye-sensitized solar cells (DSSCs) [35]. However, the use of ionic liquids adsorbed on silica particles as *free flowing* powders has given rise to the so-called supported ionic liquid phase catalysis (SILP; vide infra).

2.3. Gels from silicon alkoxides

Sol-gel processes involving silicon alkoxide precursors, in which the interstitial ionic liquid phase, first present between colloidal particles, is then confined as condensation cross-linking extends, should result in more intimate biphasic systems than the simple impregnation of oxide particles. This approach was developed a few years ago by using a non-aqueous method inspired from the pioneering work of S. Dai et al. on the preparation of aerogel-like silicas (see

below) [36], from a mixture of tetramethoxysilane (TMOS) and excess formic acid [37–39]. The method was shown to be a general route to monolith silica ionogels from ionic liquids (e.g. alkylmethylimidazolium [C_nMIm] or butylpyridinium [C₄Py] cations combined with a wide range of anions). Other authors reported the immobilization of some ionic liquids as [C_nMIm][BF₄] (*n* = 2, 4, 10, 16) or [C₄MIm][PF₆] by hydrolytic sol-gel processing using HCl aqueous solution as a catalyst [40].

Besides the preparation of ionogels, ionic liquids have been reported to have significant influence in sol-gel processes on the structure of the resulting silica-based materials, whatever used as additives or as (co-)solvents (Table 1). The effect of ionic liquids as *drying control chemical additives* was ascribed to the formation of a non volatile liquid film on the walls of pores which could protect them from the interface strains associated with the formation of meniscus on evaporation [41]. This permits the pore walls to strengthen on ageing before the solvent extraction or calcination of ILs, thus giving access to highly porous structure.

As mentioned above, the first sol-gel synthesis in an ionic liquid was reported in 2000 by S. Dai et al., from a mixture of tetramethoxysilane (TMOS) and formic acid in [C₄MIm][NTf₂] [36]. All reactants were liquid and miscible at room temperature; gelation occurred

Table 1
Syntheses of silica-based materials using ILs, either as additives or (co-)solvents.

Synthetic conditions	Catalyst (if any)	Precursor	Ionic liquid	References	
Nonhydrolytic HCOOH		TMOS	[C ₂ MIm][NTf ₂]	[36]	
		TMOS	[C ₄ MIm][NTf ₂]	[39]	
		TMOS-MTMOS			
CH ₃ COOH		APTMS	[C ₄ MIm][PF ₆]	[43]	
Hydrolytic		TMOS	[C ₄ MIm][Cl]	[41]	
		TEOS	[C _{2n+1} O _n MIm][CH ₃ SO ₃] <i>n</i> = 1,3	[114]	
		TMOS-MTMOS	[C _n MIm][Cl] <i>n</i> = 4,6 [C ₄ MIm][BF ₄] [C ₄ MPy][BF ₄]	[49]	
		HCl	TMOS	[C ₁₆ MIm][Cl] [C ₄ MIm][BF ₄]	[45,46] [47]
		TEOS-VTEOS		[C ₄ MIm][Cl]	[109]
		TEOS		[C _n MIm][BF ₄] <i>n</i> = 1,3,9,15 [C _n MIm][PF ₆] <i>n</i> = 3	[40]
		TEOS		[C ₁₆ MIm][Br]	[115]
		TMOS-MTMOS		[C ₄ MIm][BF ₄] and [C ₄ Py][BF ₄]	[116]
		NaOH	BTSE	[C ₁₆ MIm][Br]	[48]
		HF	TEOS	[C ₃ O ₁ MIm]X (<i>X</i> = CH ₃ SO ₃ , BF ₄ , PF ₆)	[51]

TMOS: tetramethoxysilane; TEOS: tetraethoxysilane; MTMOS: methyltrimethoxysilane; BTSE: bis(triethoxysilyl)ethane; VTEOS: vinyltriethoxysilane; APTMS 3: aminopropyltrimethoxysilane.

overnight, leading to transparent monoliths after curing at room temperature for three weeks. The ionic liquid was used as a template solvent; after extraction by refluxing in acetonitrile, the porous structure was shown to be close to that of aerogels prepared from molecular solvents after supercritical drying. The N_2 sorption isotherms disclosed a mesoporous structure with typical hysteresis loops. It was shown that the porosity could be adjusted by varying the ratio ionic liquid /silica (mean pore diameters in the 7–20 nm range) [42]. The use of acetic acid was reported similarly to prepare porous aminopropylsilsesquioxanes in $[C_4Mim][PF_6]$ [43].

Similarly, Deng et al. reported that $[C_4Mim][BF_4]$ and $[C_4Mim][PF_6]$ ILs could be completely washed out from the silica matrices under acetone refluxing conditions [40]. Interestingly, the porosity was shown to be influenced by the anion. Thus, in the case of $[C_4Mim][PF_6]$, mesoporous silica gels were also obtained when the ionic liquid was removed, but the corresponding average pore diameters were much larger and the pore-size distribution became quite wide relative to that of silica gels in which the same amount of $[C_4Mim][BF_4]$ was initially confined.

Controlled periodic porosity could be generated in silica-derived materials by using long chain imidazolium salts. The use of $[C_{16}Mim][Br]$ as surfactants in the preparation of MCM-41 instead of traditional $[C_{16}NMe_3][Br]$ illustrates this way [44]. Alternatively, highly ordered monolithic supermicroporous lamellar silicas were prepared under acidic conditions in $[C_nMim][Cl]$ ($n = 10, 14, 16, 18$) at temperatures above the melting points of the ILs in a so-called *nanocasting* sol-gel technique [45,46]. The lamellar arrangement was ascribed to the liquid crystal self-organization of the reaction media (Fig. 4).

In contrast, the use of $[C_4Mim][BF_4]$ led to monolithic mesoporous silica with worm-like structure [47]. Note that mesoporous organosilica materials were successfully synthesized using $[C_{16}Mim][Br]$ as a template, under basic conditions [48].

The role of the IL anions in hydrolytic sol-gel processing has been recently addressed. Pierre et al. reported the catalytic activity of alkylmethylimidazolium tetrafluoroborate and chloride IL, probably in relation to the nucleophilic character of anions [49]. Note that BF_4 anion has been reported as a powerful promoter for hydrolytic condensation of alkoxy silanes in the synthesis of mesoporous silica [50]. The synthesis of silica xerogels, using HF as a catalyst in the presence of 1-monoethylene glycol monomethylether-3-methylimidazolium cation based ILs, led to highly distinct morphologies depending on the counter anion: $[NTf_2]$

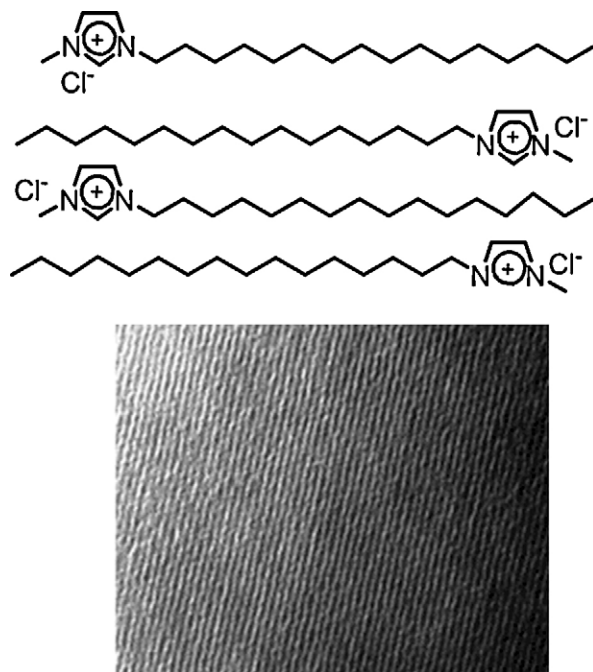


Fig. 4. Lamellar microporous structure $D_p = 1.3$ nm obtained by nanocasting.

anion induced the formation of a compact lamellar monolith with a flat surface, while $[BF_4]$ anion led to a free flowing powder of aggregated spherical particles and $[PF_6]$ anion to a porcelain-like aggregates with honeycomb shapes [51].

2.4. Gels from metal alkoxides

Parallel to silica-based ionogels, several other oxides were investigated. Among them, *titania* was the most studied. Indeed, the high photo-activity of TiO_2 currently attracts most attention for applications as photocatalysts for air and water purification, solar cells and opto-electronics. The physical and chemical properties of TiO_2 closely depend on its particle size, morphology and crystalline phase. In 2003, Nakashima and Kimikuza reported the preparation of hollow TiO_2 microspheres by means of an interfacial sol-gel reaction method in which $[C_4Mim][PF_6]$ was added to a solution of toluene containing titanium tetrabutoxide [52]. The same year, Zhou and Antonietti were the first to report the synthesis of very fine crystalline anatase particles and their assembly toward mesoporous spherical aggregates using a mixture of $TiCl_4$ and $[C_4Mim][BF_4]$ in water at $80^\circ C$ [53]. Dionysou systematically studied the synthesis and the characterization of mesoporous TiO_2 by reaction of titanium isopropoxide and water immiscible $[C_4mim][PF_6]$ [54,55]. In another work, a

peptization process involving $[\text{C}_4\text{MIm}][\text{BF}_4]$ was applied to the preparation of nanostructured anatase TiO_2 monoliths [56]. In all these studies, anatase-containing nanostructured TiO_2 particles with a high surface area and narrow pore size distribution were obtained at low temperature. Moreover, the TiO_2 nanoparticles were shown to be thermally stable, resisting to pore collapse and to anatase-to-rutile conversion on annealing. Using a very small amount of ionic liquid (one-hundredth of the earlier experiment), Choi managed to synthesize stable particles at high temperature (400 °C), which kept anatase structure even after prolonged treatment at 600 °C [57]. Finally, TiO_2 nanocrystals could be easily obtained using a microwave-assisted route [58]. The role of the ionic liquid in the sol-gel process is not so clear; Zhou and Antonietti postulated the reaction to proceed via reaction-limited-aggregation. Dyonisou proposed that $[\text{C}_4\text{MIm}][\text{PF}_6]$ acted as a capping agent due to its water immiscibility and thus prevent direct hydrolysis of titanium tetraisopropoxide resulting in the formation of completely condensed systems. Kim et al. also studied the synthesis of mesoporous TiO_2 and postulated that the essential factor for structuration was the strength of hydrogen bonds between the anion of the ionic liquid and water [59]. More recently, Liu et al. focused on the role of the IL during the crystallization process to anatase in lower temperature treatments. They evidenced higher anatase crystallinity for $[\text{C}_4\text{MIm}][\text{BF}_4]$ resulting from a better ionic liquid-water hydrogen-bonding [60].

Rutile TiO_2 nanostructures could also be obtained at room temperature from TiCl_4 [61–63]. Hu demonstrated that the formation of rutile phase only occurred when $[\text{NTf}_2]$ ILs were used. In the presence of $[\text{BF}_4]$ and $[\text{PF}_6]$ anions, anatase phases were observed [63]. This specific influence is not clear, but it could be attributed to a reversible ligand $[\text{NTf}_2]$ exchange on the Ti surface sites in the amorphous state. Increasing the amount of TiCl_4 , the whole morphology of rutile particles from nanorods to microcones and microspheres was illustrated by Zheng [61].

Recapitulative Table 2 shows the general trend to form anatase from $\text{Ti}(\text{O}^i\text{Pr})_4$ and ionic liquids as $[\text{C}_4\text{MIm}][\text{BF}_4]$ or $[\text{C}_4\text{MIm}][\text{PF}_6]$ and to form rutile from TiCl_4 and $[\text{NTf}_2]$ or halide containing ionic liquids.

The use of IL in the synthesis of *tin dioxide* is very recent. In 2008, Dong and Liu described the synthesis of 2.5 μm SnO_2 microspheres under microwave conditions using IL as templates and starting from SnCl_4 in aqueous conditions [64]. Among the ILs used, only BF_4 containing ionic liquids were shown to be able to produce these microspheres. On the other hand,

Table 2

Influence on the titanium precursor and the IL used on the TiO_2 crystal phase.

Precursor	Ionic liquid	Crystal phase	Reference
TiCl_4	$[\text{C}_4\text{MIm}][\text{BF}_4]$	Anatase	[53,55,56]
$\text{Ti}(\text{O}^i\text{Pr})_4$	$[\text{C}_4\text{MIm}][\text{PF}_6]$	Anatase	[54,57,59,60]
	$[\text{C}_4\text{MIm}][\text{BF}_4]$	Anatase	[54,58–60]
TiCl_4	$[\text{C}_4\text{MIm}][\text{Cl}^-]$	Rutile	[62]
	$[\text{C}_2\text{MIm}][\text{NTf}_2]$	Rutile	[63]
	$[\text{C}_8\text{mim}][\text{Br}^-]$	Rutile	[61]

interactions between SnO_2 and hydrophobic PF_6 anion were supposed to be too weak to promote nucleation and growth, whereas strong interactions with water would minimize the interactions with SnO_2 nuclei in the case of hydrophilic chloride anion. At the same time, using $[\text{C}_{13}\text{MIm}][\text{Br}^-]$ as template and SnCl_4 as precursor, Yan et al. reported the synthesis of nanocrystalline porous tin oxide SnO_2 materials, which showed a tetragonal cassiterite structure after annealing. These materials showed some potential for gas sensing applications [65]. In a recent work, we explored a quite different approach, using a β -diketonato stabilized tin precursor to produce translucent monolith ionogels. A major advantage over the previous results was the possibility to use a wide range of IL ($[\text{C}_4\text{MIm}][\text{BF}_4]$, $[\text{C}_4\text{MIm}][\text{PF}_6]$, $[\text{C}_4\text{MIm}][\text{Br}^-]$), thanks to the chelating ligand on the tin precursor which permitted to control the polycondensation rate [66].

The fabrication of large mesoporous *alumina* nanostructures was recently reported by Hong et al. using ionothermal synthesis starting from aluminium tri-*sec*-butoxide [67]. This technique, first described by Morris, relies on the use of an ionic liquid as both the solvent and the structure-directing agent [68]. One major advantage is that most ionic liquids have vanishingly small vapor pressures, which means that no autogenous pressure is produced on heating and that ionothermal synthesis can take place at high temperature while keeping the pressure at ambient levels. Indeed, the synthesis was performed in an open container under ambient pressure at 120 °C. Once again, hydrogen bonding and co- π - π stacking interactions induced the formation of the oxide-based structure, and finally the conversion into boehmite crystallites, as proved by FT-IR and XRD analysis. The same authors also reported the synthesis of alumina ionogels with various shapes, including 1D nanorods with hexagonal tips, straight and curved nanofibers embedded in a porous network, 3D octahedral-, polyhedral- and angular spherical shapes [69]. These hybrids were still obtained via a one-pot ionothermal

process by tuning cooperative interactions between the ionic liquid and the building blocks (i.e. by varying the nature of the IL anionic part and the humidity conditions). In the case of $[C_4MIm][BF_4]$, high proton conductivity was obtained as a result of continuous proton conduction channels and confinement effect.

The only sol-gel synthesis of *vanadia* in ionic liquid media was reported by Endres' group. These authors used two different classes of IL, pyridinium and imidazolium salts: a higher crystallinity was observed for the samples prepared from pyridinium $[NTf_2]$ in acetone, whereas a higher porosity was observed for those prepared from imidazolium $[NTf_2]$ in isopropanol as cosolvent. The surface area could be enlarged four times using acidic hydrolysis instead of pure water [70].

In some cases, *mixed oxides* make it possible to overcome some drawbacks encountered with the single oxides. For instance, TiO_2 is a good catalyst but it exhibits low surface area, whereas Al_2O_3 is stable, has acceptable surface area, but is poorly catalytically active. Accordingly, TiO_2 - Al_2O_3 mixtures are interesting for catalytic applications. Using a sol-gel synthesis in the presence of $[Pyr][NTf_2]$, amorphous alumina-titania powders were obtained. After calcinations, the surface reached around $500\text{ m}^2\cdot\text{g}^{-1}$ whereas the surfaces of boehmite and titania were around $100\text{ m}^2\cdot\text{g}^{-1}$. The authors found that the presence of alumina stabilized the anatase phase and elevated the temperature at which the phase transformation to rutile occurred [71]. Another example was given by the synthesis of mesoporous Al-MCM-41 using $[C_{16}MIm][Br]$. The material obtained was shown to have a high surface area and uniform mesopores, and to keep the tetrahedral environment of aluminum after calcination [72].

3. Ionogels, properties and applications

3.1. Stability of ionogels

Despite no accurate study of the interfacial tension between silica and IL has been performed, a strong wettability of porous silica networks by ILs was observed. In fact, monolithic silica ionogels did not undergo any expulsion of $[BMIm][NTf_2]$ when submitted to around 10 kHz centrifugation in a MAS NMR rotor probe [73].

As mentioned above, ionogels are quite stable in non polar organic solvents such as toluene or alkane, whereas the ionic liquid can generally be extracted by polar solvents such as acetonitrile, dichloromethane or ethanol. In some cases, monolith gels could be obtained after washing by extraction with a polar solvent and

then refilled with a new ionic liquid. This method made it possible to incorporate highly sensitive metal complexes (which otherwise would have decomposed under the conditions of sol-gel synthesis) within the ionogel. In the case of immersion in water, ionogels were found to be quite stable as far as the ionic liquid was non water-soluble and enough hydrophobic methyl groups were present in the silica network (i.e. some methyltrialkoxysilane was added in the starting precursor solution [42]).

As expected, the ionogels exhibited the same thermal stability as the ionic liquids alone. It is noteworthy that the organic modification of silica, by incorporation of a large amount of methyl groups, had no significant effect on the thermal stability [42].

3.2. Effect of confinement on the physicochemical properties of ionic liquids

Ionogels stemming from silicon alkoxides could be pictured as two interpenetrating continuous networks of silica and ionic liquid intermingled at the nanometer scale. Accordingly, the nanoconfined ionic liquid phase experiences a large interface with pore walls which is expected to modify its microscopic structure and dynamics with respect to the bulk phase.

^1H MAS NMR experiments carried out on $[BMIm][NTf_2]$ containing ionogels exhibited quite unexpected high resolution with respect to that usually observed in the solid state [42,73]. This showed liquid-like dynamics of confined ILs in monolithic ionogels (15 nm pore diameter silica host networks containing about 80 wt % $[C_4MIm][NTf_2]$), since a 400 Hz MAS was sufficient to average the interactions usually broadening the signals in the solid state. T_1 relaxation-time measurements, which gave dynamic information for longer spatial range correlations, confirmed that dynamics of confined ILs was only slightly slowed down [73]. Moreover, ^1H MAS NMR spectra disclosed a magnetic susceptibility gradient, as evidenced by the lack of narrowing of signals when comparing FWHM from 400 to 9000 Hz spinning rates; the resulting distribution of chemical shifts was ascribed to the fact that IL species could be localised either at the centre of the pores (where magnetic susceptibility only arose from surrounding parent anions and cations), or at the wall neighbourhood (where magnetic susceptibility was also influenced by anisotropic constraints on close IL species). Effects of wall neighbourhood on structuration were also reflected by differential scanning calorimetry (DSC) [42,74]. In fact, even though confinement did not affect the glass transition, DSC disclosed the dramatic

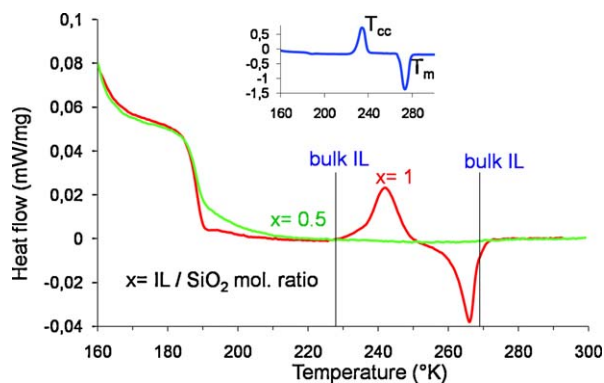


Fig. 5. DSC traces of ionogels. $x = \text{IL/Si}$ (mol/mol), insert: pristine ionic liquid $[\text{C}_4\text{MIm}][\text{TFSI}]$.

effect of confinement on both cold crystallization and melting, which even could be no longer observed on increasing the confinement, i.e. on decreasing the mean pore size (Fig. 5). It is worth noting that when cold crystallisation and melting were observed, the melting temperature (T'_m) was lowered with respect to the pristine IL (T_m), whereas the cold-crystallization temperature (T'_{cc}) was shifted to a higher value (T'_{cc}). Actually, considering the pore/solid and pore/liquid interface energies $\gamma_{p/s}$ and $\gamma_{p/l}$, respectively, the effect of confinement is to be related to the chemical features of pore walls, through a Gibbs-Thomson-like equation $(T'_{cc} - T_{cc})/T_{cc} = -2(\gamma_{p/s} - \gamma_{p/l})V_{mol}/D\lambda_f$, where V_{mol} is the molar volume of the IL, λ_f the latent heat of melting, and D the pore diameter [75].

3.3. Use of ionogels as electrolytes

Most sol-gel derived materials are electronic insulators with low charge-transfer efficiency and substrate diffusion. Besides that, ionic liquids are now well-known for their use in dye sensitized solar cells, lithium batteries, supercapacitors and fuels cells, owing to some of their properties such as non flammability, easy solvation of the selected salt (charge carrier), possible non miscibility with water. [76–79] Immobilizing ionic liquids in oxide gels offers a way to endow these oxides with ionic liquid properties, apparently antinomic. Roughly, confined ILs showed the same order of magnitude of conductivity as pristine ILs, which is consistent with their liquid-like dynamics [42]. Their ionic conductivity followed an Arrhenius-like behaviour with temperature, which, of course, could be correlated to viscosity through the Walden product if sufficient data were available. However, besides temperature, water content also influences

viscosity: only 2 wt % (20 mol %) of water in $[\text{C}_4\text{MIm}][\text{BF}_4]$ reduces its viscosity by more than 50% [80]. Although this trend strongly depends on the affinity of the IL with water ($[\text{C}_4\text{MIm}][\text{BF}_4]$ is water soluble), any IL shows a decrease in viscosity when the amount of dissolved water increases. This point is to be taken into account in ionogels, since sol-gel methods release water, alcohol and other by-products, making it difficult to ascertain the purity of the confined IL, even after a prolonged heat treatment under vacuum.

Anyway, ionogels that combine the chemical versatility of ILs with the shaping versatility of sol-gel, offer a new way to design conducting materials for electrochemical devices, such as batteries, fuel cells, electrochromic windows or photovoltaic cells. Thus, Stathatos et al. fabricated TiO_2 dye-sensitized quasi-solid-state solar cells by using an electrolyte prepared by sol-gel, which was based on silica and a mixture of a surfactant, propylene carbonate, iodine, and 1-methyl-3-propylimidazolium iodide [81]. Interestingly, an IL based on an imidazolium iodide in which the dialkylimidazolium cation was derivatized by covalent attachment of a trimethoxysilane group (namely 1-methyl-3-[3-(trimethoxy- λ^4 -silyl)propyl]-1H-imidazolium iodide) was synthesized and used as a sol-gel precursor to prepare quasi-solid-state electrolytes. Acid catalysed hydrolysis led to positively charged polyhedral cube-like silsesquioxane species, which still contained a small amount of silanol end groups that were removed after heating at 200 °C [82]. Alternatively formic acid solvolysis at 120 °C (in the absence of water) was used as well [83]. The resulting material was a tough, yellowish and transparent solid, consisting of ladder-like polysilsesquioxane species bearing imidazolium end-groups with iodide counter-ions [84]. The addition of iodine (and some imidazolium IL) resulted in quasi-solid-state redox electrolytes for dye-sensitized photoelectrochemical cells of the Graetzel type [83,85,86].

3.4. Use of ionogels in optics

Ionic liquids are very interesting as optical solvents, not only for their high stability and non-volatility, but also due to their transparency through almost the whole visible and near-infrared spectral regions. Moreover, their ionic natures permit the solubilisation of ionic coordination compounds, including lanthanides salts and complexes. Binnemans has thus demonstrated a highly photostability of lanthanides complexes in ionic liquids [87]. The development of ILs for optical applications is however limited by their liquid state.

Ionogels recently demonstrated high efficiency to immobilize lanthanides complexes [88,89]. Actually, most silica-based ionogels appear transparent to the naked eye, opening potential applications as luminescent devices. Thus, europium(III)-doped ionogels showed a very intense red photoluminescence, with a very high monochromatic purity, under ultraviolet irradiation [89]. Note that the average decay times were as long in confined IL liquid as in bulk IL (mono-exponential decays of 0.52 ms and 0.55 ms, respectively, versus 0.35 ms in solid state). Thus, it could be concluded that the coordination sphere of the complex (europium(III) tetrakis β -diketonate) was not altered upon confinement and that it experienced a liquid-like environment. Similarly Sm(III)- and Tb(III)-doped ionogels showed the same emission performance as IL solutions (Fig. 6) [88].

Ahmad took advantage of the ionic conductivity of ionogels, which have liquid electrolyte performances despite their solid state, to synthesize an electrochromic device based on tungsten oxide and Prussian blue electrodes. This device exhibited extremely fast switching kinetics (transmission variation ΔT around 90% in 2 s) [90].

3.5. Use of ionogels in catalysis and biocatalysis

Ionic liquids are extensively used in metal catalyzed reactions. However, they still are expensive, which makes it necessary to implement recovering and reusing processes. Other restrictions to their development as industrial solvents arise from their high viscosity, which implies highly energy-consuming stirring and from mass transfer limitations in biphasic systems, which makes that the sole catalyst involved in the process is

that contained in the narrow diffusion layer at the liquid-liquid (or gas-liquid) interface. Over the last years, the immobilization of ionic liquids as adsorbed thin films on high surface area supports has been proposed to circumvent these restrictions. This approach is known as supported ionic liquid catalysis phase (SILP) catalysis (Fig. 7) [91–93]. Typically, silica support beads with 25 wt % of ionic liquid loading are easily obtained as free flowing powders. This concept combines the advantages of ionic liquids with those of heterogeneous support materials and could be particularly suitable for continuous fixed-bed reactors. Actually, the layer of free ionic liquid on the carrier (the thickness of which is close to the diffusion layer) was shown to act as a reaction phase able to dissolve various homogeneous catalysts. SILP catalysis has been successfully used in miscellaneous reactions such as Friedel-Crafts reactions [94], Rh-catalyzed hydroformylations [95] and hydrogenations [96], Pd-catalyzed Heck [97,98] and Suzuki [99] reactions, and Rh-, Pd-, and Zn-catalyzed hydroaminations [100,101].

Ionogels provide alternative SILP systems [93], as the interconnected 3-D pore structure allows free transport of reactants and products, while pore diameters are small enough to prevent IL leaching. However, the processing of metal catalyzed reactions is quite different in ionogels and supported IL films. In the latter, reactants and products diffuse through the residual voids in pores, the walls of which are only coated with the liquid catalyst film. On the other hand, in ionogels, reactants and products diffuse in the 3D continuous liquid phase which fills all the pores. Actually, Deng et al. reported the enhanced catalytic performance of the carbonylation of aniline into ureas and carbamates in the presence of ionogels loaded with Rh(PPh₃)₃Cl and Pd(PPh₃)₂Cl₂ [40]. The reactions were carried out without additional organic solvent in autoclave at 135–180 °C under 5 MPa CO pressure (Fig. 7).

Recent investigations involving ionogels prepared in the presence of Pd salts have shown an effective catalytic activity for the Heck coupling reaction without leaching [102]. The ability of ionogels to be used as nanoreactors could induce some confinement effects, which have been already reported in others SILP systems. Thus, the coating of organomodified acid silica support with hydrophobic ionic liquid permitted highly selective transformations in formalin and pure water [103]. In another work [104], the immobilization of chiral hydrogenation catalysts led to high enantioselectivities (up to 74%) in the hydrogenation of acetophenone (whereas enantioselectivity of the homogeneous reaction

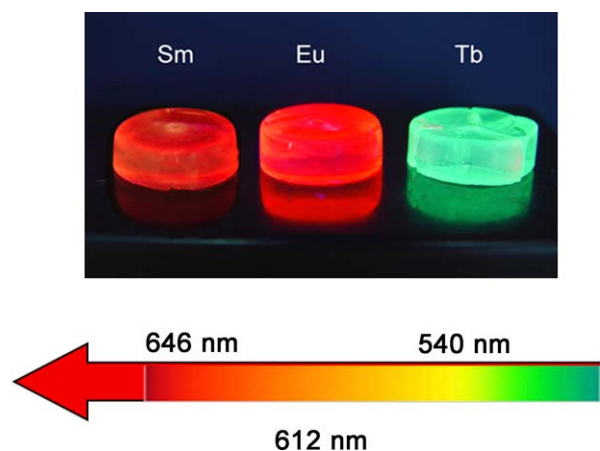
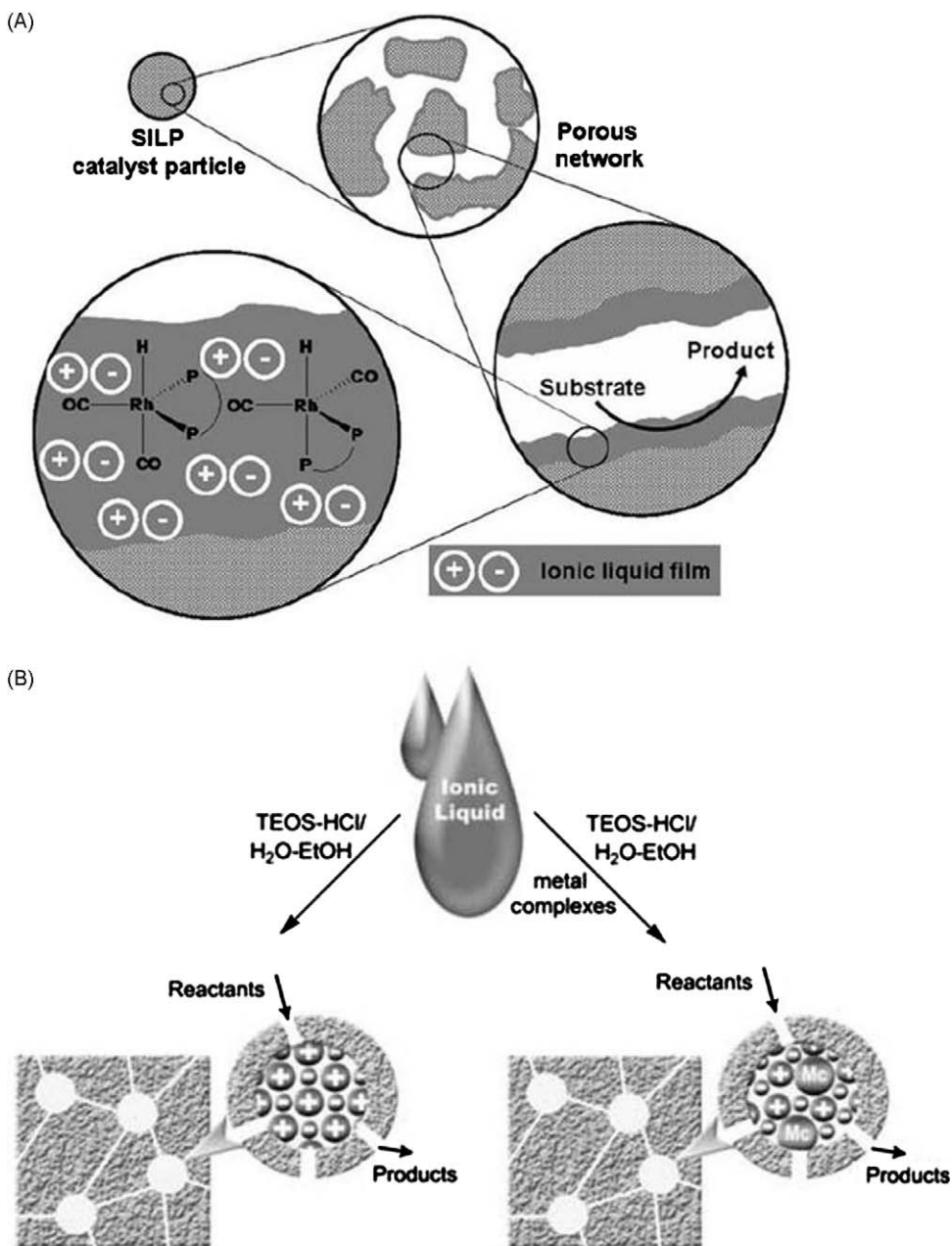


Fig. 6. Luminescence of lanthanides doped ionogels.



was null in methanol). This enhanced enantioselectivity compared to the corresponding homogeneous catalysis was attributed to confinement effects, which enhanced substrate-catalyst interactions. Actually, the formation of solvent cages around metal complexes has been postulated in ionic liquids; transition states would be modified in these cages in confined ionic liquid, promoting selectively alternative reaction pathways [105,106].

ILs have recently demonstrated attractive performances as a reaction media in *biocatalysis* [107]. The activity of biomolecules in ILs has been found to be comparable or higher than in conventional solvents and enhanced enzyme stability has been reported. The first reports of applications of ionogels to biocatalysis seem promising. Thus, the activity of horseradish peroxidase (HRP) immobilized in ionogels was shown to be about 30-fold greater than that in silica gel without IL, with an

excellent thermal stability [108]. HRP was immobilized in ionogels prepared by acidic hydrolysis of TEOS in $[C_4MIm][BF_4]$. The enzyme was thought to be protected by the IL from the detrimental effect of ethanol during the synthesis, while the interconnected pore structure of ionogels would facilitate the internal diffusion of the substrate.

3.6. Use of ionogels in sensing and biosensing

The unique combination of ionic conduction and optical properties with the possible diffusion of analytes into the immobilized IL phase makes ionogels good candidate materials for integrated electrochemical and colorimetric approaches in sensing and biosensing. Moreover, the use of IL that decreases the capillary stresses makes it easier to prepare crack-free films (for coating electrodes for instance).

Thus, sulfonaphtalein pH indicators were trapped in TEOS/VTOS ionogels (IL: $[C_4MIm][Cl]$). The resulting IL modified films showed increased wettability, reduced gel shrinkage, faster response times and better reproducibility compared to classic sol-gel films [109]. Recently, films of ionogels doped with $Ru(bpy)_3^{2+}$ displayed a fast and reversible response to gaseous oxygen. In comparison to traditional sol-gel derived thin films, the microenvironment of the complex was supposed to be not so rigid, leading to more important Stocke's shift values [110].

Enzyme immobilisation in IL confined onto electrodes surface comes under the same concept as SILP catalysis: no covalent grafting is needed and the nature of the catalyst is preserved. Some examples are based on the immobilization of enzyme-IL systems in organic hydrogels [111]. New hybrid organic-inorganic siloxane-based hydrogels entrapping IL have been recently developed for similar uses [112]. Interestingly, an amperometric biosensor was obtained by coating the surface of a glassy carbon electrode with a silica ionogel film doped with HRP and ferrocene (IL: $[C_4mim][BF_4]$) [113]. The resulting electrode had faster response in sensing hydrogen peroxide than with classic sol-gel film, with a detection limit for H_2O_2 of 1.1 μM .

4. Conclusion

The use of an ionic liquid as a solvent or a cosolvent in sol-gel processing provides an efficient way to crack-free monoliths with high specific surface areas and mesopores whose the size can be modulated by the choice of the IL and the ratio IL:Si. Ionogels result from the interpenetration of two continuous 3-D networks of

solid and ionic liquid. Studies by DSC and 1H NMR highlighted the effects of nanoconfinement of imidazolium salts, while evidencing liquid-like dynamics. However, ionogels are not only curiosity, as they open considerable fields of applications, by combining the versatility of the sol-gel process, which gives access to a wide range of supports, from pure metal oxides to organic-inorganic silica-derived hybrids and the unique advantage of ILs whose properties can be adjusted to specific tasks.

Thus, ionogels, whose preparation and shaping are very easy and cheap, form a new family of temperature-resistant solid electrolytes, which could be of interest for applications such as fuel cells, dye-sensitized solar cells and lithium batteries. Functionalization of ionogels can be achieved both by the incorporation of organic functions in the solid matrix and by encapsulation of functional molecules, metal complexes or nanoparticles in the immobilized IL phase, which opens new routes for designing materials, especially in the fields of sensors, display devices, catalysts and separation.

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