



Conductivity and viscosity properties of associated ionic liquids phosphonium orthoborates

Alejandro García ^a, Luis C. Torres-González ^a, Karinjilottu P. Padmasree ^b,
 Maria G. Benavides-García ^c, Eduardo M. Sánchez ^{a,*}

^a Laboratorio de Materiales para Almacenamiento y Conversión de Energía, Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, Cd. Universitaria, San Nicolás de los Garza N.L. 66450, México

^b CINVESTAV, Unidad Saltillo, Carr. Saltillo – Monterrey km 13.5, C.P. 25900, México

^c University of Houston-Downtown, Department of Natural Sciences, Houston, TX 77002, United States

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ABSTRACT

A new group of room temperature molten salts based on asymmetric isobutyl(trihexyl)phosphonium cation with different chelated orthoborate anions are presented in this report. The physicochemical properties of these compounds as glass transition temperature, thermal stability, viscosity and conductivity are determined and discussed on structural basis. The highest room temperature conductivity observed was for the isobutyl(trihexyl)phosphonium bis(malonate)borate. The results indicate that the prepared orthoborates have lower viscosities, better conductivities when compared to their precursor, isobutyl(trihexyl)phosphonium bromide. Our investigation has found that those new compounds have an intermediate-to-fragile behavior. We plotted the conductivity and viscosity data according to Walden's rule and found that they can be classified as an associated ionic liquid (AIL) an intermediate between a true ionic liquid and a molecular species.

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1. Introduction

Ionic liquids (ILs) are molten salts at room temperature and are composed of a cation and anion having a melting point lower than 373 K. These compounds have a variety of useful properties like low vapor pressure, high thermal and electrochemical stability, non-flammability, good solvent miscibility and high conductivity [1]. These qualities make them useful in a diversity of applications such as catalysis, electrochemistry, photochemistry, organic synthesis, solar cells, batteries and fuel cells [2,3]. Regarding ILs, generally one or both of the ions are large and should preferably be unsymmetrical [4]. These factors tend to reduce binding energy in the crystalline network giving properties to ILs such as existing in the liquid state at temperatures well below 373 K. ILs are known as designer solvents, and one of their most important advantages is their physicochemical properties and their phase behavior of the systems that can be tuned/controlled by tailoring their structures [5]. In particular, ionic liquids used for electrochemical devices include imidazolium, quaternary ammonium, pyridinium, pyrrolidinium and piperidinium derivatives [6]. Recently, phosphonium molten salts have found use in electrochemical applications. For instance, these salts have been used successfully for electrodeposition on CdS [7], alkali metals [8], Titanium [9] and Al [10], among others. Additionally, phosphonium ionic liquids

have been proposed for electrochemical devices such as capacitors [11], lithium batteries [12] and solar cells [13].

Perfluorinated-based molten salts are the common choice for electrochemical applications but they are relatively expensive and they could be hydrolyzed to generate hydrogen fluoride (HF) in the presence of water traces [14]. To overcome this situation, several alternatives had been investigated. For instance, chelated orthoborate anions of different N-containing cations have been reported by Angell's group [15]. However, they were found to have higher glass transition temperatures and room-temperature viscosities than those with perfluorinated anions. At first glance, those compounds are too viscous for most practical applications but they have many attractive properties as model IL systems for fundamental studies. Nevertheless, tighter safety regulations and cost-wise issues place a potential demand for the use of nonhalogenated electrolytes for electrochemical devices in the near future. Therefore, several orthoborate ionic liquids have been proposed as electrolyte additives to improve stability on lithium batteries [16,17] and electrochemical capacitors [18]. Our research group is seeking alternative routes to decrease glass transition and viscosity and we recently reported [19] the use of asymmetric phosphonium ILs as an attempt to hinder crystallization on an assortment of molten iodide salts. As a continuation of such efforts, we present on this work the conductivity and viscosity of new room temperature ionic liquids made by the combination of asymmetric isobutyl(trihexyl)-phosphonium cation with a variety of orthoborate anions. In particular, we compared their conductivity, viscosity and fragility behavior to similar molten systems and

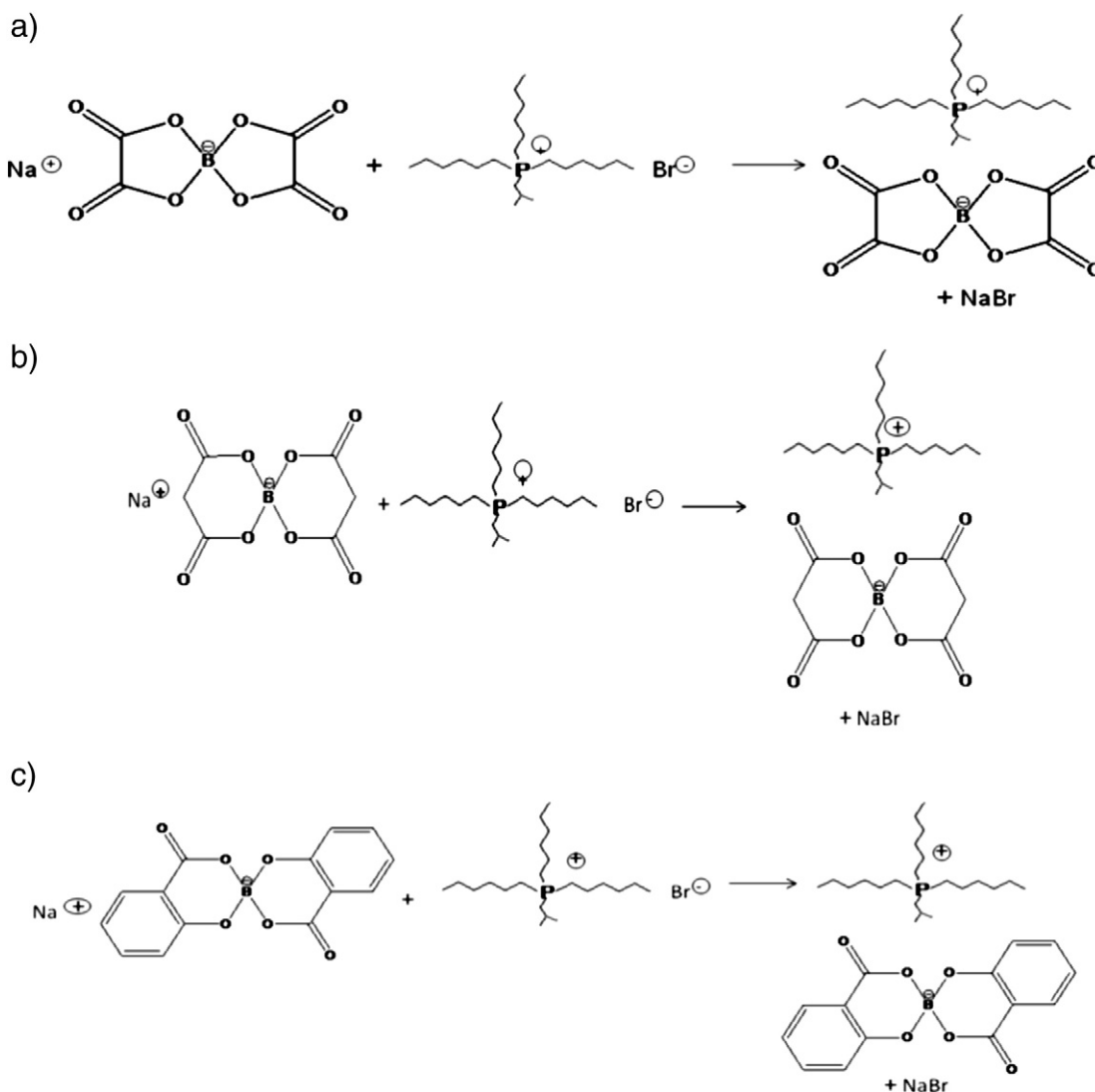
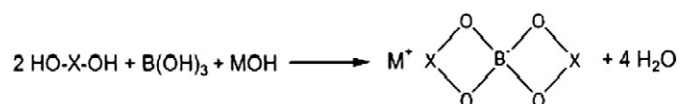
* Corresponding author.

E-mail address: eduardo.sanchezcv@uanl.edu.mx (E.M. Sánchez).

attempt to explain these properties using structural considerations. Furthermore, their conductivity and viscosity data are plotted under Walden's rule, where ion association plays a major role.

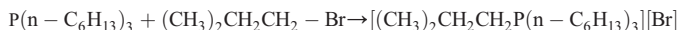
2. Experimental

All reagents used in this work were from Aldrich, except for trihexylphosphine (Cytec) and all of them were used as received. Sodium bis(oxalate)borate (NaBOB), sodium bis(salicylate)borate (NaBSB) and sodium bis(malonate)borate (NaBMB) were prepared by complete evaporation of water from the aqueous solutions of the corresponding organic acid (oxalic acid, salicylic acid and malonic acid respectively) along with boric acid and sodium hydroxide in a 2:1:1 molar ratio. This procedure was previously proposed by [15]. A white solid material was obtained on the three cases and were washed with ethanol, then filtered and dried inside a vacuum oven (Shel Lab 1410) at 353 K for two days. The reaction is as follows



where X is oxalate, malonate, and salicylate respectively.

Intermediate iso-butyl-tri-n-hexyl-phosphonium bromide (iBH₃P-Br) preparation [20] was performed according to:



where iBH₃P-Br was synthesized by refluxing 1-bromo-2-methylpropane with 10% excess of trihexylphosphine for 5 h at 423 K followed by addition of 3 parts of petroleum ether for separation. The colorless liquid was dried in a vacuum oven at 343 K for 7 days.

Phosphonium bromide was reacted with excess of sodium orthoborate salt in anhydrous acetonitrile under refluxing for 6 days at 353 K (see Fig. 1). After cooling, the precipitated sodium bromide was filtered off and the solvent in the filtrate was evaporated. The residue was dried in a vacuum oven at 353 K for one day and then dissolved in a large amount of dichloromethane. The solution was allowed to stand at room temperature in order for remaining sodium orthoborate salt to precipitate. After filtration and evaporation of the solvent, the liquid residue was dried in a vacuum oven at 363 K for 2 days to yield phosphonium orthoborate liquid.

Nuclear magnetic resonance (NMR) spectroscopy was used for structure confirmation of the orthoborates in deuterated acetonitrile.

Fig. 1. Synthesis of phosphonium orthoborates. (a) Iso-butyl-(tri-n-hexyl)-phosphonium Bis(oxalate)borate (iBH₃P-BOB), (b) Iso-butyl-(tri-n-hexyl)-phosphonium Bis(malonate)borate (iBH₃P-BMB) and (c) Iso-butyl-(tri-n-hexyl)-phosphonium Bis(salicylate)borate (iBH₃P-BSB).

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