

## Electrorheological and dielectric behavior of new ionic liquid/silica systems

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### ABSTRACT

New phosphonium-based ionic liquids, denoted, 11-carboxyundecyltriphenylphosphonium bromide (IL1) and octadecyltriphenylphosphonium iodide (IL2), were employed on the sol–gel synthesis to prepare new silica-based matrices. The fastest gelation during the sol–gel process was observed in hydrolysis/condensation of tetraethoxysilane in the presence of IL1. The confinement of ionic liquids (especially IL1) inside the silica networks was suggested by thermogravimetric analysis and Fourier transform infrared spectroscopy. The resulting ionogels present higher permittivity than pure silica and were used as the solid component for the development of new electrorheological fluids, presenting good ER behavior, mainly those prepared with IL1.

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### 1. Introduction

Electrorheological (ER) fluids are constituted by a colloidal suspension of polarizable or semi-conducting solid organic or inorganic particles in an insulating liquid medium, which exhibits drastic change in their rheological properties under an applied electric field [1]. This behavior associated with the quick and reversible viscous fluid – solid-state transition offers several potential applications as electrical clutches, dampers, robotics, servo devices, etc. The ER response depends on several parameters such as dielectric properties of the solid particle, its volume fraction, size, and morphology. Among several particles employed as component of the ER fluids, silica has been one of the most popular because of its low cost and its easy preparation with tuned properties using the well-known sol–gel process [2]. The presence of small amount of water usually enhances the ER effect of silica-based suspensions [3,4]. However, the presence of water causes several drawbacks such as narrow working temperature range, high current density, etc. Several other strategies have been developed to enhance the ER effect of silica-based suspensions. Pavlínek et al. [5] observed an improvement of the ER effect in suspensions of non-treated silica or silica particles treated with 3-aminopropyl(triethyl)-silane or 2-cyanoethyl(triethoxy)-silane. Cherif et al. [6] prepared silica

particles through the sol–gel process in the presence of chloride solution of metallic cations of cobalt or zirconium and observed a great improvement of the ER behavior of the suspensions of silica with zirconium cation trapped into its network. Agaforov et al. [7] also used the sol–gel technique to prepare silica in the presence of different amines as templates and reported a great ER effect in suspensions of mesoporous silica that contains the organic compounds. Recently, we prepared silica modified with mercapto groups and observed a good ER response of the corresponding silicone oil suspension [8].

Due to their unique properties such as excellent thermal and chemical stability, good ionic conductivity, negligible vapor pressure, ionic liquids (ILs) have been attracted enormous interest [9]. Nowadays, they can find important applications as a new “green solvent” for several organic syntheses and polymerization, as plasticizers, polymer electrolytes, etc. [10]. More recently, ILs have emerged as a versatile component for the sol–gel process, most of them involving silicon alkoxide precursors [11] They are employed as additive to assist the sol–gel process and to obtain xerogel silica with controlled morphology [12–16] or as template to obtain monolithic mesoporous silica [17,18]. Additionally, there are several papers in the literature dealing with the preparation of ionogels where the IL is confined inside the silica networks [19–21], which are of great interest on the development of electrolytic membranes. The presence of confined IL changes the dielectric properties of the silica particles and may enhance the ER properties of the corresponding suspensions in a liquid medium. Due to their

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low volatility, the corresponding fluids can be used at high temperature than those which employ volatile additives. The use of ionic components to improve the ER effect was reported by Cho et al. [22], who studied the effect of pendent ionic groups on polyaniline derivatives. Also, Sedlacik et al. [23] observed an improvement of the ER activity of titanium oxide hollow globular particles when covered by polypyrrole, which was attributed to an increase in the particle polarizability. Bicaik et al. [24] investigated the vibration damping of pure ionic liquid based on (2-hydroxyethylammonium formate) under electric and magnetic field and observed that the IL was not stimulated by magnetic field, but presented high vibration damping in the presence of low electric field.

To the best of our knowledge, there is no report in the available literature dealing with the use of silica/ionic liquid systems as a solid component in the ER fluids. Therefore, the aim of the present communication is to prepare silica particles from tetraethoxysilane through the sol–gel method in the presence of two different triphenylphosphonium-based ionic liquids and evaluate the performance of the corresponding ionogels as solid components in electrorheological fluids.

## 2. Experimental

### 2.1. Materials

Tetraethoxysilane (TEOS), ethanol, 11-bromoundecanoic acid, triphenylphosphine, and octadecyl iodide (95%) were analytical grade, supplied from Aldrich and used as received. The silicone oil was purchased from Rhodorsil 47V 500 ( $\epsilon' = 2.64$ ;  $\sigma = 1 \times 10^{-12} \text{ S cm}^{-1}$ ; kinematic viscosity  $475\text{--}525 \text{ mm}^2 \text{ s}^{-1}$ ; density  $0.97 \text{ g cm}^{-3}$ ).

### 2.2. Synthesis of phosphonium-based ionic liquids

The structures of the ionic liquids used in this work are illustrated in Fig. 1. The octadecyltriphenylphosphonium iodide (IL2) was prepared according to the literature [25]. In a typical procedure, 5 g of the triphenylphosphine and 7.3 g of the octadecyl iodide were mixed with 20 mL of toluene in a 100 mL flask under nitrogen atmosphere. The stirred suspensions were allowed to react for 24 h at  $120^\circ\text{C}$  when a yellow precipitate was formed. The reaction mixture was filtered and washed repeatedly with pentane. Most of the solvent was removed under vacuum.

The 11-carboxyundecyltriphenylphosphonium bromide (IL1) was synthesized as follows: 4.73 g of the 11-bromoundecanoic acid and 5 g of the triphenylphosphine were mixed together with 20 mL of toluene under nitrogen atmosphere. The system was reacted for 24 h at  $120^\circ\text{C}$  under stirring and nitrogen atmosphere. The reaction mixture was filtered and washed repeatedly with hexane. The structure was confirmed by  $^{13}\text{C}$  NMR spectroscopy, whose spectrum is shown in Fig. 2 (yield = 90–93%; mp =  $110^\circ\text{C}$ ).

### 2.3. Synthesis of silica particles

18.8 g (0.09 mol) of TEOS was slowly added to a stirred solution containing 24 g (1.3 mol) of distilled water and 28.4 g (0.62 mol) of ethanol. After the TEOS addition, the medium was kept under stirring at room temperature until the complete gel formation and the evaporation of the volatile compounds. The ionogels containing IL1 and IL2 were prepared similarly, with the previous addition of 1 g of IL into the water/ethanol solution.

### 2.4. Characterization

$^{29}\text{Si}$  CPMAS solid-state nuclear magnetic resonance spectra of the samples were recorded on a VARIAN spectrometer, operating at 4 MHz, 7.05 T and  $4.5 \mu\text{s}$ . It was employed a rotation speed of 4 kHz, 2 ms of contact time and pulse interval 60 s. Chemical shifts were referenced to tetramethylsilane (TMS) as external standard, 1000 accumulations during 18 h.

Dynamic light scattering (DLS) measurements were performed using the Zetasizer nanoseries Nano-ZS Malvern Instruments. Dilute solutions of silica, silica/IL1, and silica/IL2 in ethanol were employed.

Rheological measurements were performed using the Anton Paar Instruments Physical RMC 302 rheometer with electrorheological accessory (Generator HVS/ERD80 – DC), (Generator Model 609E-6 High voltage amplifier TREK with Multimeter Hameg Instruments – AC), and plate–plate geometry (PP50/E-SN12613 gap 1 mm). The suspensions were prepared by dispersing the particles in silicone oil in a concentration of 10 wt.%, with the help of ultrasonic apparatus operating at 20% amplitude for 5 min.

Dielectric properties and conductivity were measurements using the Impedance analyzer Hewlett–Packard HP, model 4192A LF operating at 5 V and at frequency range from 5 to  $10^6$  Hz.

Surface energy of modified silicas was determined with the sessile drop method using a GBX goniometer. From contact angle measurements performed with water and diiodomethane as probe liquids on disks obtained from silica powders by pressing, polar and dispersive components of surface energy were determined by using Owens–Wendt theory.

## 3. Results and discussion

### 3.1. The sol–gel processing and characterization of silica networks

The preparation of the silica particles through the sol–gel process was performed in the presence of two different ionic liquids under mild conditions, without the addition of acidic or basic catalyst. Table 1 summarizes the reaction recipes and some feature of the sol–gel process and particle density. At the beginning, the pH of the medium was around 8 for the system prepared without IL, but significantly decreased in the systems containing IL. This characteristic also affects the velocity of the sol–gel process. The gelation occurred after 8 days of stirring at room temperature for the system without IL. Systems containing IL presented a substantial de-

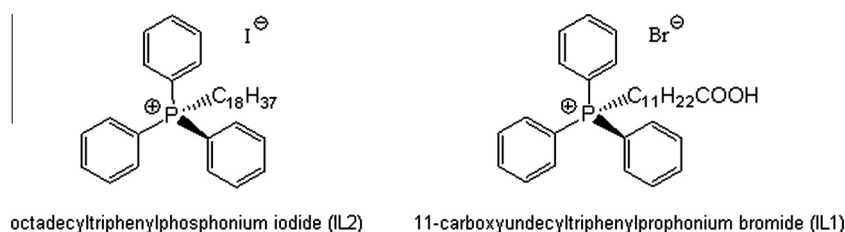


Fig. 1. Structure of the phosphonium-based ILs.

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