



Ionic liquid-functionalized crystals of barium sulfate: A hybrid organic–inorganic material with tuned hydrophilicity and solid–liquid behavior



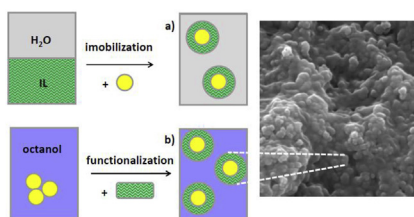
Magdalena Kowacz^{*,1}, Mateusz Marchel¹, José M.S.S. Esperança¹, Luís Paulo N. Rebelo^{*,1}

Instituto de Tecnologia Química e Biológica – António Xavier, Universidade Nova de Lisboa, Av. da República, 2780-157 Oeiras, Portugal

HIGHLIGHTS

- Hybrid organic–inorganic material: nanocrystals of BaSO₄ in ionic liquid matrix.
- Functionalized BaSO₄ with enhanced affinity to lipophilic media.
- Solid-supported water-immiscible ionic liquids (ILs) dispersed in aqueous solution.
- Molecular-scale mixing of ILs and crystal building units at the solid/IL interface.

GRAPHICAL ABSTRACT



a) Hydrophobic ionic liquids (ILs) on solid carrier dispersed in water. b) IL -functionalized hydrophilic solid dispersed in lipophilic media.

ARTICLE INFO

Article history:

Received 16 February 2015
 Received in revised form
 16 April 2015
 Accepted 24 April 2015
 Available online 29 April 2015

Keywords:

Composite materials
 Inorganic compounds
 Organic compounds
 Interfaces

ABSTRACT

A hybrid organic–inorganic material composed of barium sulfate (BaSO₄) crystals embedded within a hydrophobic ionic liquid (ILs) matrix has been synthesized. The contact between the inorganic solid and the organic coating is created by chemical interactions between the crystal surface and the ionic liquid. The material exhibits higher affinity to lipophilic media than the non-modified BaSO₄. Increased hydrophobicity is a property often sought for inorganic particles to be applied in non-polar formulations. Immobilization of water-immiscible ILs on a hydrophilic solid carrier enables their application in aqueous solutions and the creation of appreciable hydrophobic-IL/water interfaces on the dispersion of solid-like material in aqueous media.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Barium sulfate (BaSO₄) is an industrially important mineral that finds wide range of applications due to its whiteness, inertness and high density [1]. It is used as an additive in painting, coating,

plastics and medicines fibres [2,3]. BaSO₄ (barite) is one of the most important inorganic fillers. Presently polymers filled with nano-scale inorganic particles are gaining increasing scientific interest. It is because inorganic fillers are expected to enhance stiffness and impact properties of the polymer matrix [1,4,5]. Nevertheless, the surface of inorganic particles (such as that of BaSO₄) is hydrophilic. This fact poses difficulties in their dispersion in a lipophilic media [5]. Therefore, surface modification of inorganic fillers is crucial, for instance, in the formation of inorganic/polymer composites. In this context, appropriate functionalization of BaSO₄ is an important and

* Corresponding authors.

E-mail addresses: magda@itqb.unl.pt (M. Kowacz), luis.rebelo@itqb.unl.pt (L.P.N. Rebelo).

¹ www.itqb.unl.pt.

still challenging task. Some scientific reports in this field have been published [5,6] and new materials have been patented and find their application in industry [7].

From the perspective of particle functionalization the concern is about novel properties added to the solid. Nevertheless, the surface-modifying agent may also gain new characteristics upon its attachment to the solid support. Functionalizing agents used in this work are ionic liquids. Ionic liquids (ILs – substances composed almost exclusively of ions that are usually liquid at room temperature [8]) are synthesized chemicals which ions tend self-organize (in a neat liquid or in solution and at the interfaces) to present distinct nano-domains (like polar and non-polar) [9]. Their corresponding properties can be tailored to fit specific applications. One of those is the extraction of amphiphilic components (such as proteins) from aqueous media. This can be done e. g with the use of IL-based aqueous biphasic systems [10]. On the other hand, components of predominantly hydrophobic character can be solubilized in water with the aid of emulsions that can contain ILs as a dispersed phase [11,-12]. Yet, unless spontaneously created at specific conditions [13], the emulsion formulation usually requires application of high mechanical force and high concentration of stabilizing agents. Stabilizing agents hinder direct contact of the dispersed and dispersing phase. Nonetheless, for the processes that take place at the liquid/liquid interface, the creation of undisturbed extensive liquid/liquid contacts is required. In this context, hydrophobic IL/water interfaces have been examined for example as biphasic reaction fields for enzyme-catalysed reactions [14].

In this work, we explore the possibility of modifying the surface properties of inorganic crystals of barium sulfate using hydrophobic ionic liquids. On the other hand, we show that the use of a hydrophilic solid carrier may extend applications of hydrophobic ILs in aqueous media.

2. Materials and methods

2.1. Synthesis of barium sulfate

Barium sulfate (BaSO_4) crystals were prepared by a precipitation method by mixing aqueous solutions of 1 M of Na_2SO_4 and 0.1 M BaCl_2 in proportions of 2:1 (by volume). The precipitate (BaSO_4) was separated from the solution by filtration (filter pore diameter of 0.45 μm) and washed with a copious amount of Milli-Q water. BaSO_4 was either dried for 48 h at 60 °C (dry BaSO_4) or used wet as prepared (wet BaSO_4) for its further functionalization with ionic liquids (ILs): 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[\text{C}_2\text{mim}][\text{NTf}_2]$ (Iolitec), 1-hexyl-3-methylimidazolium bis(trifluoro methylsulfonyl) imide $[\text{C}_6\text{mim}][\text{NTf}_2]$ (Iolitec), 1-dodecyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide $[\text{C}_{12}\text{mim}][\text{NTf}_2]$ (Iolitec), or 2-hydroxyethyltrimethyl ammonium bis(trifluoro methylsulfonyl) imide $[\text{Ch}][\text{NTf}_2]$ (synthesized) (Fig. 1).

2.1.1. Functionalization

For each type of non-modified precipitate (dry BaSO_4 and wet BaSO_4) was added one of the following modifying agents: H_2O , 0.7 M aqueous solution of NaCl (surface etching), $[\text{C}_2\text{mim}][\text{NTf}_2]$, $[\text{C}_6\text{mim}][\text{NTf}_2]$, $[\text{C}_{12}\text{mim}][\text{NTf}_2]$, or $[\text{Ch}][\text{NTf}_2]$ (200 μl of liquid to approx. 20 mg of solid BaSO_4). Samples were vigorously mixed (by vortex) and left overnight. Subsequently 1 ml of Milli-Q water was mixed with each sample. Samples were transferred onto a filter (0.45 μm pore diameter) and washed with copious amount of Milli-Q water (approx. 45 ml). These functionalized precipitates were dried for 48 h at 60 °C and used for further characterization. These surface-modified precipitates are designated in this work as dry (or wet) BaSO_4 + modifying agent (IL, H_2O , NaCl).

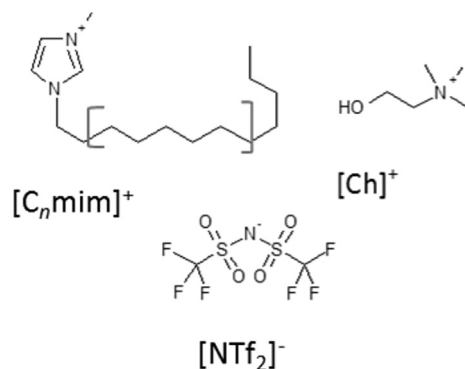


Fig. 1. Structural chemical formulas of the IL ions, $n = 2, 6, 12$. Square brackets indicate adjustable length of the cation alkyl chain.

2.1.2. Functionalization with surface etching

The hydrated BaSO_4 precipitate (wet BaSO_4) was soaked overnight in 0.7 M aqueous solution of NaCl . After this etching step, samples were filtered, washed with Milli-Q water and either dried for 48 h at 60 °C, (BaSO_4 + NaCl)dry, or further used without dehydration, (BaSO_4 + NaCl). Each type of etched (treated with NaCl) precipitate was further functionalized by ILs ($[\text{C}_2\text{mim}][\text{NTf}_2]$, $[\text{C}_6\text{mim}][\text{NTf}_2]$, $[\text{C}_{12}\text{mim}][\text{NTf}_2]$, or $[\text{Ch}][\text{NTf}_2]$) following the same procedure as described above: to the etched BaSO_4 was added one of the ILs (or H_2O), mixed and left overnight, then the sample was filtered, washed and dried before analysis. This material is designated in this work as (BaSO_4 + NaCl) or (BaSO_4 + NaCl)dry + modifying agent (IL or H_2O). A schematic representation of the BaSO_4 synthesis and functionalization can be found in [Supplementary data](#).

2.2. Characterization

2.2.1. FTIR

Fourier transform infrared attenuated total reflectance (FTIR – ATR) spectroscopy was used to access information about interactions of the modifying agents with barium sulfate crystals as well as to verify if the surface attached-ILs are being released to the aqueous solution. Therefore, functionalized and reference precipitates were analysed as prepared or, for the latter purpose, samples were soaked for 24 h in water or in 0.1 M aqueous solution of NaCl (approx. 20 mg of BaSO_4 + ILs in 200 μl of solution). The aqueous phase was then sampled, filtered through a filter with pore diameter of 0.2 μm and analysed. Measurements were performed on a IFS-66/S FTIR spectrometer from Bruker (Bruker Daltonics, MA, USA) using a single reflection ATR cell (DuraDisk). Acquisition was accomplished in the DTGS-detection mode using an accumulation rate of 258 scans at a resolution of 8 cm^{-1} at room temperature in the spectral range of 4000–600 cm^{-1} and was processed using the Opus software package (Bruker) with a wavenumber accuracy of 0.1 cm^{-1} .

2.2.2. UV–vis

UV–vis measurements were performed in order to demonstrate the ability of the IL-functionalized BaSO_4 to scavenge amphiphilic molecules from solution. Additionally UV–vis experiments enabled verifying the possibility of mobilization of the solid-supported ILs into aqueous media at lower detection limits than those provided by FTIR. For those purposes to 10 mg of each type of precipitate was added 1300 μl of Milli-Q water or to 10 mg of (BaSO_4 + NaCl)dry + $[\text{C}_{12}\text{mim}][\text{NTf}_2]$ and to 10 mg of (BaSO_4 + NaCl)dry + H_2O was added 1300 μl of aqueous solution of 0.2 mg/ml of protein

Download English Version:

<https://daneshyari.com/en/article/7923036>

Download Persian Version:

<https://daneshyari.com/article/7923036>

[Daneshyari.com](https://daneshyari.com)