PAPER

Halogen-free ionic liquids: effect of chelated orthoborate anion structure on their lubrication properties†

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In transportation vehicles, a large portion of energy is consumed to overcome friction in the engine and associated components. An efficient lubricant system has a direct impact on saving energy and material loss by reducing the friction, wear, and corrosion. Herein, halogen-free chelated orthoborate ionic liquids were designed, synthesized and then evaluated as potential lubricant additives. The effect of the orthoborate anion structure on the thermal stability, corrosion, friction, and wear properties of ionic liquids were studied. The copper strip tests revealed the non-corrosiveness of bis(mandalato)borate (BMdB), bis(salicylato)borate (BScB), and bis(malonato)borate (BMlB) anion constituted ionic liquids. Whereas, the bis(oxalato)borate (BOxB) anion, eventually developed micro-pits of corrosion owing to its lower stability and acidic nature of the decomposed product. These ionic liquids as additives to the synthetic lube base oil significantly reduced both friction and wear. The degree of friction and wear reduction was influenced by the structure of associated anions. BMdB and BScB anion constituted ionic liquids exhibited excellent thermal stability, friction-reduction, and antiwear properties, which are attributed to their compact and chemically stable structure driven by higher intermolecular interactions and rigidity of aromatic rings. The chemical analysis of tribo-interfaces suggested the formation of an ionic liquid composed tribochemical product and that enhanced the lubrication properties. Being halogen-free, these ionic liquids could be energy efficient and environmentally-friendly substitutes to the conventional friction-reducing and antiwear additives.

Introduction

Energy and the environment play important roles in everyone's life and are inextricably linked with each other. The global awareness on the sustainability of fuels, need for energy-efficient systems, and utilization/conversion of energy in environmentally benign practices have been increasing immensely because of high volatility in fuel prices and stringent environmental regulations. In this context, the energy and material losses due to high friction and wear in the transportation system leads to high fuel consumption, frequent failure of engine parts, increased greenhouse gas emission, discharge of partially oxidized fuels *etc.* An efficient lubricant can reduce these undesirable events. Friction and wear are considered to be the most damaging events to the mating surfaces of the engine. Zinc dialkyldithiophosphate (ZDDP) has been a well established antiwear and friction-reducing additive for iron based components since 1960s. Over the last two decades there has been a growing interest to reduce the use of ZDDP based lubricant additives because of their toxicity to aquatic wildlife, adverse effects to human-health and poisoning of automotive exhaust gas catalyst components.[1]

Recently, ionic liquids have been studied as versatile lubricants and lubricant additives for various engineering surfaces, because of their unique and tunable physico-chemical properties like negligible vapour pressure, wide liquid range, excellent conductivity, good thermal stability, inherent polarity *etc.*[2,3] Ionic liquids are task specific in nature and their properties can be tailored by changing the structure of constituted cation and anion. The molecular thin films of ionic liquids on solid surfaces mediate efficient lubrication relative to conventional non-polar hydrocarbon liquids and is attributed to the geometric and charge characteristics of the ionic liquids. The irregular shapes of cation and anion leads to low shear stress, revealing low friction than non-polar molecular liquids.[4] Inherent polar nature of ionic liquids facilitates their interaction with engineering surfaces under tribo-stress, resulting in boundary thin film formation. Such protective thin film of ionic liquids avoids the direct contact between mating surfaces and is believed to be responsible for the antiwear property.[5]

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Boron compounds are established as lubricious materials because of their remarkable tribochemical and high pressure properties.[6,7] The boron constituted materials, such as organoboron compounds, h-BN powder, metal borate nanoparticles *etc.* exhibit excellent friction-reducing and antiwear properties.[6,8,9] The first report on lubrication properties of ionic liquids was based on the boron constituted alkylimidazolium tetrafluoroborate (BF_4^-) ionic liquid.[10] Under tribostress, alkylimidazolium-BF_4 ionic liquid developed a tribothin film composed of FeF_2 and B_2O_3 over the steel surface, which avoids direct contact between tribo interfaces, consequently reduction in both friction and wear.[11] Phillips *et al.* have revealed that BF_4^- anion based ionic liquids break down into several reaction products mainly consisting of FeF_2, and this leads to the degradation of the lubricant fluid and corrosion of the substrate surface.[12] Over last one decade, several ionic liquids composed of imidazolium, ammonium, phosphonium, pyridinium *etc.* as cations and X^-, PF_6^-, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, $(C_2F_5)_3PF_3^-$ *etc.* as anions have been studied as lubricant and lubricant additives for diversified range of engineering surfaces and have exhibited structure dependent lubrication properties.[2,3,13] These halogenated ionic liquids have hazardous and toxic effects to the environment and are corrosive to the engineering surfaces.[14,15] The decomposition of halogenated ionic liquids under tribo-conditions and/or *via* hydrolysis by trapped water molecules evolve toxic and corrosive products, which contaminate the environment and corrode the engineering surfaces.[15,16] Besides that, high cost of halogens, particularly, fluorine based precursors and disposal/discharge of halogenated ionic liquids are big challenges for their penetration to the industrial applications. Thus, halogen-free ionic liquids have become a topic of great research interest for the energy efficient and environmentally-friendly lubricant development.

Recently, amino acids, dicyanamide, tricyanomethanide and fatty acids anions based ionic liquids were explored as halogen-free ionic liquids. These ionic liquids showed good tribological performance compared to the synthetic lube oils.[17–19] However, low thermal stability and high cost of precursors limit their usage from application perspective. Antzutkin *et al.* have developed halogen-free orthoborate anions based phosphonium ionic liquids. These hydrophobic ionic liquids as lubricants exhibited better antiwear and friction-reducing properties as compared to fully formulated engine oil.[20] Nevertheless, the stringent regulations on environment protection drives to replace the phosphorus from the lubricant composition because of its hazardous and toxic effects to environment.[21] The scope of chelated orthoborate anions based ionic liquids were further extended with imidazolium, bis-imidazolium and pyrrolidinium cations.[22–24] Herein, we report synthesis, corrosion and tribo-evaluation of chelated orthoborate anions based ammonium ionic liquids, which are halogen- and phosphorous-free. These ionic liquids having variable anion structure are evaluated for non-corrosiveness, friction-reducing and antiwear properties. Results are further compared with halogenated analogue.

Experimental section

Materials

Tetrabutylammonium bromide (99%, Loba Chemie), boric acid (99.5%, Loba Chemie), lithium carbonate (99.9%, Sigma Aldrich), salicylic acid (99.8%, Merck), malonic acid (99%, Sigma Aldrich), mandelic acid (99%, Sigma Aldrich), oxalic Acid (99%, Merck Chemicals) and sodium tetrafluoroborate (97%, Alfa Aesar) were used without further purification for the synthesis of ionic liquids. The dichloromethane (DCM; AR grade, Loba Chemie) was used for ionic liquid extraction. The polyethylene glycol (mol. weight: 200; PEG 200) was procured from Alfa Aesar was used as synthetic lube base oil.

Synthesis and NMR characterization of ionic liquids

Tetrabutylammonium bis(salicylato)borate (TBA-BScB). The lithium salt of BScB, an anionic precursor was prepared by mixing salicylic acid (2.762 g, 20 mmol) in an aqueous solution of lithium carbonate (0.367 g, 5 mmol) and boric acid (0.619 g, 10 mmol) at 60 °C temperature for 2 hours. In the next step, TBA-Br (3.224 g, 10 mmol), a cationic precursor, was gradually added to the freshly prepared solution of lithium-BScB and heated the reaction mixture at 50 °C for 2 hours. This led to the formation of an organic layer composed of TBA-BScB ionic liquid. The TBA-BScB was extracted using DCM and then washed with distilled water several times to remove all unreacted bromide content. The DCM was then removed under reduced pressure and TBA-BScB ionic liquid was dried in vacuum oven at 80 °C for 48 hours. The preparation of TBA-BScB was confirmed by ^{1}H and ^{13}C NMR analyses. ^{1}H NMR (CDCl$_3$, ppm): 0.8–0.9 (t, 12H, N(CH$_2$)$_3$CH$_3$), 1.3 (m, 8H, N(CH$_2$)$_2$CH$_2$), 1.5 (q, 8H, NCH$_2$CH$_2$), 3.1 (t, 8H, NCH$_2$), 6.8–6.9 (m, 4H, C$_6$H$_4$), 7.29–7.39 (m, 2H, C$_6$H$_4$), 7.86–7.95 (dd, 2H, C$_6$H$_4$). ^{13}C NMR (ppm): 173.30, 165.19, 161.77, 159, 30, 136.43, 130.60, 118.73, 118.26, 115.36, 58.5, 23.5, 19, 13. Yield: 95%, physical state (at 24 °C): off-white wax.

Tetrabutylammonium bis(mandelato)borate (TBA-BMdB). TBA-BMdB was prepared by following the TBA-BScB preparation procedure using mandelic acid (3.043 g, 20 mmol) as an ingredient to anionic precursor, instead of salicylic acid. The preparation of TBA-BMdB was confirmed by ^{1}H and ^{13}C NMR analyses. ^{1}H NMR (CDCl$_3$, ppm): 0.85–0.88 (t, 12H, N(CH$_2$)$_3$CH$_3$), 1.2–1.27 (m, 8H, N(CH$_2$)$_2$CH$_2$), 1.36–1.39 (q, 8H, NCH$_2$CH$_2$), 2.92–2.95 (t, 8H, NCH$_2$), 5.2 and 5.3 (s, 2H, CH$_2$–C$_6$H$_5$), 7.22–7.26 (m, 2H, C$_6$H$_4$), 7.27–7.32 (m, 4H, C$_6$H$_4$), 7.58–7.65 (m, 4H, C$_6$H$_4$). ^{13}C NMR (ppm): 177.95, 40.29, 140.01, 131.79, 129.65, 128, 127.32, 126.44, 126.32, 126.23, 126.14, 78.26, 78.01, 58.26, 23.64, 19.49, 13.58. Yield: 94%, physical state (at 24 °C): off-white gel.

Tetrabutylammonium bis(malonato)borate (TBA-BMlB). TBA-BMlB was prepared by following the TBA-BScB preparation procedure using malonic acid (2.081 g, 20 mmol) as an ingredient to anionic precursor, instead of salicylic acid. The preparation of TBA-BMlB was confirmed by ^{1}H and ^{13}C NMR analyses. ^{1}H NMR (CDCl$_3$, ppm): 0.92–0.95 (t, 12H, N(CH$_2$)$_3$CH$_3$), 1.35–1.42 (m, 8H, N(CH$_2$)$_2$CH$_2$), 1.58–1.64 (q, 8H,

NCH$_2$CH$_2$), 3.2–3.3 (t, 8H, NCH$_2$), 3.35 (s, 4H, CO–CH$_2$_CO). ^{13}C NMR (ppm): 173.55, 58.83, 38.43, 24.03, 22.13, 19.69, 13.68. Yield: 91%, physical state (at 24 °C): off-white semi-solid.

Tetrabutylammonium bis(oxalato)borate (TBA-BOxB). TBA-BOxB was prepared by following the TBA-BScB preparation procedure using oxalic acid (1.800 g, 20 mmol) as an ingredient to anionic precursor, instead of salicylic acid. The preparation of TBA-BOxB was confirmed by ^{1}H and ^{13}C NMR analyses. ^{1}H NMR (CDCl$_3$, ppm): 0.92–0.95 (t, 12H, N(CH$_2$)$_3$CH$_3$), 1.34–1.42 (m, 8H, N(CH$_2$)$_2$CH$_2$), 1.58–1.64 (q, 8H, NCH$_2$CH$_2$), 3.26–3.33 (t, 8H, NCH$_2$). ^{13}C NMR (ppm): 158.77, 58.88, 24.05, 19.70, 13.68. Yield: 86%, physical state (at 24 °C): off-white waxy-solid.

Tetrabutylammonium tetrafluoroborate (TBA-BF$_4$). TBA-BF$_4$ was prepared by the metathesis of TBA-Br (3.224 g, 10 mmol) and NaBF$_4$ (1.098 g, 10 mmol) in water for two hours at 60 °C under continuous stirring. The organic layer of reaction product composed of TBA-BF$_4$ was extracted using DCM and then washed with distilled water several times to remove all bromide content. The DCM was separated by distillation under the reduced pressure and TBA-BF$_4$ ionic liquid was dried in vacuum oven for 48 hours at 80 °C. The preparation of TBA-BF$_4$ was confirmed by ^{1}H and ^{13}C NMR analyses. ^{1}H NMR (CDCl$_3$, ppm): 0.91–0.94 (t, 12H, N(CH$_2$)$_3$CH$_3$), 1.33–1.39 (m, 8H, N(CH$_2$)$_2$CH$_2$), 1.51–1.58 (q, 8H, NCH$_2$CH$_2$), 3.11–3.14 (t, 8H, NCH$_2$). ^{13}C NMR (ppm): 58.47, 23.77, 19.61, 13.60. Yield: 89%, physical state (at 24 °C): white solid.

Characterization of ionic liquids

The preparation of all ionic liquids was confirmed by their Fourier Transform Infrared (FTIR) and ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) analyses. FTIR spectra of all ionic liquids were recorded using Nicolet 8700 research spectrometer at 4 cm^{-1} resolution. The ^{1}H and ^{13}C NMR spectra of all ionic liquids were collected using Bruker Av III 500 MHz Spectrometer. Thermal decomposition properties of these ionic liquids were probed by a thermal analyzer (Diamond, PerkinElmer) under the flow of nitrogen (50 ml min^{-1}) at thermal rate of 10 °C min^{-1}. The viscosities at 40 and 100 °C, and viscosity index of each ionic liquid (2 wt%) in polyethylene glycol (PEG 200) synthetic lube base oil were measured as per the ASTM D445 and ASTM D2270 standard test methods, respectively. The corrosion properties of these ionic liquids were carried out using a copper strip as a substrate. In each test, a freshly polished copper strip was dipped in a vial containing 2 wt% of ionic liquid in PEG 200 at 100 °C for 3 hours. After the test, copper strip was washed thoroughly to remove the traces of ionic liquids. Corrosion pits, eventually developed on the copper strips, and changes in color were thoroughly examined by optical microscopy, Field Emission Scanning Electron Microscopy (FESEM) and elemental mapping.

Tribo-evaluation of ionic liquids

All lubrication tests were conducted on four-ball tribo tester (Ducom, India) following the ASTM D4172 standard test method. In a typical test, three steel balls (ϕ = 12.7 mm) were fixed in a pot containing the lube sample and fourth ball was rotated over these stationary balls under specific load and rotating speed. PEG 200 was used as a reference lube base oil throughout the study. All ionic liquids were kept in vacuum at 80 °C for 48 hours, prior to their tribo-evaluation. The known quantity of each ionic liquid was mixed with PEG 200 by normal stirring at ambient condition. All ionic liquids exhibited excellent miscibility with PEG 200. Blend of each ionic liquid in PEG 200 was used for lubrication test. Friction coefficient as a function of time for each sample was measured at a load of 392 N and rotating speed of 1200 for the one hour. Temperature of lube sample was maintained as 75 °C throughout the experiment. The structural features of the worn area of the steel balls, lubricated with different types of ionic liquid samples, were examined by FESEM using an FEI Quanta 200F. The elemental composition and distribution of elements on surfaces of the worn balls were examined by Energy Dispersive X-ray Spectroscopy (EDX). Coefficient of friction and wear scar diameter values reported here are the mean of three different tests of each sample. Furthermore, the error bar of each result is provided to understand the repeatability of test results.

Results and discussion

The chelated orthoborate ionic liquids comprising variable anions were prepared by metathesis of lithium salt of chelated orthoborate with TBA-Br in equimolar amount. Total four ionic liquids with aromatic and aliphatic structures (Fig. 1) were prepared to probe their structural effects on the thermal stability, corrosion and tribo-physical properties. The TBA-BF$_4$ ionic liquid was prepared as a halogenated analogue for comparison study. The synthesis of these ionic liquids were confirmed by their FTIR and NMR (^{1}H and ^{13}C) characterizations. The vibrational peak assignments of all ionic liquids are extracted in Table 1 and their respective spectra are shown as Fig. S6 (ESI†). FTIR spectra of TBA-BMdB and TBA-BScB ionic liquids showed weak vibrational peaks in the range of 3068–3030 cm^{-1} and a strong peak in the range of 1577–1557 cm^{-1}, which are ascribed to ν(C–H) and ν(C=C), respectively, revealing the presence of aromatic rings. These vibrational peaks are absent in rest of the ionic liquids because of their aliphatic nature. The strong vibrational features in the range of 3000–2800 cm^{-1} are attributed to the symbolic signature of methylene and methyl units of alkyl groups present in the TBA cation of all ionic liquids. The vibrational signatures in the region of 1800–1600 cm^{-1} are assigned to ν(C=O) and ν_a(O–C=O) stretching mode of COO group.[25] The ν_s(O–C=O) vibrational signature was splitted into two peaks in the range of 1275–1240 cm^{-1}, revealing the complex nature of carboxylate groups in the chelated orthoborate anions. The broad peaks in the range of 1200–900 cm^{-1} are attributed to ν_a(B–O) and ν(C–O), representing the tetrahedral chelated orthoborate complex. Two additional vibrations in the range of 801–768 and 725–696 are assigned to the ν_s(B–O) signature, and suggested the presence of chelated orthoborate complex.[26] These characteristic vibrational peaks confirmed the synthesis of chelated orthoborate ionic liquids. Besides that, the broad vibrational peaks at 1110–1036 cm^{-1}, attributed to the stretching modes of
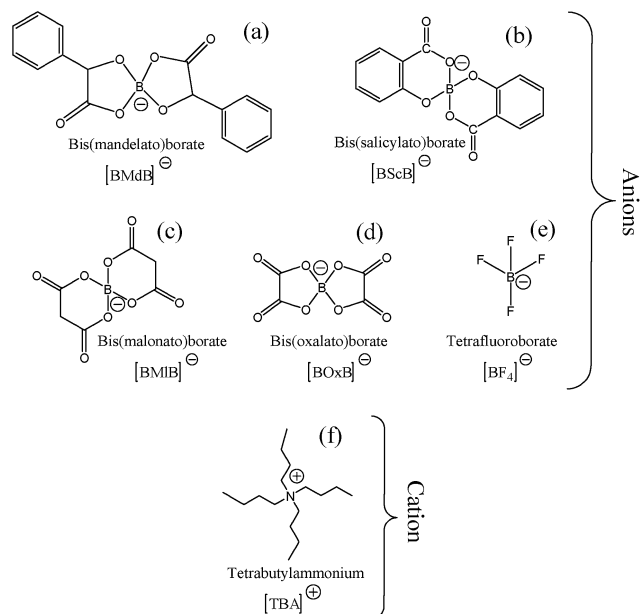
Fig. 1 Structural illustration of boron based anions (a) BMdB, (b) BScB, (c) BMlB, (d) BOxB and (e) BF$_4$. (f) TBA cation.

Fig. 2 Thermal decomposition of TBA-BMdB, TBA-BScB, TBA-BOxB and TBA-BF$_4$ ionic liquids at thermal rate of 10 °C min^{-1} under the nitrogen flow.

B–F and it confirmed the presence of BF$_4^-$ anion in the TBA-BF$_4$ ionic liquid.[27]

The thermal decomposition properties of synthesized ionic liquids were probed over the temperature range of 35 to 450 °C. Fig. 2 explicitly shows that TBA-BMdB and TBA-BScB ionic liquids exhibited higher thermal stability than TBA-BOxB ionic liquid. The higher thermal stability of TBA-BMdB and TBA-BScB ionic liquids are attributed to the presence of aromatic rings in their chelated structure, which provides higher intermolecular interactions and rigidity to their anionic moieties. It was noted that TBA-BMdB and TBA-BScB ionic liquids thermally decomposed in the range of 300–400 °C, whereas TBA-BOxB ionic liquid decomposed at moderately low thermal range, i.e. 200–270 °C. Thermal stability of ionic liquids were also measured in terms of nucleophilicity and coordinating nature of anions.[28] The BF$_4$ anion is considered as less nucleophilic and non-coordinating in nature, hence exhibited good thermal stability. Table 2 shows the TGA temperatures for 10, 20, 30 and 50% thermal loss of each ionic liquid, which are higher for
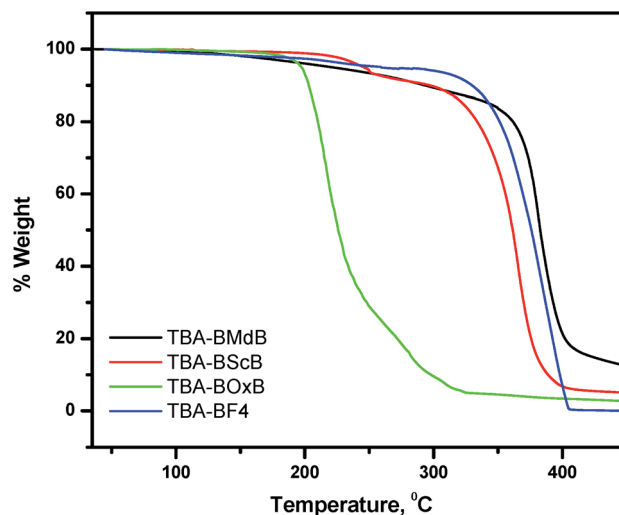
aromatic ring constituent TBA-BMdB and TBA-BScB ionic liquids compared to their aliphatic analogues.

Presence of halogen, phosphorus, and sulfur constituent components in the lubricant system facilitates the corrosion events and damages the engineering surfaces. Herein, corrosion property of each ionic liquid was probed by copper strip test method using 2 wt% blend of each ionic liquid in PEG 200. A freshly polished copper strip was exposed to ionic liquid blend for three hours at 100 °C. After thoroughly washing, the changes in structural features of each sample was examined by optical and electron microscopy. Fig. 3 shows the optical and electron microscopic images of the copper strips exposed to PEG 200 and 2 wt% blend of each ionic liquid. The copper strip, exposed to TBA-BOxB, exhibited corrosion pits (Fig. 3e$_i$) distributed throughout the substrate. These pits couldn't be revealed in optical images, however, electron microscopic images unambiguously demonstrated the sub-micron-to-few microns size pits. Furthermore, the elemental distribution images revealed that these pits are mainly composed of copper and oxygen (Fig. 4b). Owing to poor stability, BOxB tends to develop acidic products (oxalate), which might have interacted

Table 1 Infrared vibration frequencies of synthesized ionic liquids and their vibrational assignment

TBA-BScB	TBA-BMdB	TBA-BMlB	TBA-BOxB	TBA-BF$_4$	Vibrational assignment
3068, 3042	3062, 3030	—	—	—	ν(C–H), aromatic ring
2964, 2938, 2876	2963, 2935, 2876	2989, 2959, 2874	2962, 2937, 2875	2987, 2960, 2875	ν_a & ν_s(C–H), CH$_2$/CH$_3$ groups
1700, 1684	1738	1728	1805, 1778	—	ν(C=O)
1611	1601	1626	1625	—	ν_a(COO)
1577	1557	—	—	—	ν(C=C), aromatic
1478, 1466	1486, 1453, 1381	1473, 1456, 1381	1487, 1473, 1383	1472, 1379	δC–H, CH$_2$/CH$_3$ groups
1268, 1244	1271	1286, 1240	1275, 1244	—	ν_s(COO)
1200–900	1200–900	1200–900	1200–900	—	ν_a(B–O)/ν(C–O)
—	—	—	—	1108–1036 b	ν(B–F)
768, 698	770, 739, 694	796, 738	801, 740, 725	—	ν_s(B–O)

Table 2 Thermal loss of ionic liquids as deduced from thermogravimetric pattern of respective ionic liquid

Ionic liquids	TGA temperature for % weight loss, °C			
	10%	20%	30%	50%
TBA-BMdB	293.4	361.7	373.5	382.8
TBA-BScB	297.1	333.9	347.3	361.4
TBA-BOxB	203.1	210.2	215.2	225.9
TBA-BF$_4$	329.9	351.3	361.9	375.9

with copper substrate and developed the corrosion pits. The copper strip, exposed to TBA-BF$_4$ was significantly corroded and developed plenty of corrosion pits (Fig. 3f$_{i–ii}$). The element overlay images (Fig. 4c) explicitly showed that the corrosive pits are composed of fluorine, oxygen and copper, and are distributed throughout the substrate. However, the surface features of copper strips, exposed to TBA-BMdB, TBA-BScB and TBA-BMlB ionic liquids were found to remain intact without any damage. These results suggested that TBA-BMdB, TBA-BScB and TBA-BMlB ionic liquids, which are halogen-free, do not corrode the copper strips, whereas, presence of fluorine in TBA-BF$_4$, facilitated the corrosive events. Considering the non-corrosive properties, chelated orthoborate ionic liquids were then examined for their lubrication properties.

All tribological tests were conducted using steel balls in rolling contact geometry under the load of 392 N for one hour at 75 °C temperature. The average coefficient of friction and WSD for the PEG 200 were found as ~0.17 and 1275 μm, respectively. The TBA-BScB was used as a representative ionic liquid for the
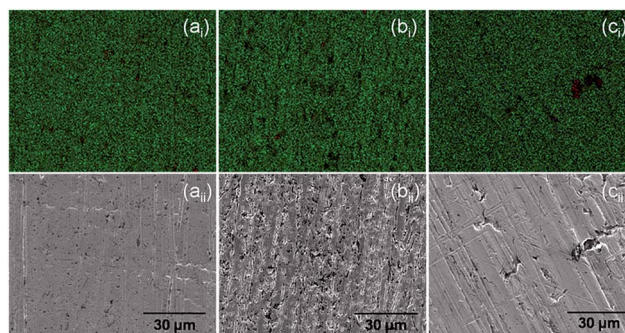

Fig. 4 Overlay elemental mapping and corresponding FESEM images of copper strips exposed to 2 wt% blends of (a$_{i–ii}$) TBA-BScB, (b$_{i–ii}$) TBA-BOxB and (c$_{i–ii}$) TBA-BF$_4$ ionic liquids in PEG 200 at 100 °C for 3 hours. The green, red and blue pixels represent copper, oxygen and fluorine, respectively.

dose optimization in PEG 200. Fig. 5 show gradual reductions in both friction and WSD with increasing the dose of TBA-BScB, and no further measurable changes were observed beyond the 2 wt% dose. These results revealed that 2 wt% dose of TBA-BScB is good enough to provide the efficient lubrication performance by interacting with tribo-interfaces and reduced both friction and WSD by ~60 and ~47%, respectively, compared to PEG 200. An addition of 2 wt% dose of each ionic liquid in PEG 200 has slightly improved the kinematic viscosities and viscosity index (Table S1, ESI†). This is attributed to the high viscosities of these ionic liquids and their excellent miscibility, which are important for their efficient performance in lubricant applications.

Fig. 6 compare the changes in coefficient of friction as a function of contact time for steel balls lubricated by PEG 200 and 2 wt% blends of TBA-BMdB, TBA-BMlB and TBA-BF$_4$ ionic liquids. PEG 200 is an additive-free lube base oil and under the tribo-stress, it is unable to hold the lube thin film between steel balls interfaces, resulting in high friction. The presence of boron based ionic liquids showed significant reductions in friction coefficient (Fig. 6). The inherent polarity of these ionic
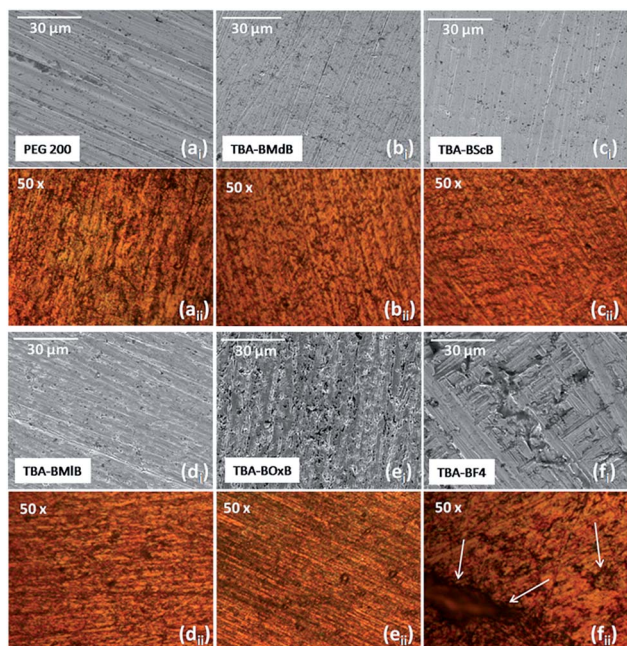

Fig. 3 FESEM and optical images of copper strips exposed to (a) PEG 200, and 2 wt% blends of (b) TBA–BMdB, (c) TBA–BScB, (d) TBA–BMlB, (e) TBA–BOxB, and (f) TBA–BF4 ionic liquids in PEG 200 for 3 hours at 100 °C.
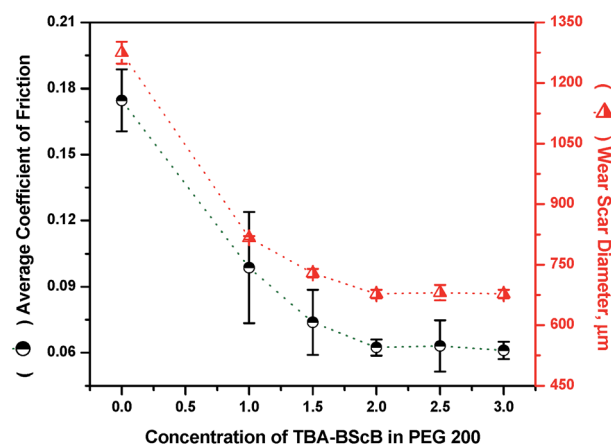

Fig. 5 Changes in coefficient of friction and WSD as a function of TBA-BScB ionic liquid dose in PEG 200. Load: 392 N, rotating speed: 1200 rpm, temperature: 75 °C, test duration: 1 hour.

liquids is believed to provide strong adsorption to the steel surfaces and forms the tribo-thin film of low shear strength, which reduces the friction significantly. Fig. 7 revealed that the degree of friction and WSD reductions are strongly monitored by the chemical structure of constituted anions. Among these ionic liquids, TBA-BMdB provided maximum reduction in both friction (~65%) and WSD (~55%) and was slightly better than the performance of TBA-BScB ionic liquid. The excellent friction-reducing and antiwear properties of TBA-BMdB and TBA-BScB ionic liquids were attributed to the compact, rigid and stable structure of BMdB and BScB anions, provided by two six-membered aromatic rings in each anion. The BMlB and BOxB anions based ionic liquids too reduced both friction and WSD, however, their tribo-performance was relatively poor. Furthermore, it was revealed that TBA-BOxB ionic liquid has poor thermal stability and its decomposed acidic (oxalic acid) product leads to corrosive events. As a result, TBA-BOxB showed higher friction and WSD compared to other chelated orthoborate ionic liquids.

Fig. 8 shows FESEM images of worn surface of steel balls lubricated by PEG 200 and 2 wt% blend of each ionic liquid. The worn area lubricated by PEG 200 exhibited very high WSD (~1275 μm) with lot of uneven features attributed to the plastic deformation on the steel surface under the tribo-stress, suggesting the direct contact between the steel balls. The 2 wt% dose of ionic liquids in PEG 200 reduced the WSD significantly and generates comparatively smoother features on the worn surfaces of steel balls (Fig. 8). Among all ionic liquids, maximum antiwear property was achieved by TBA-BMdB ionic liquid and was attributed to the compact, rigid and stable structure of BMdB anion. Furthermore, the EDX analyses of steel balls were carried out to probe the elemental composition of tribo-chemical thin film developed on the worn surfaces. The FESEM micrographs and corresponding elemental distribution images of worn area of steel balls lubricated with 2 wt% of each ionic liquid, explicitly illustrated uniform distribution of boron
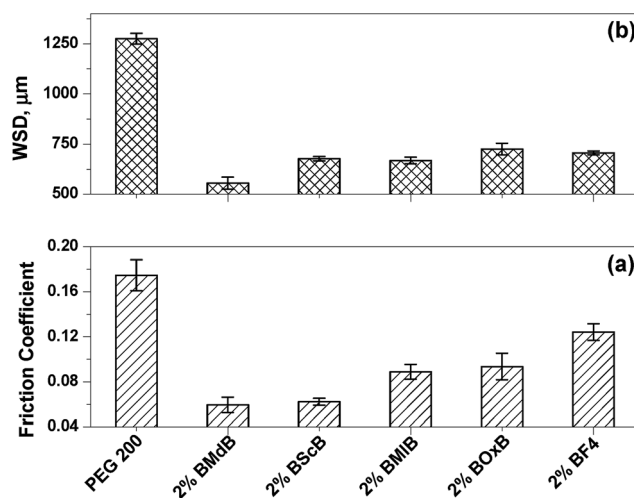

Fig. 7 Comparison of (a) coefficient of friction and (b) WSD of steel balls lubricated with PEG 200 and 2 wt% blend of TBA ionic liquids consisting variable anions, in PEG 200. Load: 392 N, rotating speed: 1200 rpm, temperature: 75 °C, test duration: 1 hour.

and nitrogen (Fig. 9a–d). In these ionic liquids, boron and nitrogen are characteristics elements of anion and cation, respectively, and are uniformly distributed on the worn area of steel balls. These results suggested that the tribo-chemical thin film on the steel balls are composed of ionic liquids or its tribo-chemical product.

In order to probe the effect of halogen, the friction and wear properties of fluorine constituted TBA-BF$_4$ ionic liquid was examined under identical condition (Fig. 7). Though, TBA-BF$_4$ showed reduction in both friction and wear, the tribo-performance was noted poorer compared to the chelated orthoborate ionic liquids. The elemental images (Fig. 9e) illustrated regular distribution of fluorine along with boron and nitrogen, throughout the worn surface. Usually, BF$_4$ anion based ionic liquid developed a tribo-thin film composed of FeF$_2$ and B$_2$O$_3$ over the steel surface,[11] and such tribo-chemical thin film reduced both the friction and wear. The corrosion results (Fig. 4) and poor tribo-performance suggested corrosive products generation by BF$_4^-$ anion constituted ionic liquids, which could be further facilitated by trapped water molecules in the lubricant. Probably, the corrosive events compromised the tribo-performance of TBA-BF$_4$ ionic liquid, and thus, poorer lubrication properties compared to the chelated orthoborate ionic liquids.

Elemental mapping results showed that chelated orthoborate ionic liquids have generated a tribo-chemical thin film on the steel interfaces, which was composed of tribo-chemical product of ionic liquids with the steel. The exact mechanism and role of ionic liquids in tribo-chemical thin film formation is believed to be complex because of inherent polarity of ionic liquids, rich boron chemistry, and hard nature of the boron. Usually, under the tribo-stress, metal surfaces induced the positive charge,[29] where the chelated orthoborate anions could be adsorbed and then counter cation TBA would have provided the layering structure through electrostatic attractions and
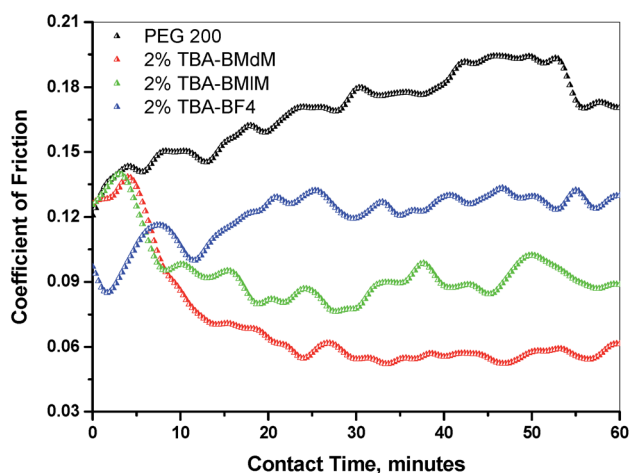

Fig. 6 The evolution of coefficient of friction with contact time for PEG 200, 2 wt% of TBA–BMdB, TBA–BMlB, and TBA–BF$_4$ ionic liquids individually blended in PEG 200. Load: 392 N, rotating speed: 1200 rpm, temperature: 75 °C, test duration: 1 hour.
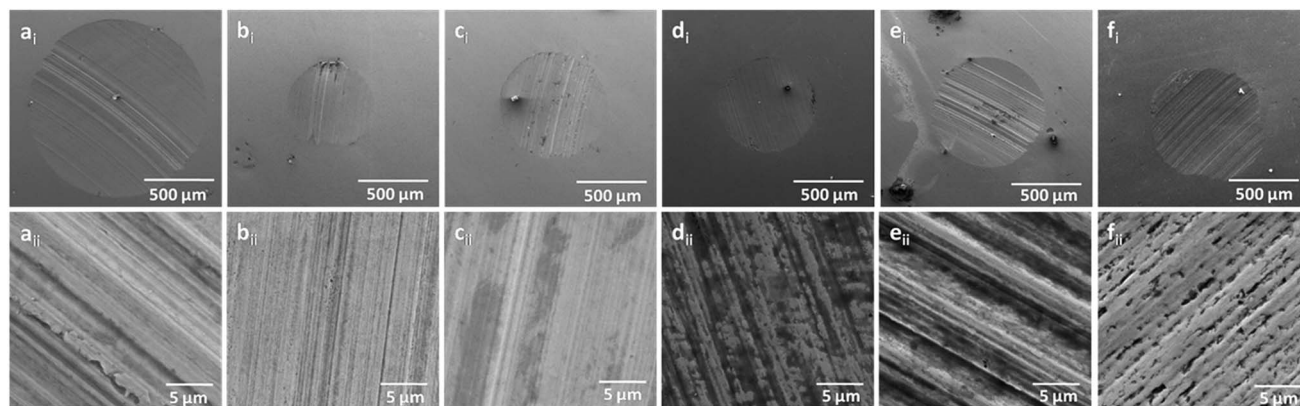
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Fig. 8 FESEM images of the worn surfaces of steel balls lubricated with (a$_{i-ii}$) PEG 200 and 2 wt% blends of (b$_{i-ii}$) TBA–BMdB, (c$_{i-ii}$) TBA–BScB, (d$_{i-ii}$) TBA–BMlB (e$_{i-ii}$) TBA–BOxB and (f$_{i-ii}$) TBA–BF$_4$ ionic liquids in PEG 200. Load: 392 N, rotating speed: 1200 rpm, temperature: 75 °C, test duration: 1 hour.
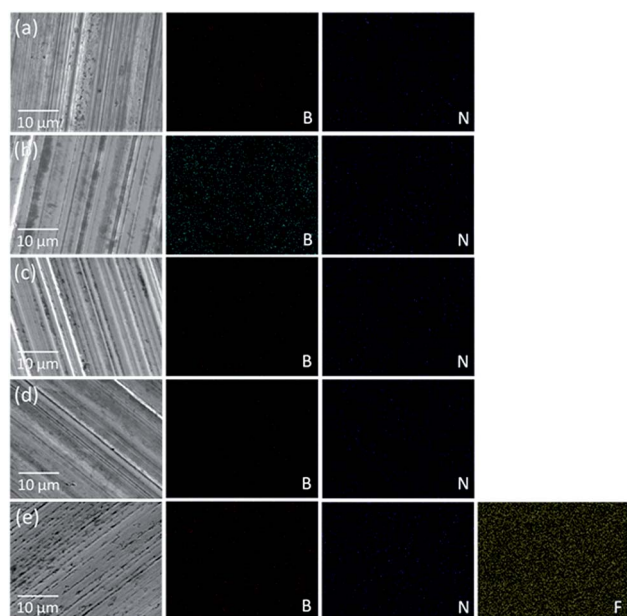

Fig. 9 Elemental mapping of worn area lubricated with 2 wt% of (a) TBA–BMdB, (b) TBA–BScB, (c) TBA–BMlB, (d) TBA–BOxB and (e) TBA–BF$_4$ in PEG 200. The uniform distribution of boron, and nitrogen revealed the presence of ionic liquids or its decomposed products in the tribo-chemical thin film. Furthermore, strong and uniform abundance of fluorine on TBA–BF$_4$ lubricated worn ball revealed the existence of fluorine based product on the tribo-interfaces. Load: 392 N, rotating speed: 1200 rpm, temperature: 75 °C, test duration: 1 hour.

generated the physico-chemically adsorbed tribo-thin film. This mechanism is further supported by the layering structure of ionic liquids confined between the two surfaces,[4] which provided low shear strength, and thus a significant reduction in the friction. The tribo-chemical thin film developed by chemical interaction of ionic liquids and their decomposed products with steel interfaces could be an alternate to justify the tribo-mechanism. Furthermore, elemental mapping results support the development of such tribo-chemical thin film. Recently, Oganov et al. have revealed that under the high pressure boron

generates partial negative charge,[7] which might facilitate the interaction of chelated orthoborate anions with steel surfaces and forms the tribo-thin film. Furthermore, the very hard nature of boron[30] is understood to provide durable tribo-thin film, which protects the steel interfaces and reduces wear significantly. Being halogen- and phosphorus-free, these ionic liquids offer an energy-efficient, environment-friendly, and economic alternative to the conventional halogenated ionic liquids for the lubrication applications.

Conclusion

The focus of this work was (a) to develop halogen- and phosphorus-free ionic liquids as energy efficient and environment-friendly lubricant additives for the steel based engineering surfaces, and (b) to established the correlation between structure of anion and tribo-physical properties of ionic liquids. In this study, chelated orthoborate ionic liquids, having structural variations in their anionic moieties, were synthesized and then thoroughly characterized by NMR (¹H and ¹³C) and FTIR. The aromatic rings constituted TBA-BMdB and TBA-BScB ionic liquids exhibited higher thermal stability compared to their aliphatic analogous (TBA-BMlB and TBA-BOxB). The higher stability of former ionic liquids was attributed to higher intermolecular interactions and rigidity to their anionic moieties. The copper strip test results revealed non-corrosive nature of TBA-BMdB, TBA-BScB and TBA-BMlB ionic liquids, whereas, halogen-constituted TBA-BF$_4$ ionic liquid developed several corrosion pits under identical conditions. The hydrolysis and decomposed product of TBA-BF$_4$ ionic liquid were found to facilitate the corrosion events, as revealed by elemental mapping of corroded areas. All synthesized ionic liquids are miscible with synthetic lubricant PEG 200. The 2 wt%, as an optimized dose of TBA-chelated orthoborate ionic liquids in PEG 200, remarkably improved the friction-reducing and antiwear properties. Among chelated orthoborate ionic liquids, TBA-BMdB and TBA-BScB showed better lubrication properties. Elemental mapping on the worn surfaces suggested the formation of tribo-chemical thin film composed of ionic

liquids and their tribo-chemical products with the steel surfaces. The inherent polarity of ionic liquids, rich boron chemistry, coulombic force induced layering structure of ionic liquids, hard nature of boron *etc.* collectively play the role for development of the tribo-chemical thin film on the contact interfaces of steel balls, which not only reduces the friction, but also protects tribo-interfaces. These results promise great potential of boron based ionic liquids for industrial lubricant applications.

Acknowledgements

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