



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Probing the local environment of hybrid materials designed from ionic liquids and synthetic clay by Raman spectroscopy



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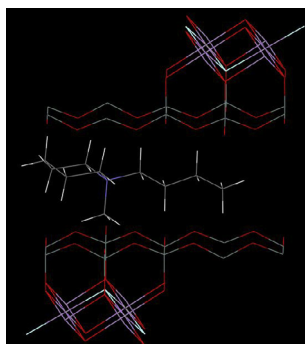
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HIGHLIGHTS

- Laponite and ionic liquids forming cations nanomaterials have been prepared and characterized.
- FT-Raman was employed to investigate the environment of confined organic cations.
- Organic cations are located parallel to the clay slab with a relatively disordered structure.
- The environment probed by these intercalated cations is similar to ionic liquids with TFSI anion.

GRAPHICAL ABSTRACT

In this work, FT-Raman spectroscopy was employed to investigate the local environment probed by ionic-liquid-forming cations in a confined interlayer space of synthetic Laponite clay. Comparison of Raman spectra of pure ionic liquids and the hybrid materials and quantum chemistry calculations was performed to probe the local environment experienced by the confined cations.



ARTICLE INFO

Article history:

Received 22 August 2013
Received in revised form 12 November 2013
Accepted 13 November 2013
Available online 25 November 2013

Keywords:

Clay
Ionic liquid
Raman spectroscopy
Hybrid material

ABSTRACT

Hybrid organic–inorganic material containing Laponite clay and ionic liquids forming cations have been prepared and characterized by FT-Raman spectroscopy, X-ray diffraction, and thermal analysis. The effect of varying the length of the alkyl side chain and conformations of cations has been investigated by using different ionic liquids based on piperidinium and imidazolium cations. The structure of the *N,N*-butylmethyl-piperidinium cation and the assignment of its vibrational spectrum have been further elucidated by quantum chemistry calculations. The X-ray data indicate that the organic cations are intercalated parallel to the layers of the clay. Comparison of Raman spectra of pure ionic liquids with different anions and the resulting solid hybrid materials in which the organic cations have been intercalated into the clay characterizes the local environment experienced by the cations in the hybrid materials. The Raman spectra of hybrid materials suggest that the local environment of all confined cations, in spite of this diversity in properties, resembles the liquid state of ionic liquids with a relatively disordered structure.

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Introduction

Laponite RD is a synthetic smectite-type clay and has a 2:1 layered structure, *i.e.* each layer is formed by one central octahedral sheet $\text{MgO}_4(\text{OH})_2$ placed between two tetrahedral sheets,

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SiO₄ [1,2]. Due to isomorphous substitution of some Mg²⁺ in the octahedral sheet by Li⁺, a residual negative charge on the surface of the slab is developed. Hence, in order to neutralize this negative charge, alkaline or alkaline earth cations are situated into the interlayer space [2,3]. Making use of the moderate negative surface charge, ion exchange reaction can take place, prompting the exchange of the interlayer cations by different species, including organic cations. By exploring this property, hybrid organic-inorganic materials can be yielded using soft chemistry [3–8].

The term hybrid organic-inorganic material comprises several different materials, which combine organic species and structured inorganic materials [3,8]. Among hybrid materials, polymer-clay nanocomposites are being the most investigated systems due to the improvement of mechanic and thermal properties achieved by the composite compared to the pure polymer [3,8–15]. A serious drawback might be faced in the preparation of polymer-clay nanocomposite of non-polar and low thermal stability polymers, which prevent its preparation by the melting process. Thus, an alternative route is available by using polymer solution and the exfoliated clay in non-polar solvent. However, the clay swelling necessary for its exfoliation is hardly accomplished with non-polar solvent due to low hydrophilicity of clays. In this regard, new composites with suitable hydrophobic properties are highly required for preparing polymer-clay nanocomposites [11,15,16]. Hydrophobic modified clays have been prepared by intercalating surfactant [17–20] and ionic liquids [21]. For instance, new hybrid materials formed by Kaolinite and Montmorillonite clay and ionic liquids have been investigated as promising systems for advanced functional applications [22–26]. Not only neutral clays, like Kaolinite, but also those whose surface is negatively charged, have been studied. By using ion exchange reaction, the exchangeable ions are replaced by ionic-liquid-forming cations [21]. Clay hydrophobicity can be adjusted by exploring the tuning property of ionic liquids as achieved by varying the structure of cations.

Ionic liquids usually contain asymmetric large organic cations and more simple anions such as Cl⁻, BF₄⁻, PF₆⁻, CF₃⁻ and SO₃⁻. Common cations include derivatives of imidazolium, piperidinium, pyrrolidinium, alkylammonium etc. These bulky species avoid crystal packing, thus lowering melting or glass transition temperatures [27–29]. Thus, room temperature molten salt, or simply ionic liquid, is a denomination now accepted for purely ionic systems with melting below +100 °C [29]. Certainly, the most important application of ionic liquids is alternative solvent in organic chemistry synthesis, where the non-volatile characteristics make them more environmental friendly than usual organic solvents [29]. Other important applications of ionic liquids are electrolytes for batteries and electrodepositions [29]. On the other hand, the amphiphilic nature of these cations implies that beyond coulombic interactions, significant van der Waals, dipole, and also hydrogen bond interactions are simultaneously present in ionic liquids [30,31]. This characteristic feature of ionic liquids makes them good solvents for molecular or ionic solutes, polar or non-polar species, gases etc. with many applications in extraction processes. The tuning property of ionic liquids achieved by varying the cation structure can be explored to adjust clay hydrophobicity.

Usually, the characterization of either ionic liquid modified clays or organic-inorganic hybrid materials has been performed extensively by thermogravimetric analysis (TG), X-Ray diffraction (XRD), and/or infrared spectroscopy (IR) [20,21,24,32–37]. In the vast majority of the studies, the later technique has been used to confirm the presence of organic cation into the interlayer space by observing the new bands arising from normal modes of the organic cation. It is less common, however, the study of these materials by Raman spectroscopy. Several properties, for instance, hydrogen bonding [38], conformation of alkyl chains [39], ionic pair formation in solutions of lithium salts in ionic liquids

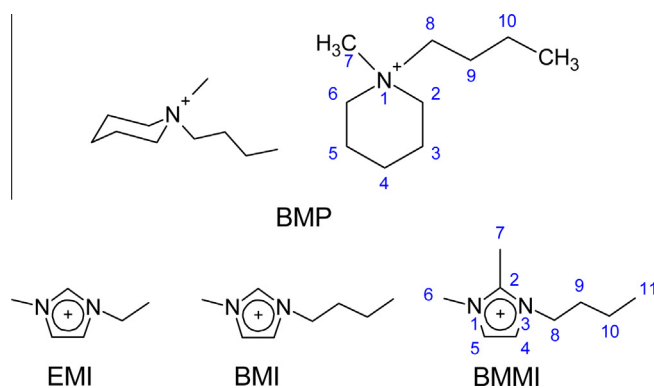


Fig. 1. Structure of ionic liquids precursors cations. BMP means (*N,N*-butyl-methyl-piperidinium), EMI (1-ethyl-3-methylimidazolium), BMI (1-butyl-3-methylimidazolium) and BMMI (1-butyl-2,3-dimethylimidazolium).

[40–42], relaxation process [43], and intermolecular vibration [43] have been investigated by means of Raman spectroscopy of ionic liquids. Therefore, Raman spectroscopy can be used to indicate the presence of cations into the clay and also employed as a tool for providing information about the local environment probed by the cation into the interlayer space.

In this work, we use Raman spectroscopy to investigate the local environment probed by ionic-liquid-forming cations in a confined space. In this regard, we prepared hybrid organic-inorganic materials, in which Laponite RD was modified with four different ionic-liquid-forming cations showed in Fig. 1. These cations were properly chosen in order to evaluate effects of chain length, ability of developing hydrogen bond, and electronic delocalization of their positively charged region. Usual techniques for characterizing hybrid organic-inorganic materials, namely mass spectrometry coupled thermogravimetric analyses (TG-MS) and XRD were also used.

Methods

Materials

Laponite (LAP), RD grade, was obtained from Southern Clay Products Inc and was used as received. It has an empirical formula of Na_{0.7}⁺[(Si₈Mg_{5.5}Li_{0.3})O₂₀(OH)₄]_{0.7}⁻ (charge deficiency of 0.7 charge per unit cell) and a cation exchange capacity of 50–55 mmol per 100 g [44]. *N,N*-butyl-methyl-piperidinium bromide (BMPBr), *N,N*-butyl-methyl-piperidinium bis(trifluoromethylsulfonyl)imide (BMPTFSI), 1-*n*-butyl-2,3-dimethylimidazolium bromide (BMMIBr) and 1-*n*-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide (BMITFSI) were synthesized following the procedure previously reported [45]. 1-*n*-butyl,3-methylimidazolium bromide (BMIBr) and 1-*n*-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide (BMMITFSI), 1-ethyl-3-methylimidazolium ethylsulphate (EMIEtSO₄) (Merck), 1-ethyl-3-methylimidazolium chloride (EMICI) (Aldrich) were used as received.

Preparation of ion-exchanged layered silicates

Standard ion exchange procedures were employed for the preparation of hybrid materials. Briefly, in the BMPLAP preparation, 0.5 g of BMPBr (2.1 mmol) was added to a suspension containing 1.0 g (1.3 mmol) of Laponite RD and 100 mL of deionized H₂O. This mixture was stirred at room temperature for 24 h. The solid was collected by filtration and subsequently washed exhaustively with deionized H₂O until an Ag_(aq)⁻ test indicated the absence of halide anions. The filter cake was dried at 120 °C for 5 h, ground, and the final powder was stored under vacuum with silica gel

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