



The role of ether-functionalized ionic liquids in the sol–gel process: Effects on the initial alkoxide hydrolysis steps



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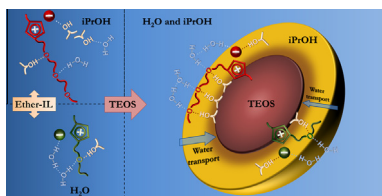
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GRAPHICAL ABSTRACT



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ABSTRACT

The ether-functionalized imidazolium ionic liquids (IL) applied in the silica sol–gel process demonstrated a defined coordination potential. These IL display the capacity to control the system organization from the reactions' first moments through a dynamic system-assembling ability, being the sum of ionic and physical interactions, i.e. Coulomb forces, H-bonding and London forces. The initial hydrolysis steps of tetraethyl orthosilicate (TEOS) in the presence of these IL were followed by Fourier transform infrared spectroscopy (FTIR) and dynamic light scattering (DLS), both in time-resolved experiments, in an attempt to correlate the structuring and the bonding dynamics of these systems.

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1. Introduction

The sol–gel process is a powerful source for the preparation of surface and interface controlled materials, allowing the physico-chemical properties tuning from the first stages of preparation.

Technology driven materials with unique properties can be prepared, including highly homogenous structures or finely controlled secondary phases [1,2]. Ionic liquids (IL) are salts with ionic-covalent crystalline structures presenting melting temperatures up to 100 °C. Due to the unusual imidazolium derived IL's characteristics, e.g. structural organization and high thermal and chemical stability, these have shown great potential as templates for the synthesis of inorganic materials. Some IL do not only act as templates, but also stabilize the structures formed, thus working as an efficient template–solvent and in some cases a

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template–solvent–reactant [3,4]. This explains the interest in understanding the physicochemical characteristics of IL–solvent mixtures. The pure imidazolium IL exist as self-assembled polymeric supramolecular structures, driven by hydrogen bonding (H-bond) and π – π stacking, as well as Coulomb coupling and London forces depending on the IL molecular structure, among the cations and anions. Differently, IL–solvents mixtures present highly complex structures (inclusion structures, triple ions, ion pairs, solvent separated ions), which are concentration dependent [3]. The elucidation of these structures, and their correlation with the formation conditions, are of great interest for applications in colloidal solution-based systems. For instance, this structural organization of the original sol determines the continuous polycondensation and subsequent network formation [2,5].

Nowadays, ether-functionalized IL are popular due to successful applications in the fields of deep-eutectic solvents, electrochemistry and materials with biological interfaces [6,7]. In general, the functionalization of imidazolium cations with alkyloxy or alkyloxyalkyl groups leads to reduced viscosity, crystallinity, melting temperature and glass transition temperature; and also to increased polarity, hydrophilicity and H-bond capability, when compared to their aliphatic analogs [6]. Furthermore, this set of physicochemical changes leads to increased water solubility and conductivity [8–10]. These characteristics are a reflex of the high chain flexibility predominating over the polarity of the ether groups, the higher rotational freedom and reduced lattice energy promoted by the ether groups [9,11,12]. Also, the ether chains compete with anions for cation interactions and, as a result, the cation–anion interactions are weakened, resulting in the formation of cation dimers in ether-functionalized IL [13,14]. Interestingly, the alkoxy chain can be designed in different lengths and shapes, allowing a fine tuning of these physicochemical properties for particular applications [6].

Since the first reports on using IL as templates for the sol–gel process and materials science [15], their structural similarities to usual surfactants, summed to their unique properties, make them ideal candidates for replacing traditional surfactants applied in the preparation of periodic porous networks [16,17]. This ability of IL to act as template is due to their interfacial interaction with the growing material. Based on the special molecular structures of some of these imidazolium based IL, a mechanism called *hydrogen bond-co- π – π stack* was proposed [16,18]. This should be responsible for the IL induced formation of the tridimensional porous systems in the formation of, e.g., silica via the sol–gel method. In this particular case, the H-bond induced IL anion–silanol interaction forces the orientation of this anion. Consequently, the cation also tends to align with the growing silica surface, driven by Coulomb coupling forces with the anion. The fluid state of the sol system favors the necessary molecular relocation, which is further promoted by the additional π -interactions among the imidazolium rings [18].

The use of this strategy, despite of being fairly recent, is already quite consolidated in the literature, including successful attempts of our group to obtain morphologically controlled sol–gel silica by using different classes of IL [5,19]. This approach was extended to the *in situ* formation of silica-filler polymer nanocomposite systems, where the IL could serve as multifunctional agents, providing materials with significantly improved mechanical properties [20–22]. Ether-functionalized imidazolium IL also showed media dependent electrical conductivity enhancements [23], forming in the presence of water H_3O^+ and a new species that inhibits charge transfer processes on an electrode surface [8]. The H_3O^+ formation in the presence of water allows these IL to act as bifunctional morphology controller-catalysts when applied into the sol–gel process [19]. Importantly, previous works focused only on the IL's participation in the final stages of sol–gel process, when the condensed

phase was dominant in the growing network [5,16–19,21]. However, information about the initial sol–gel stage involving the hydrolysis step and IL's interactions with the reaction mixture, in spite of its crucial role in the system structure evolution, is very scarce. Differently, this study is an attempt to elucidate the ether-functionalized IL's mechanism of action in the phase structure evolution (by DSL) and the kinetics (by FTIR) of TEOS hydrolysis in the sol–gel process, since the first reaction moments. Herein, is also reported about the individual roles of IL's cation side chain length and anion (Fig. 1), as well as the synergic action with the applied co-solvent.

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS), isopropyl alcohol (*i*PrOH), ethyl alcohol (EtOH) and hydrochloric acid (HCl) were used as received (Sigma–Aldrich).

2.2. IL synthesis

A straightforward synthetic pathway was chosen for the preparation of halide-free ether-functionalized imidazolium IL, as presented in the literature [24]. The first reaction step consisted in the preparation of methanesulfonate ester alkylating agents by the treatment of the corresponding alcohols (i.e., 2-methoxyethanol and triethylene glycol monomethyl ether) with methanesulfonyl chloride, in the presence of triethylamine. The obtained alkylating agents were then reacted with 1-methylimidazole to obtain the respective IL: 1-monoethylene glycol monomethyl ether-3-methylimidazolium methanesulfonate ($C_3OMImMeS$), 1-triethylene glycol monomethyl ether-3-methylimidazolium methanesulfonate ($C_7O_3MImMeS$) and 1-triethylene glycol monomethyl ether-3-methylimidazolium tetrafluoroborate ($C_7O_3MImBF_4$) (Fig. 1). 1H and ^{13}C NMR confirmed the purity of the synthesized IL.

2.3. Synthesis of sol–gel silica

Hydrolysis and condensation of TEOS was performed in either *i*PrOH or EtOH solutions, using IL (2.5 wt.% relative to the content

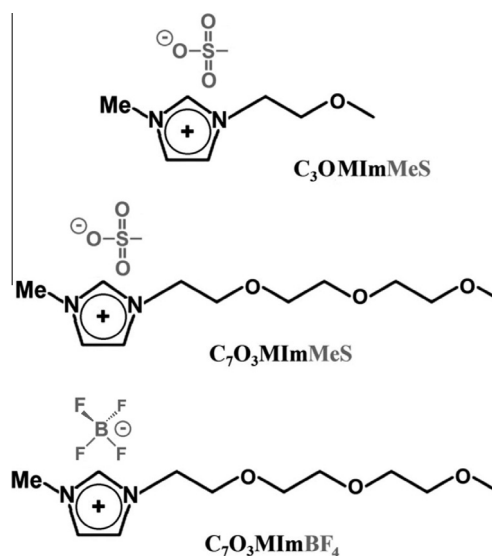


Fig. 1. Ether-functionalized IL used in this study.

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