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PAPER

# Novel halogen-free chelated orthoborate–phosphonium ionic liquids: synthesis and tribophysical properties†

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Received 11th April 2011, Accepted 18th May 2011

DOI: 10.1039/c1cp21139k

We report on the synthesis, characterisation, and physical and tribological properties of halogen-free ionic liquids based on various chelated orthoborate anions with different phosphonium cations, both without halogen atoms in their structure. Important physical properties of the ILs including glass transition temperatures, density, viscosity and ionic conductivity were measured and are reported here. All of these new halogen-free orthoborate ionic liquids (hf-BILs) are hydrophobic and hydrolytically stable liquids at room temperature. As lubricants, these hf-BILs exhibit considerably better antiwear and friction reducing properties under boundary lubrication conditions for steel–aluminium contacts as compared with fully formulated (15W-50 grade) engine oil. Being halogen free these hf-BILs offer a more environmentally benign alternative to ILs being currently developed for lubricant applications.

## 1. Introduction

Ionic liquids (ILs) are salts, which are liquid at temperatures <100 °C. The cations are generally organic compounds with low symmetry, while anions are usually weak base inorganic or organic species.<sup>1</sup> ILs exhibit many unusual properties compared to molecular liquids, which make them useful in a wide range of applications.<sup>2</sup> Some of their unique properties include, in certain cases, favorable solubility of organic and inorganic compounds, relatively high ionic conductivity, low vapour pressure, high thermal stability, low flammability and designability of cations and anions for specific applications.<sup>3</sup> ILs are already providing unique capabilities in organic synthesis,<sup>4,5</sup> catalysis,<sup>6–8</sup> and electrochemistry,<sup>9–11</sup> and used as recyclable solvents for a variety of chemical reactions and in separation processes,<sup>12,13</sup> as active pharmaceutical ingredients,<sup>14,15</sup> as

alternatives to traditional organic diluents for solvent extraction of metal ions,<sup>16–18</sup> and as functional materials.<sup>19–21</sup>

Ionic liquids can be synthesised for specific applications by targeting the molecular design of both the cations and anions. A chemical functionality can be selected to provide a specific property required in the IL. Functionalised ILs are of particular interest for controlling processes at solid–IL interfaces. Ions of an IL may either physisorb or chemisorb at a surface, forming a thin interfacial layer. A physisorbed ionic liquid layer (PhILL) on surfaces of a solid matrix can be either organic or inorganic in nature. A chemisorbed ionic liquid layer (ChILL) is formed when ionic moieties are chemically bonded to surface active sites of the matrix.<sup>22</sup> It has been reported that ILs may form both physisorbed and chemisorbed surface films on ceramic surfaces and on a variety of light metals such as lithium, aluminium, magnesium and their alloys.<sup>23–25</sup>

A recently emerging application of ILs has been in challenging tribological contacts. During the past decade, ILs have been extensively investigated as lubricants, additives to lubricants and as thin films. Ye *et al.* has reported that ILs can be used as versatile lubricants at tribological contacts with a wide variety of materials including steel, aluminium, copper, silicon dioxide, silicon nitride, aluminium oxide and sialon ceramics.<sup>26</sup> The interest in ILs as novel lubricants in various applications is steadily increasing due to their unique combination of physical, chemical and tribological properties.<sup>27–30</sup> Recent reviews have summarised advances in tribological applications of ILs as future lubricants reducing friction and wear at the interfaces of both ferrous and non-ferrous materials.<sup>31–34</sup>

The most studied ILs in tribological applications usually contain tetrafluoroborate (BF<sub>4</sub><sup>−</sup>) and hexafluorophosphate

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† Electronic supplementary information (ESI) available: Synthesis and characterisation detail, ESI-MS and (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>11</sup>B) NMR spectra of all the synthesised halogen-free orthoborate ionic liquids (hf-BILs) and 3D images of the discs. See DOI: 10.1039/c1cp21139k

(PF<sub>6</sub><sup>−</sup>) anions.<sup>35,36</sup> It is known that compounds containing boron and/or phosphorous have excellent tribological properties under high pressures and elevated temperatures in the lubricated contacts.<sup>37–40</sup> Tribochemical processes that take place at the interfaces lubricated with boron-based ILs lead to formation of surface layers containing B<sub>2</sub>O<sub>3</sub> and BN,<sup>41,42</sup> similarly, metal phosphates are formed from phosphorous-containing ILs.<sup>43–45</sup> These layers protect surfaces from a direct surface-to-surface contact and reduce both friction and wear. However, BF<sub>4</sub><sup>−</sup> and PF<sub>6</sub><sup>−</sup> anions have high polarity and absorb water. These anions are very sensitive to moisture and may hydrolyse to produce hydrogen fluoride among other products. These products cause corrosion by various tribochemical reactions, which can damage the substrate in the mechanical system.<sup>46–48</sup> In addition, halogen containing ILs may release toxic and corrosive hydrogen halides to the surrounding environment.<sup>49,50</sup> Replacing BF<sub>4</sub><sup>−</sup>, PF<sub>6</sub><sup>−</sup> and other hydrophilic or halogen containing anions with more hydrophobic or halogen-free anions is one of the possible ways to avoid corrosion and toxicity.<sup>51</sup> Therefore, the development of new hydrophobic and halogen-free anions containing ILs is highly desired in industrial applications. Recently, Yang *et al.* have prepared two chelated orthoborate ILs, 1-butyl-3-methylimidazolium bis(oxalato)borate and 1-hexyl-3-methylimidazolium bis(oxalato)borate and studied their thermodynamic properties.<sup>52</sup> These authors have found that ILs of this type have high heat capacities and elevated glass-transition temperatures (235–240 K) compared to ILs with the same cations but different halogen-containing anions.

Despite the important human health and environmental problems and urgency for proper lubrication of the new mechanical systems, ILs with hydrophobic and halogen-free boron based anions are yet to be established in tribological applications. In this study, we, therefore, report on the development, physicochemical and tribological characterisation of new halogen-free orthoborate ionic liquids (hf-BILs). A new family of hf-BILs was systematically synthesised and a detailed study of their physicochemical properties, including thermal behaviour, density, viscosity, ionic conductivity, and tribological properties, was carried out. The tribological properties were studied with 100Cr6 steel balls on AA2024 aluminium disc in a rotating pin-on-disc test. To the best of our knowledge, this is the first tribological study on halogen-free, hydrophobic and hydrolytically stable boron based anions containing ILs. This development may provide a platform to the researchers and lubricant companies for designing novel lubricants with improved tribological and environmental performances. A detailed tribological study of hf-BILs for ferrous and other non-ferrous materials is in progress and will be published elsewhere.

## 2. Experimental section

### 2.1 Chemicals

Boric acid (BDH, 99.8% purity), lithium carbonate (Aldrich, 99.99% purity), mandelic acid (Merck, for synthesis), malonic acid (Merck, for synthesis), oxalic acid (Merck, for synthesis), salicylic acid (UNILAB Australia, >99.5% purity),

tributyloctylphosphonium chloride (Cytec), tributyltetradecylphosphonium chloride (Cytec), trihexyltetradecylphosphonium chloride (Cytec) and dichloromethane were used as received.

### 2.2 Synthesis

All these novel hf-BILs were synthesised by using a slightly modified methods reported in the literature.<sup>53,54</sup> Only one representative example of the synthesis is given below, while synthetic details including yields, and MS (ESI) and NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, <sup>11</sup>B) data for other hf-BILs are given in ESI.†

**2.2.1 Synthesis of tributyl-octylphosphonium bis(mandelato)-borate [P<sub>4,4,4,8</sub>][BMB].** Mandelic acid (3.043 g, 20 mmol) was added slowly to an aqueous solution of lithium carbonate (0.369 g, 5 mmol) and boric acid (0.618 g, 10 mmol) in 50 mL water. The solution was heated up to about 60 °C for two hours. The reaction was cooled to room temperature and tributyl-octylphosphonium chloride (3.509 g, 10 mmol) was added. The reaction mixture was stirred for two hours at room temperature. The organic layer of reaction product formed was extracted with 80 mL of CH<sub>2</sub>Cl<sub>2</sub>. The CH<sub>2</sub>Cl<sub>2</sub> organic layer was washed three times with 100 mL water. The CH<sub>2</sub>Cl<sub>2</sub> was rotary evaporated at reduced pressure and the product was dried in a vacuum oven at 60 °C for 2 days. A viscous colorless ionic liquid was obtained in 84% yield (5.30 g).

MS (ESI) calcd for [C<sub>20</sub>H<sub>44</sub>P]<sup>+</sup> *m/z* 315.4; found *m/z* 315.3; calcd for [C<sub>16</sub>H<sub>12</sub>O<sub>6</sub>B]<sup>−</sup> *m/z* 311.0; found *m/z* 311.0.

<sup>1</sup>H NMR (400.17 MHz, CDCl<sub>3</sub>): 7.625–7.590 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.315–7.240 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.236–7.215 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 5.312 (d, 1H, <sup>4</sup>*J*<sub>HH</sub> = 2.8 Hz, C<sub>6</sub>H<sub>5</sub>–CH), 5.233 (d, 1H, <sup>4</sup>*J*<sub>HH</sub> = 3.6 Hz, C<sub>6</sub>H<sub>5</sub>–CH), 1.926–1.854 (m, 8H, P–CH<sub>2</sub>), 1.360–1.227 (m, 24H, –CH<sub>2</sub>–), 0.930–0.844 (m, 12H, CH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (100.62 MHz, CDCl<sub>3</sub>): 177.93, 177.84, 140.25, 140.12, 128.06, 127.31, 127.19, 126.44, 126.37, 126.13, 31.62, 30.58, 30.42, 28.86, 27.93, 27.28, 24.30, 24.16, 23.73, 23.32, 22.55, 21.40, 18.67, 18.47, 14.04, 13.27 ppm.

<sup>31</sup>P NMR (161.99 MHz, CDCl<sub>3</sub>): 33.528 ppm.

<sup>11</sup>B NMR (129.39 MHz, CDCl<sub>3</sub>): 10.874 ppm.

### 2.3 Physicochemical characterisation

NMR experiments were conducted on a Bruker Avance 400 (9.4 T) with a 5 mm broadband autotunable probe with Z-gradients at 30 °C. NMR spectra were collected and processed using spectrometer “Topspin” 2.1 software. <sup>1</sup>H and <sup>13</sup>C spectra were referenced to internal TMS and CDCl<sub>3</sub>. External references were employed in the <sup>31</sup>P (85% H<sub>3</sub>PO<sub>4</sub>) and <sup>11</sup>B (Et<sub>2</sub>O·BF<sub>3</sub>).

The positive and negative ion electrospray mass spectra were obtained with a Micromass Platform 2 ESI-MS instrument.

Water content in hf-BILs was determined using a 831 Karl Fischer Coulometer (Metrohm). Duplicate measurements were carried out for each sample.

An Anton-Paar DMA 5000 density meter was used to measure the density in a temperature range from 20 to 90 °C.

Viscosity was measured with an AMVn Automated Microviscometer (Anton-Paar falling ball type viscometer) in a temperature range from 20 to 90 °C using a sealed sample tube.

Differential scanning calorimetric (DSC) measurements were performed with a Q100 TA instrument to study thermal behavior of hf-BILs. A sample with an average weight

of 7–9 mg was sealed in an aluminium pan, cooled to  $-120\text{ }^{\circ}\text{C}$  and then heated up to  $50\text{ }^{\circ}\text{C}$  at a scanning rate of  $10.0\text{ }^{\circ}\text{C min}^{-1}$ . The glass transition temperatures,  $t_g$ , were determined as the onset of the transition on DSC graphs. Measurements were performed twice for each ionic liquid and the mean values and standard deviations are given in Results and Discussion.

Thermogravimetric analyses (TGA) were performed using a Netzsch STA 409 instrument at a rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  and argon flow rate of  $100\text{ mL min}^{-1}$ . The sensitivity of this STA instrument is  $\pm 1\text{ }\mu\text{g}$ .

Conductivity was measured by using electrochemical impedance spectroscopy with a Solatron SI 1260 impedance/gain phase analyzer connected to a Solatron 1296 dielectric interface. A platinum wire electrode conductivity cell, calibrated with  $0.01\text{ M}$  aqueous KCl, was filled and sealed.

## 2.4 Tribological properties

The wear tests were conducted at room temperature ( $22\text{ }^{\circ}\text{C}$ ) on a Nanovea pin-on-disk tester according to ASTM G99 using  $6\text{ mm}$  100Cr6 ball surface in contact with a  $45\text{ mm}$  diameter AA2024 aluminium disc. Composition, hardness and surface roughness of the steel balls and aluminium discs are given in Table SI-42 in ESI.†  $0.1\text{ mL}$  of lubricant was used in each test. Experiments were conducted at loads of  $20$  and  $40\text{ N}$  for a sliding distance of  $1000\text{ m}$  and at a speed of  $0.2\text{ m s}^{-1}$ . Coefficient of friction was recorded throughout the test. The wear scar depth was measured using a Dektak 150 stylus profilometer.

## 3. Results and discussion

### 3.1 Synthesis and characterisation of halogen-free chelated orthoborate ionic liquids

A complete synthetic procedure for each hf-BIL is described in detail in the experimental section. In general, as illustrated in Scheme 1, the reaction started with a carboxylic acid (mandelic acid, salicylic acid, malonic acid or oxalic acid), boric acid and lithium carbonate in a  $2:1:1$  molar ratio. After heating for  $2$  hours at about  $60\text{ }^{\circ}\text{C}$ , the reaction mixture was cooled down to room temperature. The reaction product, the lithium borate salt, was not isolated but rather continued to the next step

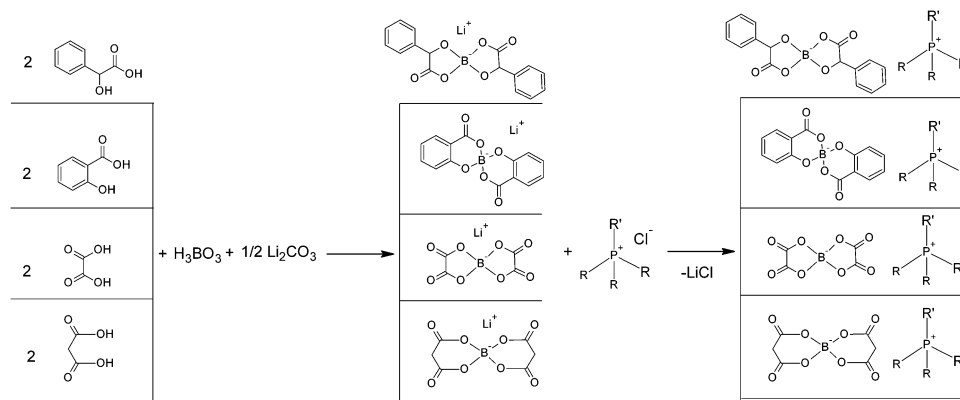
of metathesis. In the second step, phosphonium chloride was added to the reaction mixture and stirred during  $2$  hours at room temperature. The reaction product, an organic layer, was extracted with dichloromethane and washed with distilled water to remove traces of the byproduct, lithium chloride. The final products of hf-BILs were first rotary evaporated at  $60\text{ }^{\circ}\text{C}$  for  $2$  hours to remove  $\text{CH}_2\text{Cl}_2$  and traces of water mixed with either  $\text{CH}_2\text{Cl}_2$  or hf-BILs. Then the products were dried in a vacuum oven at  $60\text{ }^{\circ}\text{C}$  for not less than  $48\text{ h}$ . After nine months of storage water content in hf-BILs before and after additional drying in a vacuum oven at  $60\text{ }^{\circ}\text{C}$  for  $48\text{ h}$  was found to be  $1.40\text{--}0.21$  and  $0.33\text{--}0.03\%$ , respectively (except for  $[\text{P}_{6,6,6,14}][\text{BOB}]$ , for which water content was found to be  $2.33$  and  $2.03\%$ , respectively) as determined using a Metrohm 831 Karl Fischer titration (see Table SI-1 in ESI†). Chemical structures of the cations and anions of the synthesised hf-BILs are shown in Scheme 2. The structures and purity of all these hf-BILs were characterised by an electrospray ionisation mass spectrometry (ESI-MS) and multinuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{11}\text{B}$ ) NMR spectroscopy. The data obtained confirmed the structure and purity of all synthesised hf-BILs.

### 3.2 Hydrophobicity and hydrolytic stability

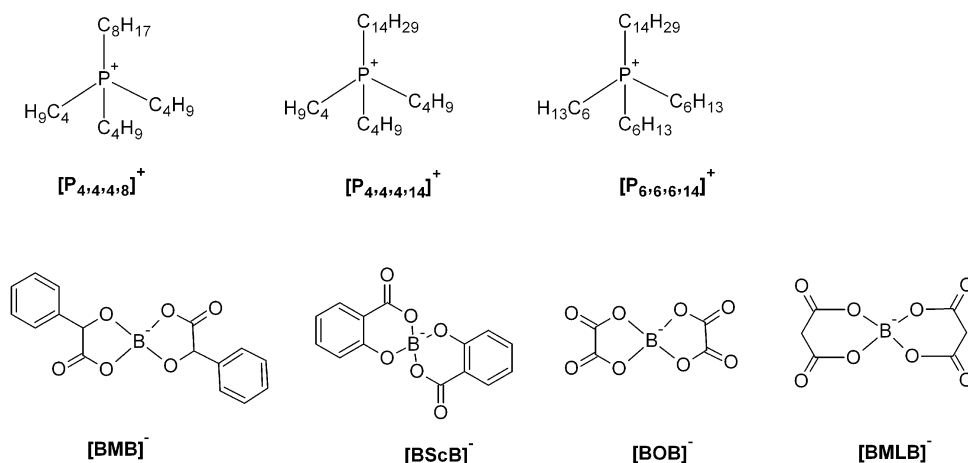
The hf-BILs investigated in this work are composed of different chelated orthoborate anions with phosphonium cations with different alkyl chains length. The longer alkyl chains make them hydrophobic and liquid at room temperature. These hf-BILs can readily dissolve in almost all the common polar organic solvents, but, when added to water, round oil beads are produced at the bottom of the container, indicating low miscibility with water. A small droplet of  $[\text{P}_{6,6,6,14}][\text{BScB}]$  was put in distilled water and left in the water for  $10$  days to confirm the hydrolytic stability of these hf-BILs. There was no change in appearance. The sample was analysed by ESI-MS; peaks at  $m/z$   $483.5$  and  $m/z$   $283.0$  for  $[\text{C}_{32}\text{H}_{68}\text{P}]^+$  and  $[\text{C}_{14}\text{H}_8\text{O}_6\text{B}]^-$ , respectively, confirmed the hydrolytic stability of these hf-BILs (see Fig. SI-6 and SI-7 in ESI†).

### 3.3 Thermal behaviour

Fig. 1 shows the differential scanning calorimetry (DSC) traces of the hf-BILs under discussion. All these hf-BILs are liquids at room temperature and they exhibit glass transitions ( $t_g$ ) below room temperature (from  $-44\text{ }^{\circ}\text{C}$  to  $-73\text{ }^{\circ}\text{C}$ ).

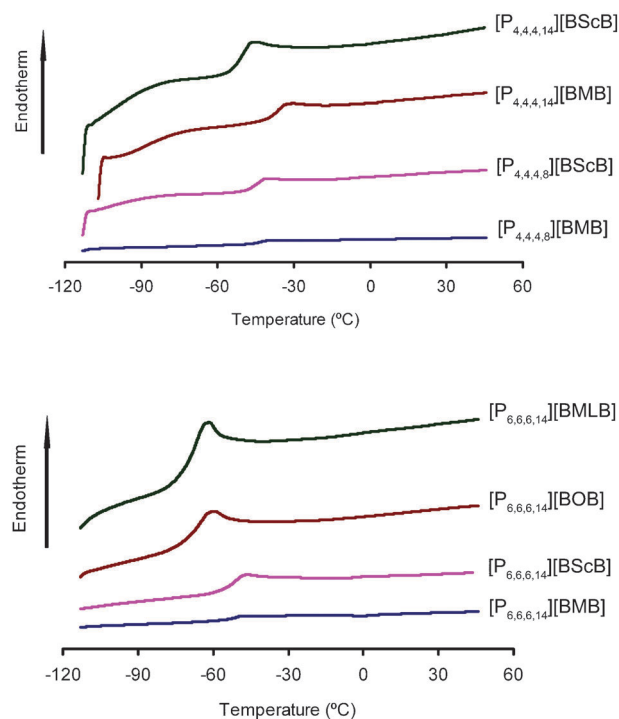


**Scheme 1** General synthetic method used to synthesise hf-BILs.



**Scheme 2** Structural illustration of ionic components of the hf-BILs investigated in this work.

Onset of  $t_g$  values in the DSC traces for these hf-BILs are tabulated in Table 1. It is known that  $t_g$  of orthoborate ionic liquids are higher than those for the corresponding salts of the



**Fig. 1** DSC thermograms of hf-BILs.

fluorinated anions.<sup>54</sup>  $t_g$  values for the orthoborate ionic liquids with the cation,  $P_{66614}^+$ , and with different anions decrease in the following order  $[BMB]^- > [BScB]^- > [BOB]^- > [BMLB]^-$ . hf-BILs with  $[BMB]^-$  and  $[BScB]^-$  have considerably higher  $t_g$  values compared with these of hf-BILs containing  $[BOB]^-$  and  $[BMLB]^-$ , most probably because of the phenyl rings present in the structure of the former anions ( $[BMB]^-$  and  $[BScB]^-$ ).

For the orthoborate anions with different phosphonium cations, a decrease in  $t_g$  values is observed with an increase in size of the alkyl chains in the cations. This trend is more pronounced for hf-BILs with the  $[BScB]^-$  anion, where  $t_g$  falls in the order  $[P_{4,4,4,8}]^+ (-48.9 \pm 0.7^\circ\text{C}) > [P_{4,4,4,14}]^+ (-55.4 \pm 1.2^\circ\text{C}) > [P_{6,6,6,14}]^+ (-56.6 \pm 0.6^\circ\text{C})$  (see Table 1). Del Sesto *et al.* have observed a similar trend for ionic liquids of phosphonium cations with bis[trifluoromethylsulfonyl]imide ( $\text{NTf}_2$ ) and dithiomaleonitrile ( $\text{dtmn}$ ) anions.<sup>55</sup> The lowest  $t_g$  of hf-BILs (down to  $-72.8 \pm 0.2^\circ\text{C}$ ) for  $[P_{6,6,6,14}][BMLB]$  are reached with the  $[P_{6,6,6,14}]^+$  as cation, probably because of the larger size, lower symmetry and a lower packing efficiency of this cation. All of these hf-BILs showed glass transitions and no melting or crystallisation peaks in accord with the results obtained previously for other phosphonium ILs.<sup>56</sup>

Fig. 2 represents a TGA curve for  $[P_{6,6,6,14}][BMB]$ . This plot indicates that hf-BILs exhibit good thermal stability with no significant weight loss up to  $370^\circ\text{C}$ . Note that decomposition of  $[P_{6,6,6,14}][BMB]$  occurs in a single step with a total weight loss of 91%. The maximum weight loss occurs between  $400$  and  $450^\circ\text{C}$ .

**Table 1** Physical properties of hf-BILs

hf-BILs	Density equation $d = b - at/\text{g cm}^{-3}$ (where $t$ is in $^\circ\text{C}$ )			$E_a(\eta)/\text{kcal mol}^{-1}$	$t_g/^\circ\text{C}$ from DSC measurement
	$a$	$b$	$R^2$		
$[P_{4,4,4,8}][BMB]$	$7 \times 10^{-4}$	1.0784	0.9991	12.2	$-46.8 \pm 0.3$
$[P_{4,4,4,14}][BMB]$	$7 \times 10^{-4}$	1.0541	0.9998	12.7	$-43.8 \pm 0.4$
$[P_{6,6,6,14}][BMB]$	$6 \times 10^{-4}$	1.0208	0.9995	11.6	$-56.1 \pm 0.4$
$[P_{4,4,4,8}][BScB]$	$7 \times 10^{-4}$	1.0919	0.9999	11.9	$-48.9 \pm 0.7$
$[P_{4,4,4,14}][BScB]$	$6 \times 10^{-4}$	1.0532	0.9998	10.8	$-55.4 \pm 1.2$
$[P_{6,6,6,14}][BScB]$	$7 \times 10^{-4}$	1.0333	1	10.6	$-56.6 \pm 0.6$
$[P_{6,6,6,14}][BOB]$	$6 \times 10^{-4}$	0.9571	0.9998	11.6	$-71.5 \pm 0.6$
$[P_{6,6,6,14}][BMLB]$	$6 \times 10^{-4}$	0.9865	0.9996	10.0	$-72.8 \pm 0.2$



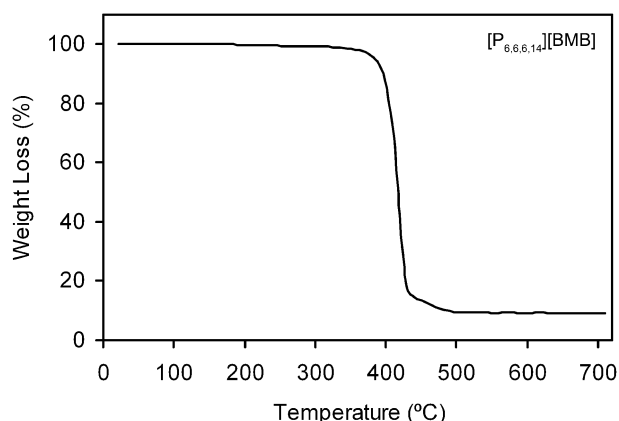


Fig. 2 A TGA curve for  $[P_{6,6,6,14}][BMB]$ .

### 3.4 Density

Fig. 3 shows a linear variation of densities with temperature for hf-BILs. By comparing the effect of anions on the density of hf-BILs, the densities decrease in the following order  $[BScB]^- > [BMB]^- > [BOB]^- > [BMLB]^-$ . For the same anion, the density of hf-BILs decreases with an increase in the size of the cation as  $[P_{4,4,4,8}]^+ > [P_{4,4,4,14}]^+ > [P_{6,6,6,14}]^+$ . The density values of  $[P_{4,4,4,14}][BMB]$  and  $[P_{4,4,4,14}][BScB]$  are very similar at all measured temperatures. Density of hf-BILs decreases with an increase in the length of alkyl chains in cations, because the van der Waals interactions are reduced and that lead to a less efficient packing of ions. The parameters characterising density of these hf-BILs as a function of temperature are tabulated in Table 1. For increasing temperatures from 20 °C to 90 °C, the density of hf-BILs decreases linearly. This behaviour is usual for ionic liquids.<sup>57</sup>

### 3.5 Viscosity

Fig. 4 shows temperature dependences of viscosities of the hf-BILs. These dependences can be fit to an Arrhenius form of equation for viscosity  $\eta = \eta_0 \exp(E_a(\eta)/k_B T)$ , in the whole temperature range studied. Here  $\eta_0$  is a constant and  $E_a(\eta)$  is the activation energy for viscous flow. Activation energies,  $E_a(\eta)$ , for different hf-BILs are tabulated in Table 1. Some of these hf-BILs have shown very high viscosity in the temperature range between 20 °C and 30 °C, which was not measurable by the viscometer used in this study. However, viscosity of the

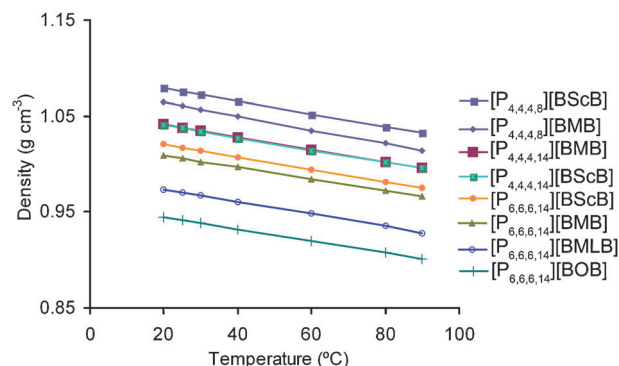


Fig. 3 Densities of hf-BILs as a function of temperature.

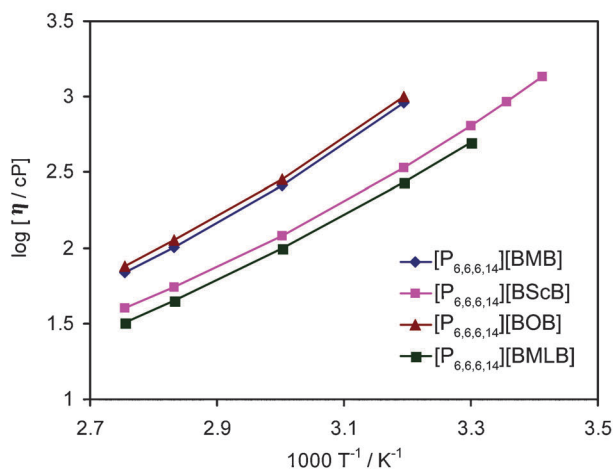
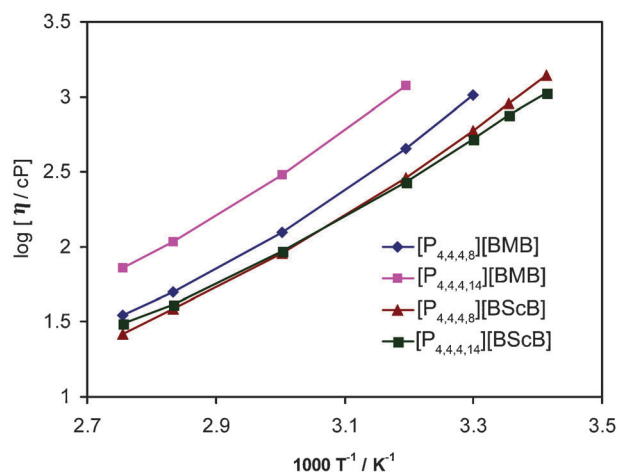


Fig. 4 Arrhenius plot of viscosity for the synthesised hf-BILs as a function of temperature.

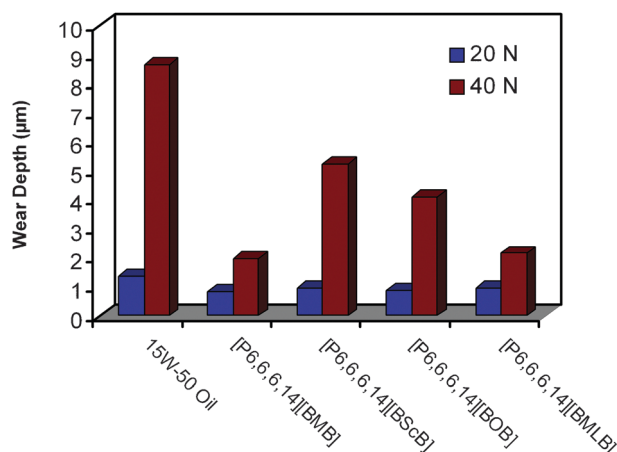
Table 2 Tribological properties of the synthesized chelated orthoborate ionic liquids for a steel–aluminium contact

Lubricant	20 N load		40 N load	
	Wear depth/μm	Friction coefficient	Wear depth/μm	Friction coefficient
15W-50 Oil	1.37	0.09	8.68	0.102
$[P_{6,6,6,14}][BMB]$	0.84	0.07	1.98	0.067
$[P_{6,6,6,14}][BScB]$	0.95	0.08	5.25	0.085
$[P_{6,6,6,14}][BOB]$	0.88	0.06	4.10	0.063
$[P_{6,6,6,14}][BMLB]$	0.97	0.07	2.17	0.068

hf-BILs decreases markedly with an increase in temperature (from *ca.* 1000 cP at *ca.* 20 °C down to *ca.* 20 cP at *ca.* 90 °C, see Fig. 4). Viscosity of ionic liquids typically depends on electrostatic forces and van der Waal interactions, hydrogen bonding, molecular weight of the ions, geometry of the ions (related to the conformational degree of freedom, their symmetry and flexibility of alkyl chains), charge delocalisation, nature of substituents and coordination ability.<sup>58–60</sup> For a given cation,  $[P_{6,6,6,14}]^+$ , the viscosities fall in the order  $[BMB]^-$  ( $E_a = 11.6 \text{ kcal mol}^{-1}$ )  $>$   $[BOB]^-$  ( $E_a = 11.6 \text{ kcal mol}^{-1}$ )  $>$   $[BScB]^-$  ( $E_a = 10.6 \text{ kcal mol}^{-1}$ )  $>$   $[BMLB]^-$  ( $E_a = 10.0 \text{ kcal mol}^{-1}$ ) (see Table 1).

### 3.6 Tribological properties

The use of aluminium alloys has been rapidly expanding in recent years due to their high strength to weight ratio, good corrosion resistance and high thermal conductivity. However, aluminium alloys due to their relatively poor wear resistance have limited use in the tribological contacts lubricated by oils with commercial additives such as zinc dialkyldithiophosphates.<sup>61</sup> Ionic liquids



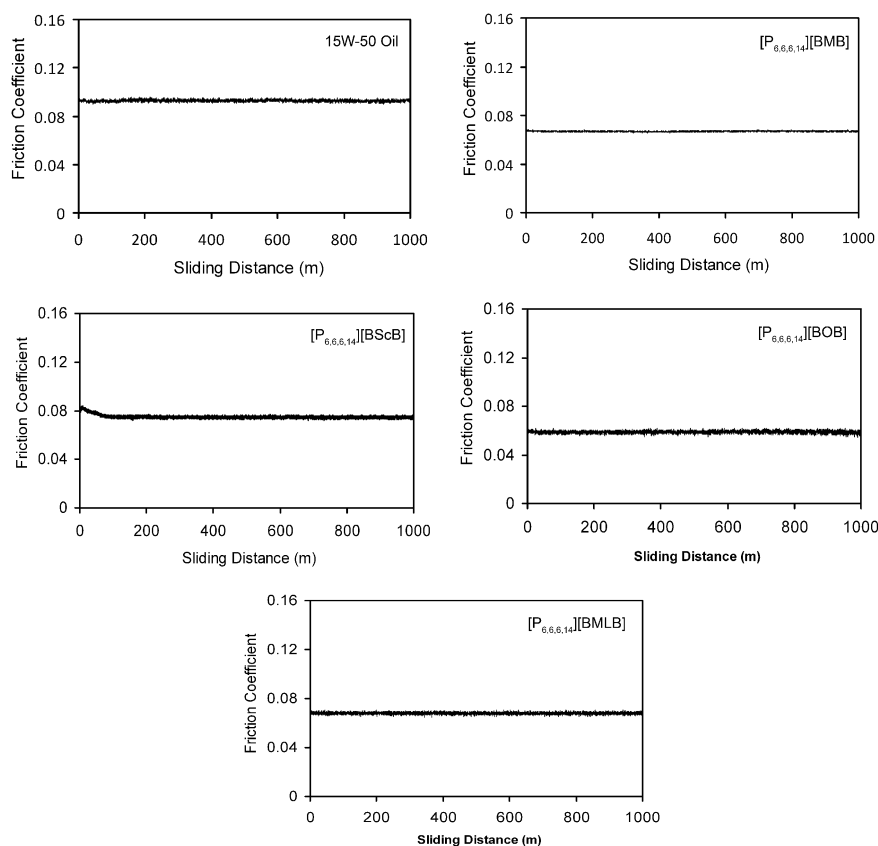
**Fig. 5** Wear depths for 100Cr6 steel against AA2024 aluminium lubricated by novel hf-BILs in comparison with 15W-50 oil. Measurements were performed at 20 N (blue) and 40 N (red) loads during 1000 m sliding distance.

containing  $\text{BF}_4^-$  and  $\text{PF}_6^-$  anions have shown promising results for steel–aluminium contacts.<sup>46,62,63</sup> For these reasons, we evaluate the tribological performance of the synthesised hf-BILs in steel–aluminium contacts.

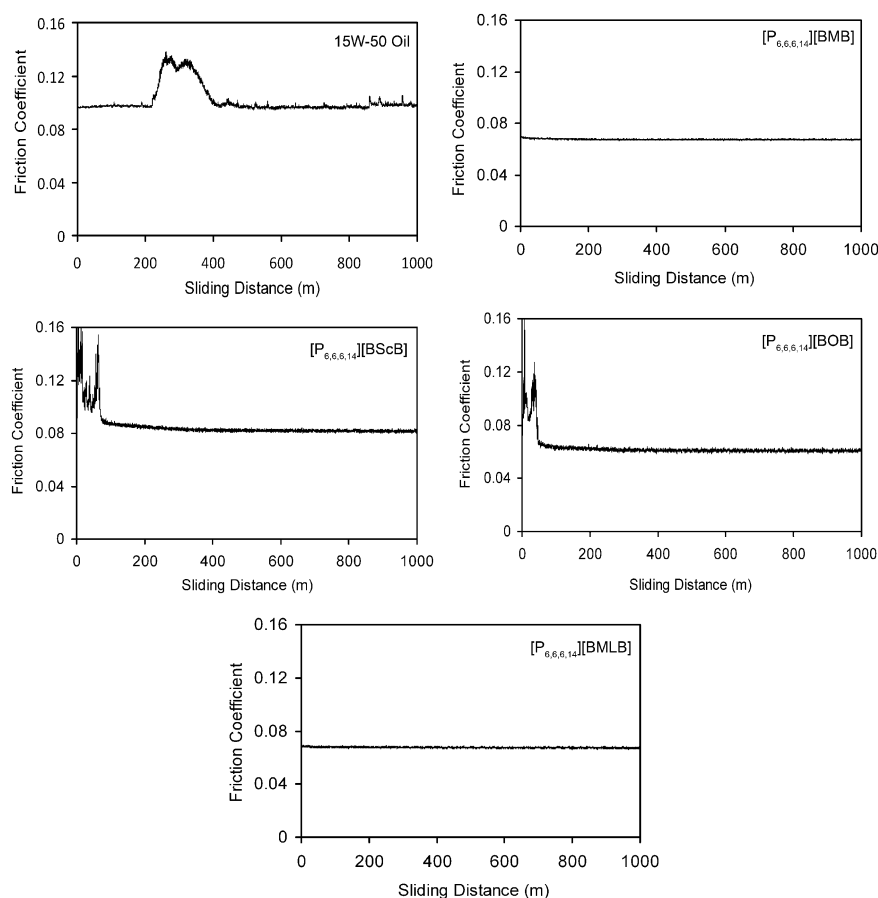
Tribological properties of selected hf-BILs were investigated in the pin-on-disc tribometer, where pure ionic liquids were put onto the surface of an aluminium disc rotating against a steel ball. Tribological data for the selected hf-BILs were compared with the 15W-50 at loads of 20 and 40 N for a sliding distance of 1000 m, Table 2 and Fig. 5. The wear depths for the 15W-50 are 1.34 μm and 8.69 μm at 20 N and 40 N loads, respectively. All of the tested hf-BILs provided significantly reduced wear rates (by 40% to 75%) of the aluminium alloy compared to the 15W-50. For example, in the case of [P<sub>6,6,6,14</sub>][BMB] the wear depths are 0.84 μm and 1.98 μm at 20 N and 40 N loads, respectively.

Similarly, all tested hf-BILs showed lower average friction coefficients compared to 15W-50. The average friction coefficients for the 15W-50 are 0.093 and 0.102 at 20 N and 40 N respectively. Friction coefficients for [P<sub>6,6,6,14</sub>][BMB] are 0.066 and 0.067 at 20 N and 40 N loads, respectively. In general, hf-BILs provide 20% to 35% lower friction than the 15W-50.

Fig. 6 and 7 show time-traces of the friction coefficient for the selected hf-BILs and the 15W-50 at 20 N (Fig. 6) and 40 N (Fig. 7) during 1000 m sliding distance. The friction coefficients are stable at 20 N for both the 15W-50 and hf-BILs. There is no increase in the friction coefficients until the end of the test



**Fig. 6** Variation of the friction coefficient with the sliding distance in the tribological test at 20 N load for 100Cr6 steel against AA2024 aluminium lubricated by hf-BILs in comparison with commercial 15W-50 oil.



**Fig. 7** Variation of the friction coefficient with the sliding distance in the tribological test at 40 N load for 100Cr6 steel against AA2024 aluminium lubricated by hf-BILs in comparison with 15W-50 oil.

for all lubricants examined here. The friction coefficients for hf-BILs are lower than those for 15W-50 at all times of the tests (see Fig. 6).

At the load of 40 N the friction coefficient for the 15W-50 varies considerably with the sliding distance. At the beginning of the test, the friction coefficient remains stable for a short duration *ca.* 200 m and then rapidly increases to a higher value. This high friction level is maintained until *ca.* 400 m before returning to the original level. In the beginning of the test a tribofilm separates the surfaces and prevent them from a direct metal-to-metal contact. A sudden increase in the friction coefficient is evidence that the tribofilm formed by standard additives present in 15W-50 is not stable on aluminium surfaces (see Fig. 7).

In contrast, the novel hf-BILs exhibited different trends compared to the 15W-50.  $[P_{6,6,6,14}][BMB]$  and  $[P_{6,6,6,14}][BMLB]$  showed no increase in the friction coefficient over the whole test period. Friction coefficients for  $[P_{6,6,6,14}][BScB]$  and  $[P_{6,6,6,14}][BOB]$  were high and unstable for a short period before stabilizing at lower friction levels until the end of the tests. This initial increase in the friction coefficient is due to the lack of a boundary film while the recovery of the friction coefficient is because of the formation of a thin layer on the surface. Since there is no increase in the friction coefficient after the initial 50 m sliding distance, it appears that the friction coefficients would remain stable if the tests were allowed to continue. This indicates the

formation of stable and hard tribofilms on the aluminium alloy surfaces from hf-BILs lubricants.

Zhang *et al.*<sup>64</sup> have recently reported that nitrile-functionalised ILs with  $BF_4^-$  anion have considerably better tribological performance in steel–steel and steel–aluminium contacts than ILs with  $NTf_2^-$  and  $N(CN)_2^-$  anions. It was suggested that the  $BF_4^-$  anion has excellent tribological performance but unfortunately the detailed mechanism was not described. The uncertainty in the proper mechanism for improved interfacial and tribological properties of boron arises because boron's chemistry and phase behaviour are rather complex.<sup>65</sup>

It is possible that the excellent tribological behaviour of the hf-BILs is due to their interaction with the substrate at the high temperatures and pressures present in the contact area. Low energy electrons are emitted from the contact point between the surfaces during the sliding motion, making the environment highly reducing towards the lubricant and leaving a positively charged surface. At such high temperatures and pressures these boron compound may break down reductively into fragments of reactive species containing boron. Recently, Tse<sup>66</sup> and Oganov *et al.*<sup>67</sup> have found that elemental boron has a partially negative charge under pressure that would allow it to interact with the positively charged metal surfaces because of the electrostatic interaction. In the case of the hf-BIL and an aluminium alloy surface, this interaction may result in the formation of a boundary film on the aluminium alloy surface.



Because boron is a superhard material,<sup>68,69</sup> the boundary film should be hard enough to protect the aluminium alloy surface against damage during interfacial processes at high temperature and pressure.

### 3.7 Conductivity

Ionic liquids conduct *via* ion mobility because they are composed of ions. Conductivity of ILs strongly depends on viscosity, ion size, molecular weight, density and ion association. Viscous ILs exhibit lower conductivities due to the hindered mobility of the normally bulky and asymmetric ions.<sup>70</sup> Increased anion–cation interaction has been found to be one of the main factors controlling the amount of ion pairing and ion mobilities in liquids.<sup>71,72</sup> This is a reason that wet ILs usually exhibit higher conductivities than neat ILs themselves.<sup>73</sup> The conductivity of the selected hf-BILs was measured over a temperature range from  $-50\text{ }^{\circ}\text{C}$  to  $100\text{ }^{\circ}\text{C}$ . A comparison of the temperature dependence of ionic conductivity of  $[\text{P}_{6,6,6,14}][\text{BMB}]$  and  $[\text{P}_{6,6,6,14}][\text{BScB}]$  ionic liquids is made in Fig. 8. The results show that both these hf-BILs have similar conductivities in the whole temperature range studied (from  $-50\text{ }^{\circ}\text{C}$  to  $100\text{ }^{\circ}\text{C}$ ). For example, the conductivity,  $\sigma$ , at  $-50\text{ }^{\circ}\text{C}$  is  $6.86 \times 10^{-11}\text{ Scm}^{-1}$  for  $[\text{P}_{6,6,6,14}][\text{BMB}]$  and  $8.85 \times 10^{-12}\text{ Scm}^{-1}$  for  $[\text{P}_{6,6,6,14}][\text{BScB}]$ , while at  $100\text{ }^{\circ}\text{C}$   $\sigma = 2.42 \times 10^{-4}\text{ Scm}^{-1}$  for  $[\text{P}_{6,6,6,14}][\text{BMB}]$  and

$\sigma = 2.88 \times 10^{-4}\text{ Scm}^{-1}$  for  $[\text{P}_{6,6,6,14}][\text{BScB}]$ . This behaviour was expected because of similar  $t_g$  values of these two hf-BILs ( $-55\text{ }^{\circ}\text{C}$  for  $[\text{P}_{6,6,6,14}][\text{BMB}]$  and  $-56\text{ }^{\circ}\text{C}$  for  $[\text{P}_{6,6,6,14}][\text{BScB}]$ ) and a comparable size and molecular weight of anions  $\text{BMB}^-$  (MW =  $311.0\text{ g mol}^{-1}$ ) and  $\text{BScB}^-$  (MW =  $283.0\text{ g mol}^{-1}$ ). It is interesting to compare conductivity of these novel hf-BILs with previously reported data obtained in other groups: Conductivity of  $[\text{P}_{6,6,6,14}][\text{BScB}]$  is much higher compared to 1-butyl-3-methylimidazolium bis(salicylato)borate  $[\text{BMI}][\text{BScB}]$ <sup>54</sup> at low temperatures ( $<50\text{ }^{\circ}\text{C}$ ). However,  $\sigma$  of these ionic liquids are comparable at high temperatures ( $>80\text{ }^{\circ}\text{C}$ ). These differences are probably because of a high fluidity and a low glass transition temperature ( $t_g = -56\text{ }^{\circ}\text{C}$ ) of  $[\text{P}_{6,6,6,14}][\text{BScB}]$  compared to that for  $[\text{BMI}][\text{BScB}]$  ( $t_g = 21.5\text{ }^{\circ}\text{C}$ ), which is a very viscous liquid at  $t < 50\text{ }^{\circ}\text{C}$ .<sup>54</sup> Interestingly, for  $[\text{P}_{6,6,6,14}][\text{BMB}]$  the slope of  $\log(\sigma)$  vs.  $T^{-1}$  changes at  $T \approx 270\text{ K}$  (see Fig. 8, top). This temperature point, though not clearly visible in DSC (see Fig. 1), may correspond to a phase transition in this hf-BIL. This will be further studied and reported elsewhere.

## 4. Conclusions

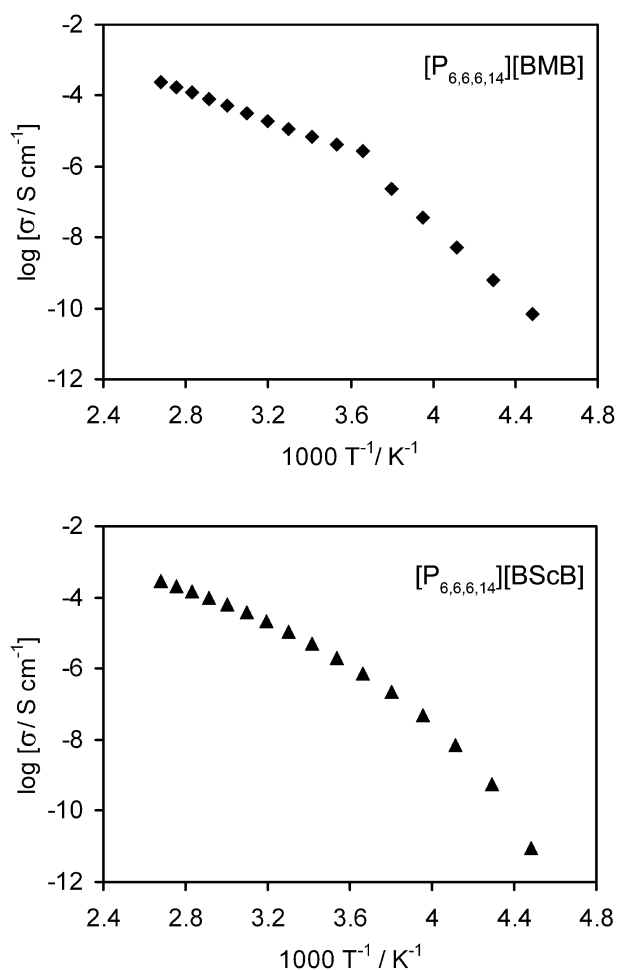
In this study, our research interest is centered on boron based ionic liquids composed of stable orthoborate anions to avoid hydrolysis and protect the environment during their use in industrial applications. We have designed and synthesised a new family of ionic liquids composed of chelated orthoborate anions and phosphonium cations. The structures and purity of the synthesised halogen-free orthoborate ionic liquids (hf-BILs) have been confirmed by electrospray ionization mass spectrometry (ESI-MS) and multinuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{11}\text{B}$ ) NMR spectroscopy. All these hf-BILs showed low melting points (from  $-44\text{ }^{\circ}\text{C}$  to  $-73\text{ }^{\circ}\text{C}$ ) and high viscosity, however, viscosity considerably decreased upon heating. Friction and wear properties of these hf-BILs as lubricants were evaluated in comparison with fully formulated (15W-50 grade) engine oil for the steel–aluminium contact. The hf-BILs showed lower friction and wear rates compared with the 15W-50. The hydrolytic stability, low melting points, high viscosities and outstanding tribological properties for steel–aluminium contacts make hf-BILs attractive as environmentally friendly alternative lubricants.

## Acknowledgements

The financial support (a stipend for FUS) provided by the Foundation in memory of J. C. and Seth M. Kempe and Swedish Research School in Tribology is gratefully acknowledged. MF, DRM and AS are grateful for the support of the Australian Research Council under its Discovery Projects and Federation Fellowship (DRM) schemes.

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**Fig. 8** Arrhenius plot of ionic conductivity for selected hf-BILs in the temperature range from  $-50\text{ }^{\circ}\text{C}$  to  $100\text{ }^{\circ}\text{C}$ .

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