



# Physicochemical characterisation of aqueous solutions of tetra-alkyl-ammonium-sulfonic acid ionic liquid



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## ABSTRACT

Zwitterionic ionic liquids (ILs) exhibit excellent characteristics when employed as electrolytes in water electrolysis. A good example of these ILs is 3-triethylammonium-propanesulfonic acid tetrafluoroborate ionic liquid (TEA-PS.BF<sub>4</sub> IL), which has great advantages like high efficiency and high current density when used as an electrolyte in water electrolysis. The excellent performance of TEA-PS.BF<sub>4</sub> IL in relation to other electrolytes and its promising use in electrochemical and other applications is better understood through the physicochemical properties of TEA-PS.BF<sub>4</sub> ionic liquid. Linear dependence between the density and IL molar concentration (0.001 M to 0.70 M) was observed; moreover, the viscosity did not change significantly at low concentrations but at high concentrations. In dilute aqueous solutions, TEA-PS.BF<sub>4</sub> IL showed the behaviour predicted by the Kohlrausch law and it was possible to calculate the value of the diffusion coefficient of IL. The molar conductivity was calculated with the Nernst-Haskell equation, the self-diffusion coefficients of ions at infinite dilution were calculated with the Nernst-Einstein equation and the hydrodynamic radius of each ion was calculated with the Stokes-Einstein equation. Comparison of the TEA-PS.BF<sub>4</sub> with other ILs showed that it has the highest diffusion coefficient ( $1.77 \times 10^{-9} \text{m}^2 \text{s}^{-1}$ ).

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## 1. Introduction

In the past 20 or 30 years, ionic liquids (ILs) have been one of the most exciting scientific discoveries in chemical science. Nowadays, the most accepted definition of an IL is a low melting salt that melts at or below 100 °C, which is normally composed of a large asymmetric organic cation and an inorganic or organic anion [1–5]. ILs are novel materials with many interesting properties including low vapour pressure, wide liquid phase regions, solubility in a wide range of organic solvents and high conductivity and stability [6–10]. Therefore, they are good candidates for a number of challenging applications, such as acting as solvents in chemical reactions in organic, inorganic, polymer chemistry and electrochemistry [11–13].

Because of their high ionic conductivity and wide electrochemical windows, ionic liquids are excellent candidates for electrolytes and avoiding corrosion. Their unique combination of properties is suitable for a wide range of applications in electrochemical technologies as solvent-free electrolytes in various devices and processes [13], such as rechargeable lithium batteries [3,4,14,15], fuel cells [16–18], electrochemical capacitors [19,20], dye-sensitised solar cells [21,22] and electrolyzers [10,23].

Among the many ILs that exist, Brønsted–Lewis acidic combined ionic liquids display excellent characteristics for use in water electrolysis. As we know, both Lewis and Brønsted acid sites are important for acid catalysed reactions and ionic liquid functionalised with both Lewis and Brønsted acid sites would become more efficient. Such combined ionic liquids have the characteristics of both Brønsted and Lewis acids. Their preparation is usually based on the synthesis of a Brønsted acid containing one or more functional groups proton donor and a halide anion followed by reaction with a metal chloride or fluoride [8,24,25].

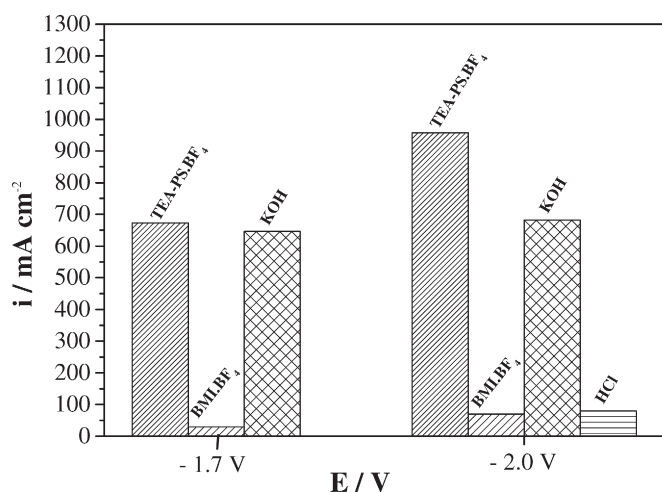
A good example of Brønsted–Lewis acid ionic liquid is 3-triethylammonium-propanesulfonic acid tetrafluoroborate ionic liquid (TEA-PS·BF<sub>4</sub>). When used as electrolyte in water electrolysis it offers great advantages like high efficiency (exceeding 93%) and high current density (between 80 at 960 mA cm<sup>-2</sup>) [10,26].

Such excellent behaviour is accompanied by an increase in the amount of hydrogen produced from the water electrolysis. Comparison of the results for TEA-PS.BF<sub>4</sub> with those of other electrolytes like KOH, BMI.BF<sub>4</sub> IL and HCl verifies the exceptional performance of this IL. For example, at –1.7 V, systems using BMI·BF<sub>4</sub> (0.7 M) and KOH (0.7 M) produce current densities of 35 and 650 mA cm<sup>-2</sup>, respectively, and when TEA-PS.BF<sub>4</sub> (0.7 M and pH 0.8) is used the system produces 670 mA cm<sup>-2</sup>. When the applied potential is 2.0 V, systems using BMI.BF<sub>4</sub> (0.7 M), KOH (0.7 M) and HCl (pH 0.8) produce current densities of 70, 682 and 80 mA cm<sup>-2</sup>, respectively, and used TEA-PS.BF<sub>4</sub> (0.7 M and pH 0.8) the system produces 960 mA cm<sup>-2</sup>. Fig. 1 compares the behaviour of different systems and different potentials applied.

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**Fig. 1.** Effect of the potential on the current density used to perform water electrolysis with different electrolytes: TEA-PS·BF<sub>4</sub> (0.7 M and pH 0.8), BMI·BF<sub>4</sub> (0.7 M), KOH (0.7 M) and HCl (pH 0.8). Conditions: 298 K; working electrode surface: Pt [10].

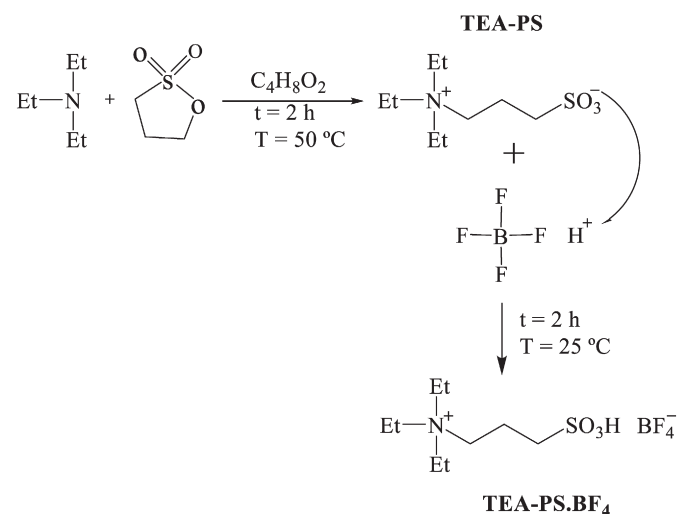
Analysis of the results shows the excellent performance of TEA-PS·BF<sub>4</sub> in relation to other electrolytes and suggests a promising future for this IL in electrochemical and other applications. Therefore, it is essential to acquire more details about this IL, such as the physicochemical properties of TEA-PS·BF<sub>4</sub> ionic liquid, including its density, viscosity, and conductivity, and determination of the diffusion coefficient at infinite dilutions.

The aim of this paper is to describe the physicochemical properties of TEA-PS·BF<sub>4</sub> IL in infinite dilutions for better understanding of the behaviour of TEA-PS·BF<sub>4</sub> IL as electrolyte in water electrolysis and in other electrochemical devices.

## 2. Experimental

### 2.1. Synthesis of TEA-PS and TEA-PS·BF<sub>4</sub>

TEA-PS and TEA-PS·BF<sub>4</sub> were prepared as described in previously published reports [10,27] and as shown in Fig. 2. In a typical reaction, 1,3-propanesultone (51.38 g) and triethylamine (42.46 g) are mixed with ethyl acetate (20 mL). The reaction is stirred at 50 °C for 2 h and filtered, producing a white solid. The precipitate is washed with three 10 mL aliquots of ethyl acetate and dried at 100 °C for 2 h, producing



**Fig. 2.** Synthesis of 3-triethylammonium-propanesulfonic acid tetrafluoroborate ionic liquid.

3-triethylammonium-propanesulfonate (TEA-PS) as a white powder in 61% yield [10]. <sup>1</sup>H NMR (300 MHz, DMSO, ppm): δ 1.18 (t, 3 H), 1.89 (m, 2 H), 3.21 (m, 2 H), 3.42 (m, 2 H).

TEA-PS·BF<sub>4</sub> was prepared by reacting TEA-PS (1:1) tetrafluoroboric acid (HBF<sub>4</sub>) at room temperature. After 2 h at 90 °C, the water was removed under reduced pressure, producing 75.98 g of 3-triethylammonium-propanesulfonic acid tetrafluoroborate ionic liquid (TEA-PS·BF<sub>4</sub>), a white viscous liquid, in 96 % yield [10]. <sup>1</sup>H NMR (300 MHz, DMSO, ppm): δ 1.17 (t, 3 H), 1.88 (m, 2 H), 3.22 (m, 2 H), 3.32 (m, 2 H), 4.23 (s, 1 H). <sup>13</sup>C NMR (75 MHz, DMSO, ppm): δ 7.00, 17.78, 47.35, 51.97, 54.88.

### 2.2. Density measurements

When determined the densities were used TEA-PS·BF<sub>4</sub> IL solutions in different concentrations. A volumetric pipette 5 mL, previously calibrated, was used as standard. The determinations followed the equation  $d = m/V$ , where  $d$  is the density of solutions in  $g \cdot cm^{-3}$ ,  $m$  is mass in g of IL weight and  $V$  is the volume solution used for weighing, as determined by previous calibration. All measurements were performed under controlled temperature of 298 K and in triplicate.

### 2.3. Viscosity measurements

Viscosity measurements were carried out for TEA-PS·BF<sub>4</sub> IL solutions in different concentrations, in an Ostwald viscometer, under controlled temperature of 298 K. Calculation of viscosity was performed with the equation  $\eta = kt\rho$  where  $\eta$  is viscosity (cP),  $\rho$  is the solution density, viscosity  $k$  is a constant,  $t$  is time of flow, and  $t$  is the flow average of five times measured in the Ostwald viscometer.

### 2.4. Conductivity measurements

The specific conductivities of the solutions were measured using a Hach Sension 7 conductivity meter. Measurements were taken of electrolyte solutions under controlled temperature of 298 K.

## 3. Results and discussion

The following physicochemical properties were determined for TEA-PS·BF<sub>4</sub> IL: density, viscosity and conductivity, in addition to determination of the diffusion coefficient and the hydrodynamic radius, in order to evaluate its potential use as aqueous electrolyte in electrochemical processes.

### 3.1. Density

The results of the determination of the densities for aqueous solutions of TEA-PS·BF<sub>4</sub> IL versus concentration are shown in Fig. 3, the IL molar concentration ranges from 0.001 to 0.70 M.

As shown in Fig. 3, there is a linear dependence between the density and IL molar concentration. In concentrated IL aqueous solutions, the density is greater because of the higher molecular weight of the solute (311  $g \cdot mol^{-1}$ ) relative to the solvent. Consequently, when the mass of solute decreases, the density decreases. The same behaviour was also observed by Ries et al. [28] when they investigated the densities of binary mixtures like BMI·BF<sub>4</sub> IL, by Królikowska and colleagues et al. [29] when they investigated the densities of aqueous mixtures of some ionic liquids like 1-ethyl-1-methyl-piperidinium ethylsulfate (EMPIP·EtSO<sub>4</sub>), 1-ethyl-1-methylmorpholinium ethylsulfate (EMMOR·EtSO<sub>4</sub>) and 1-ethyl-1-methylpyrrolidinium ethylsulfate (EMPYR·EtSO<sub>4</sub>); and by Liu et al. [30], who also found similar behaviour when they studied the physicochemical properties of binary systems involving imidazoles and water. In all previously reported cases, the densities of ILs are higher when they are in pure state. With the increase of water content, the density

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