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Halogen-free imidazolium/ammonium-bis(salicylato)borate ionic liquids as high performance lubricant additives†

Rashi Gusain, Raghuvir Singh, K. L. N. Sivakumar and Om P. Khatri*

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Halogen-free bis(salicylato)borate anion based ionic liquids having imidazolium and ammonium cations, were designed, synthesized, characterized and then evaluated as potential lubricant additives. Owing to the high polarity, high London dispersive forces and high rigidity associated with the bulk size and ring structure of the bis(salicylato)borate anion, these ionic liquids possess very high viscosities. The interaction of these ionic liquids with contact surfaces has been found to be strongly influenced by the van der Waals interactions in the ionic liquids, which increases with an increase of the alkyl chain length, particularly, for the imidazolium cations. As lubricant additives, both imidazolium and ammonium ionic liquids markedly improve the friction-reducing and anti-wear properties of PEG 200 lube base. Microstructural images and element mapping of the worn surfaces of steel balls reveal that these ionic liquids form tribo-films, which reduces both the friction and wear. Being halogen-, phosphorus-, and sulfur-free, bis(salicylato)borate ionic liquids not only protect contact surfaces from tribo-corrosive events but also keep the environment green and clean. These ionic liquids offer an environmentally friendly alternative to conventional halogenated ionic liquids being currently developed for lubricant applications.

Introduction

The need to conserve energy and to protect the environment has propelled an interest in the development of green and energy efficient lubricants and lubricant additives, which can keep the surfaces of working parts separate under all loads, temperatures and speeds, reduce the friction and wear significantly, dissipate the heat from the contact surfaces, and increase the life of sliding machine tools by protecting contact surfaces. In this context, ionic liquids have been explored in recent years as lubricants and lubricant additives.[1–4] Ionic liquids are salts of organic cations and inorganic/organic anions, where the charges on these ions are highly diffuse, consequently, most of them are liquids at <100 °C. Ionic liquids possess a combination of unique and tunable physico-chemical characteristics such as low volatility, good thermal stability, non-flammability, and excellent conductivity, which makes them potent candidates for tribological applications. The flexibility in molecular structure with a diverse range of cations and anions makes ionic liquids versatile lubricants for different engineering surfaces. Therefore, ionic liquids can be designed for task-specific purposes, considering the nature of the sliding surfaces and the lube base stock. A first report by Ye *et al.* demonstrated the potential of ionic liquids as versatile lubricants for the contact surfaces of steel, aluminium, copper, SiO_2 and ceramics.[5] They found excellent friction reduction and anti-wear performance. Since then, the interest in ionic liquids as novel lubricants, lubricant additives and lubricious thin films has gradually increased. Different types of ionic liquids with imidazolium, ammonium, phosphonium, pyridinium, pyrrolidinium, *etc.* as cations and halides, PF_6^-, BF_4^-, NO_3^-, ClO_4^-, Tf_2N^-, $BETI^-$, FAP^-, *etc.* as anions have been studied for their tribological potential.[5–13] The inherent polar nature of ionic liquids facilitates their interaction with sliding surfaces, resulting in lube film formation. Such lube films of ionic liquids avoid metal-to-metal contact, and consequently result in a reduction in friction and wear. Most of the ionic liquids studied for lubricant applications, contain halogens, sulphur and phosphorus either in simple or complex form (halides, tetrafluroborate, hexaflurophosphate, bis(trifluoromethanesulfonyl)amide, trifluoromethanesulfonate, phosphates, sulfates, *etc.* as anions and phosphonium, *etc.* as cation), which are prone to interact with moisture. In particular, hydrophilic ionic liquids having halides, phosphates and sulphates are more prone to hydrolyze.[14–17] Eventually, such interactions facilitate corrosive events, under tribological conditions (high temperature and pressure) and can damage the contact surfaces in mechanical systems. Therefore, the development of halogen-, sulphur- and phosphorus-free ionic liquids is urgently required

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CSIR – Indian Institute of Petroleum, Mohkampur, Dehradun-248005, India. E-mail: opkhatri@iip.res.in; Fax: +91 135 2660202

† Electronic supplementary information (ESI) available: Information on wear scar diameter and FTIR spectra of all the ionic liquids used in this study. See DOI: 10.1039/c3ra43052a

for industrial lubricant applications, not only to reduce friction and loss of material from contact surfaces but also to protect the environment.

The miscibility of ionic liquids with lube base is very important for their efficient performance as lubricant additives and is dependant on their molecular structure. Smolenski *et al.*developed an oil-miscible trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate ionic liquid as a potential additive, which showed significant reduction of both friction and wear.[18] The presence of long alkyl chains facilitates its miscibility with various hydrocarbon oils. Recently, Antzutkin *et al.* have designed halogen-free chelated orthoborate–phosphonium ionic liquids as lubricants.[19] These ionic liquids exhibited considerably better anti-wear and friction-reducing properties, compared with fully formulated 15W-40 engine oil. However, from the environmental viewpoint, the presence of phosphorus is of serious concern. In further development, tricyanomethanide $[C(CN)_3]^-$ and tetracyanoborate $[B(CN)_4]^-$ anions based ionic liquids have been designed to eliminate halogen, sulphur and phosphorous.[20] However, these ionic liquids as lubricants showed no significant improvement in their tribological properties.

Herein, we report the synthesis, characterization and the tribo-evaluation of bis(salicylato)borate anion based ionic liquids. Two series of ammonium and imidazolium ionic liquids were evaluated as lubricant additives using PEG 200 as a lube base on a four-ball tribo-test machine. These ionic liquids have shown significant reduction in both friction and wear. The microstructural and elemental analysis of the worn surfaces of steel balls, based on FESEM and EDX measurements, respectively, revealed the role of the ionic liquids in the improvement of lubrication characteristics.

Experimental

Materials

1-Methylimidazole (99%, Sigma Aldrich), tetrabutylammonium bromide (GR, Merck Chemicals), tetraoctylammonium bromide (98%, Sigma Aldrich), dioctylamine (98%, Sigma Aldrich), formic acid (GR, Merck Chemicals), formaldehyde (41%, SD Fine Chemicals), 1-bromopentane (purum, Fluka), boric acid (99.5%, Loba Chemie), lithium carbonate (99.9%, Sigma Aldrich), salicylic acid (99.8%, Merck Chemicals) were used without further purification as precursors for the synthesis of the ionic liquids. 1-Butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (BMI-FAP, Merck Chemicals), and 1-butyl-3-methylimidazolium dibutylphosphate (BMI-DBP, Sigma Aldrich) ionic liquids were used without further purification.

Synthesis and NMR characterization of ionic liquids

Tetrabutylammonium bis(salicylato)borate (TBA-BScB). First, the lithium salt of bis(salicylato)borate was prepared by mixing salicylic acid (2.762 g, 20 mmol) in an aqueous solution of lithium carbonate (0.734 g, 10 mmol) and boric acid (0.619 g, 10 mmol).[21] The solution was heated at 60 °C for 2 hours under continuous stirring. Then tetrabutylammonium bromide (10 mmol) was added to this solution and heated for a further 2 hours. This led to the formation of an organic layer composed of TBA-BScB ionic liquid in the reaction product, which was extracted using dichloromethane. This was followed by washing of TBA-BScB with pure water until no more bromide ions were detected in the water. Finally, dichloromethane was removed under reduced pressure and the extracted product was dried in a vacuum oven at 80 °C under reduced pressure for 48 hours. The preparation of TBA-BScB was confirmed by ^{1}H and ^{13}C NMR analyses. ^{1}H NMR ($CDCl_3$, ppm): δ 0.8–0.9 (t, 12H, $N(CH_2)_3CH_3$), 1.3 (m, 8H, $N(CH_2)_2CH_2$), 1.5 (q, 8H, NCH_2CH_2), 3.1 (t, 8H, NCH_2), 6.8–6.9 (m, 4H, C_6H_4), 7.29–7.39 (m, 2H, C_6H_4), 7.86–7.95 (dd, 2H, C_6H_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.

Tetraoctylammonium bis(salicylato)borate (TOA-BScB). Tetraoctylammonium bis(salicylato)borate (TOA-BScB) was prepared by following the TBA-BScB preparation procedure using tetraoctylammonium bromide (10 mmol) as a cationic precursor, instead of tetrabutylammonium bromide. The preparation of TOA-BScB was confirmed by ^{1}H and ^{13}C NMR analyses. ^{1}H NMR ($CDCl_3$, ppm): δ 0.84–0.87 (t, 12H, $N(CH_2)_7CH_3$), 1.19–1.24 (m, 40H, $NCH_2CH_2(CH_2)_5CH_3$), 1.46–1.52 (m, 8H, $NCH_2CH_2(CH_2)_5CH_3$), 3.0–3.11 (t, 8H, $NCH_2(CH_2)_6CH_3$), 6.8–6.9 (m, 4H, C_6H_4), 7.28–7.34 (m, 2H, C_6H_4), 7.87–7.89 (dd, 2H, C_6H_4). ^{13}C NMR (ppm): 173.09, 165.33, 161.89, 159.47, 134.54, 130.71, 129.73, 58.57, 31.61, 28.97, 26.12, 22.58, 21.58, 21.77, 14.07.

Dioctylmethylpentylammonium bis(salicylato)borate (DOMPA-BScB). Dioctylmethylpentylammonium bis(salicylato)borate (DOMPA-BScB) was prepared by following the TBA-BScB preparation procedure using dioctylmethylpentylammonium bromide (10 mmol) as a cationic precursor, instead of tetrabutylammonium bromide. Prior to this, dioctylmethylpentylammonium bromide was prepared by heating a mixture of formic acid (0.55 mol, 21 ml), dioctylamine (0.4 mol, 32 ml) and formaldehyde (1.2 mol, 23 ml) in a round bottom flask at 100 °C for 8 hours in the presence of boiling stones.[22] Finally, an equimolar amount of 1-bromopentane was added to the freshly prepared dioctylmethylamine and the reaction mixture was heated at 100 °C for 24 hours under continuous stirring to afford dioctylmethylpentylammonium bromide. The preparation of DOMPA-BScB ionic liquid was confirmed by ^{1}H and ^{13}C NMR analyses. ^{1}H NMR ($CDCl_3$, ppm): δ 0.815–0.874 (m, 9H, CH_2CH_3), 1.19–1.29 (m, 24H, $NCH_2CH_2(CH_2)_5CH_3$ and $NCH_2CH_2(CH_2)_2CH_3$), 1.52–1.54 (m, 6H, $NCH_2CH_2(CH_2)_5CH_3$ and $NCH_2CH_2(CH_2)_2CH_3$), 2.951 (s, 3H, NCH_3), 3.10–3.14 (t, 6H, $NCH_2(CH_2)_6CH_3$ and $NCH_2(CH_2)_3CH_3$), 6.8–6.9 (m, 4H, C_6H_4), 7.27–7.40 (m, 2H, C_6H_4), 7.86–7.89 (dd, 2H, C_6H_4). ^{13}C NMR (ppm): 165.46, 159.39, 134.78, 129.66, 119.06, 118.41, 115.34, 61.57, 55.50, 48.38, 31.58, 28.95, 28.07, 26.08, 23.74, 22.56, 22.10, 21.82, 14.07, 13.73.

3-Ethyl-1-methylimidazolium bis(salicylato)borate (EMIM-BScB). 3-Ethyl-1-methylimidazolium bis(salicylato)borate (EMIM-BScB) was prepared by mixing an equimolar (10 mmol) quantity of lithium salt of bis(salicylato)borate and 3-ethyl-1-methylimidazolium bromide (10 mmol) at 60 °C for 2 hours under continuous stirring. The prepared EMIM-BScB ionic liquid was extracted using dichloromethane and washed a couple of times with pure water to remove the inorganic salt. Finally, dichloromethane was removed under reduced pressure and the extracted product was dried in a vacuum oven at 80 °C under reduced pressure for 48 hours to afford the EMIM-BScB ionic liquid. Prior to this, 3-ethyl-1-methylimidazolium bromide was prepared by mixing an equimolar amount of ethyl bromide and 1-methylimidazole in a round bottom flask and heating the reaction mixture at 75 °C for 36 hours under a nitrogen atmosphere with continuous stirring. The prepared 3-ethyl-1-methylimidazolium bromide was purified by washing with ethyl acetate and then used for the synthesis of EMIM-BScB. The preparation of EMIM-BScB was confirmed by ^{1}H and ^{13}C NMR analyses. ^{1}H NMR ($CDCl_3$, ppm): δ 1.25–1.35 (t, 3H, $NCH_2C\mathit{H}_3$), 3.15 (s, 3H, $NC\mathit{H}_3$), 3.8–3.9 (t, 2H, $NC\mathit{H}_2CH_3$), 6.78–6.9 (m, 4H, C_6H_4), 7.15–7.27 (d, 2H, $C\mathit{H}$), 7.3–7.4 (m, 2H, C_6H_4), 7.75–7.89 (dd, 2H, C_6H_4), 8.9 (s, 1H, $C\mathit{H}$). ^{13}C NMR: 165.82, 161.67, 159.11, 135.72, 135.37, 123.46, 121.67, 119.44, 119.02, 117.09, 114.87, 44.92, 35.98, 14.88.

3-Butyl-1-methylimidazolium bis(salicylato)borate (BMIM-BScB). 3-Butyl-1-methylimidazolium bis(salicylato)borate (BMIM-BScB) was prepared by following the EMIM-BScB preparation procedure using 3-butyl-1-methylimidazolium bromide (10 mmol) as a precursor, instead of 3-ethyl-1-methylimidazolium bromide. The preparation of BMIM-BScB was confirmed by ^{1}H and ^{13}C NMR analyses. ^{1}H NMR ($CDCl_3$, ppm): δ 0.79–0.82 (t, 3H, $N(CH_2)_3C\mathit{H}_3$), 1.15–1.19 (h, 2H, $N(CH_2)_2C\mathit{H}_2$), 1.61–1.67 (q, 2H, $NCH_2C\mathit{H}_2$), 3.73 (s, 3H, $NC\mathit{H}_3$), 3.96–3.99 (t, 2H, $NC\mathit{H}_2$), 6.8–6.9 (m, 4H, C_6H_4), 7.124–7.128 (d, 2H, CH), 7.36–7.39 (m, 2H, C_6H_4), 7.82–7.86 (dd, 2H, C_6H_4), 8.9 (s, 1H, CH). ^{13}C NMR (ppm): 173.29, 165.80, 161.73, 159.21, 136.32, 135.10, 129.59, 123.42, 121.93, 119.30, 118.37, 116.99, 114.97, 49.63, 36.10, 31.67, 19.26, 13.24.

3-Hexyl-1-methylimidazolium bis(salicylato)borate (HMIM-BScB). 3-Hexyl-1-methylimidazolium bis(salicylato)borate (HMIM-BScB) was prepared by following the EMIM-BScB preparation procedure using 3-hexyl-1-methylimidazolium bromide (10 mmol) as a precursor, instead of 3-ethyl-1-methylimidazolium bromide. The preparation of HMIM-BScB was confirmed by ^{1}H and ^{13}C NMR analyses. ^{1}H NMR ($CDCl_3$, ppm): δ 0.80–0.83 (t, 3H, $N(CH_2)_5C\mathit{H}_3$), 1.17–1.22 (h, 6H, $N(CH_2)_2(C\mathit{H}_2)_3$), 1.685–1.712 (q, 2H, $NCH_2C\mathit{H}_2$), 3.79 (s, 3H, $NC\mathit{H}_3$), 4.0–4.03 (t, 2H, $NC\mathit{H}_2$), 6.85–6.95 (m, 4H, C_6H_4), 7.09–7.10 (d, 2H, $C\mathit{H}$), 7.37–7.39 (m, 2H, C_6H_4), 7.83–7.88 (dd, 2H, C_6H_4), 9.23 (s, 1H, $C\mathit{H}$). ^{13}C NMR (ppm): 172.54, 165.83, 161.84, 159.26, 136.39, 135.08, 130.64, 129.61, 123.40, 121.90, 119.26, 118.41, 117.23, 114.99, 49.93, 36.13, 30.91, 29.79, 29.73, 25.73, 22.27, 13.88.

Characterization of ionic liquids

Fourier transform infrared (FTIR) spectra of all the ionic liquids were recorded using a Thermo-Nicolet 8700 Research spectrophotometer with a 4 cm^{-1} resolution. The viscosity and density of the ionic liquids were measured simultaneously in a Stabinger viscometer (Anton Paar, model SVM3000). The changes in viscosities and densities of the ionic liquids as a function of temperature were measured up to 363 K. Field emission scanning electron microscopy (FESEM) images of the worn surface areas of the steel balls were taken using an FEI Quanta 200F. The elemental composition and mapping of the worn surface area of the steel balls were carried out by using energy dispersive X-ray spectroscopy (EDX) to probe the chemical composition of the tribo-film.

Friction and wear tests

Lubrication characteristics in terms of friction coefficient and wear scar diameter (WSD) for ionic liquids blended with PEG 200 were evaluated on a four-ball test machine. Details of the WSD are provided in the ESI.† PEG 200 is an additive-free lube base oil. In a typical experiment, a 12.7 mm steel ball under the load was rotated against three stationary steel balls clamped in the holder. All the tests were carried out as per the ASTM D4172 standard test method at a load of 392 N with a rotating speed of 1200 rpm for an hour. The temperature of the sample was maintained as 75 °C throughout the experiment. During these experiments, the four balls were covered with a lube sample, which was used for the wear and friction evaluation. The morphological features of the worn areas of the steel balls, lubricated with different types of ionic liquid samples were examined by field emission scanning electron microscopy.

Results and discussion

Bis(salicylato)borate, a chelated orthoborate anion, was synthesized by using a mixture of salicylic acid, boric acid and lithium carbonate. Tetraalkylammonium bis(salicylato)borate

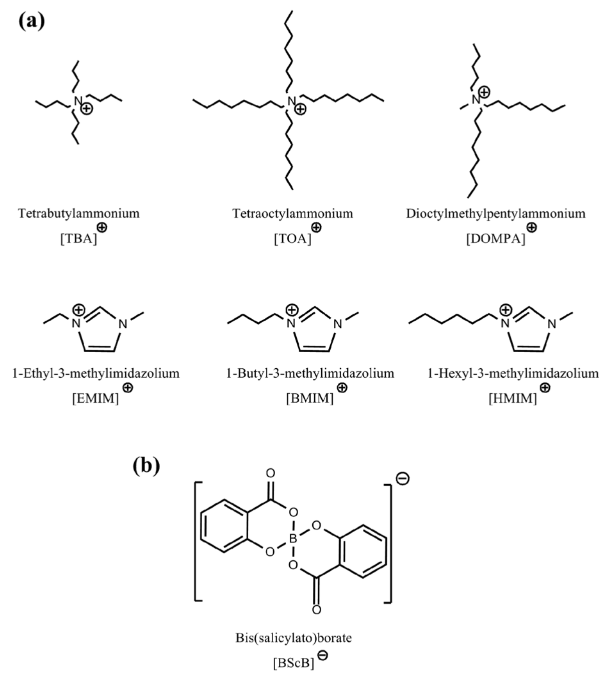


Fig. 1 Structural illustration of (a) ammonium and imidazolium cations, and (b) bis(salicylato)borate anion.

Table 1 Infrared vibration frequencies of ionic liquids with their vibrational assignment

Ammonium cation			Imidazolium cation			
TBA-BScB	TOA-BScB	DOMPA-BScB	EMIM-BScB	BMIM-BScB	HMIM-BScB	Vibrational assignment
3069w, 3041w	3065w, 3041w	3065w, 3041w, 3015w	3151s, 3112s,b	3150s, 3110m, 3083m	3149s, 3111s,b	ν(C–H), aromatic groups
2964s, 2938s, 2876s	2955s, 2927s, 2856s	2956s, 2928s, 2857s	2982w, 2939w, 2853w	2961s, 2933m, 2872s	2960s, 2935s, 2869s	ν_a & ν_s(C–H), CH_2/CH_3 groups
1683s	1685s	1684s	1681s	1680s	1685s	ν(C=O)
1611s	1611s	1610s	1609s	1608s	1610s	ν_a(COO)
1577w	1580w	1579w	—	—	—	ν(C=C), aromatic
—	—	—	1575m	1575w	1575m	ν(C–N/C–C), imidazolium ring, ν(C=C), aromatic
1465s	1466s	1468s	1467s	1469s	1468s	δ C–H, CH_2 groups
1269s, 1244s	1269s, 1242s	1268s, 1242s	1268s, 1243s	1267s, 1241s	1266s, 1244s	ν_s(COO), split peaks
1200–900	1200–900	1200–900	1200–900	1200–900	1200–900	ν_a(B–O)/ν(C–O)
768s, 699s	759s, 698s	759s, 698s	762s, 699s	761s, 700s	753s, 697s	ν_s(B–O)

and alkylmethylimidazolium bis(salicylato)borate ionic liquids were prepared by metathesis of lithium bis(salicylato)borate with tetraalkylammonium and alkylmethylimidazolium halides, respectively. A total of six ionic liquids, three under each category, having variable alkyl groups (Fig. 1) attached to ammonium and imidazolium ionic liquids were prepared to probe their effect on tribological properties. The preparation of these ionic liquids was confirmed by their NMR and FTIR analyses. The vibrational peak assignments of ammonium and imidazolium bis(salicylato)borate ionic liquids are presented in Table 1. FTIR spectra (Fig. S2, ESI†) of these ionic liquids showed strong vibrational peaks in the range of 3000–2800 cm^{-1} associated to alkyl groups,[23–25] of ammonium and imidazolium cations. Ammonium bis(salicylato)borate ionic liquids exhibited weak vibrations in the range of 3080–3000 cm^{-1}, which are attributed to ν(C–H), revealing the presence of an aromatic ring in the bis(salicylato)borate anion. However, in imidazolium ionic liquids, in addition to these weak signatures, new strong vibrational peaks appeared in the range of 3160–3080 cm^{-1} which are attributed to ν(C–H) of the imidazolium rings.[23] The other characteristic vibrational peaks at 1685 and 1610 cm^{-1} are attributed to ν(C=O) and ν_a(COO) functionalities. The ν_s(COO) vibrational signature was divided into two peaks at 1268 and 1242 cm^{-1}, revealing the complex carboxylate group in the bis(salicylato)borate anion.[26] Further, the strong vibrations in the range of 1200–900 cm^{-1} are attributed to the ν_a(B–O) in tetrahedral boron complexes. Two additional vibrations were present at ~760 and ~698 cm^{-1} representing the ν_s(B–O) signature in bis(salicylato)borate anion. As a whole, these vibrational characteristics show the preparation of ammonium and imidazolium bis(salicylato)borate ionic liquids.

Ionic liquids based on chelated orthoborate anions were found to have high glass transition temperatures and very high viscosities at room temperature than those with perfluorinated anions such as bis(trifluoromethane)sulfonimide, trifluoromethanesulfonyl, tetrafluoroborate, *etc.*[27] In general, the viscosity of ionic liquids is governed by multiple factors including van der Waals interactions, coulomb force, hydrogen bonding, ion size, polarizability of the ions, degree of freedom within the ion, *etc.*[28] Herein, the high viscosities of BScB based ionic liquids was found to be due to (a) high dipole–dipole attractions determined by the high polarity (containing two carbonyl groups), (b) high London dispersion forces, determined by the bulkier size of bis(salicylato)borate anion and (c) high rigidity (comprising two six-membered aromatic rings and

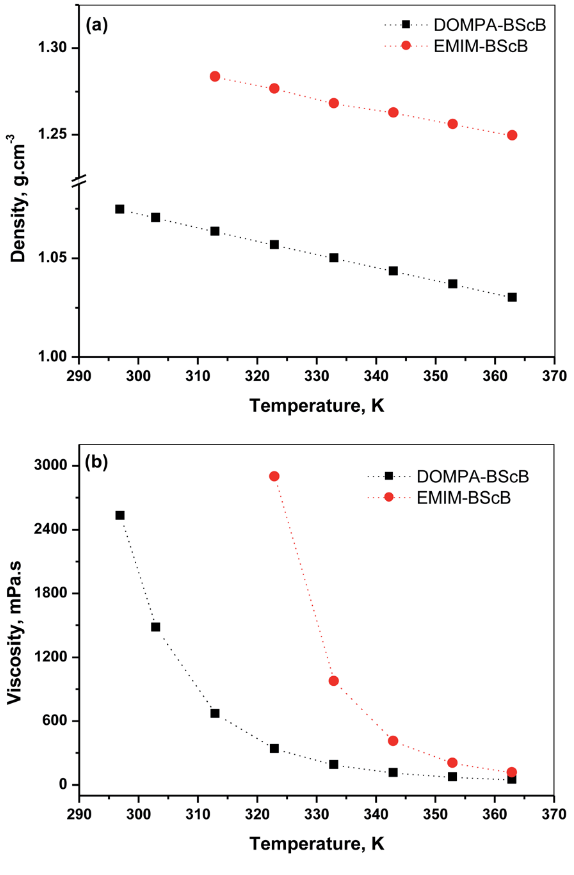


Fig. 2 (a) Density and (b) viscosity of DOMPA-BScB and EMIM-BScB ionic liquids as a function of temperature.

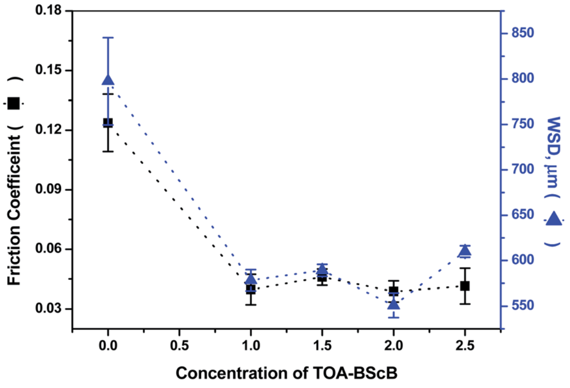


Fig. 3 Changes in friction coefficient and WSD for TOA-BScB ionic liquid as a function of concentration blended with PEG 200 under a load of 392 N, speed of 1200 rpm, and temperature of 75 °C for one hour.

two five membered rings) of the bis(salicylato)borate anion. The structure of the cation also influences the viscosity of the ionic liquids. In bis(salicylato)borate ionic liquids, aromatic imidazolium cations have a higher density and viscosity than aliphatic ammonium cations (Fig. 2). The imidazolium ionic liquids significantly loose their fluidity with an increase in the alkyl chain length attached to the imidazolium ring. The longer the chain length the further the van der Waals interaction force, resulting in a change from a wax-to-solid form of the HMIM-BScB. Fig. 2 shows the temperature dependence of the density and viscosity of the DOMPA-BScB and EMIM-BScB ionic liquids, selected as representative examples from the imidazolium and ammonium cation series. The densities were found to reduced linearly with increasing temperature as reported earlier.[29] The viscosity of bis(salicylato)borate anion based ionic liquids was found to change significantly with temperature (Fig. 2b). The thermal kinetic energy of ionic liquids molecules increase with an increase of temperature, as a result, the viscosities of EMIM-BScB and DOMPA-BScB decrease markedly with an increase of temperature.

The synthesized halogen-free BScB anion based ionic liquids were further evaluated for their lubrication potential using PEG 200 as the lube base stock. Fig. 3 shows the average friction coefficient and WSD for different doses of TOA-BScB ionic liquid blended with PEG 200 under a load of 392 N. The average friction coefficient and WSD for PEG 200 were about 0.123 and 797 μm, respectively. A 1% (w/v) dose of TOA-BScB resulted in a significant reduction of both the friction coefficient and WSD . A further increase of the TOA-BScB concentration resulted in no significant change in friction coefficient, however, the WSD was found to be at a minimum at a concentration of 2%. Therefore, a 2% dose was considered to be the optimum concentration for further studies. These results reveal that TOA-BScB as an additive, played a positive role in remarkably improving the lubrication properties of PEG 200.

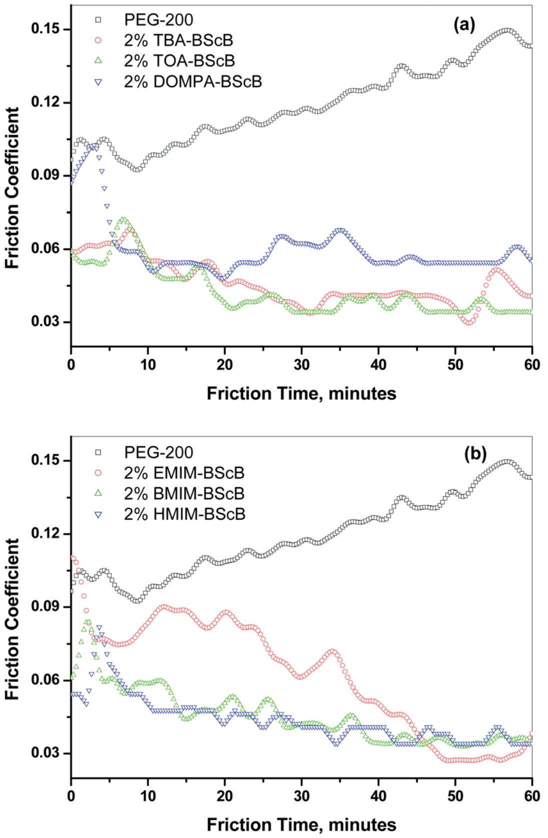


Fig. 4 Changes in friction coefficient *versus* time for (a) ammonium ionic liquids (TBA-BScB, TOA-BScB and DOMPA-BScB) and (b) imidazolium ionic liquids (EMIM-BScB, BMIM-BScB and HMIM-BScB) blended with PEG 200. Concentration of ionic liquids: 2% w/v, load: 392 N, rotating speed: 1200 rpm, temperature: 75 °C, and test duration: 1 hour.

Fig. 4 illustrates the variation in friction coefficient with time for steel balls lubricated with ammonium and imidazolium-BScB ionic liquids blended with PEG 200. The friction coefficient of PEG 200 was found to gradually increase with time. An absence of friction and wear modifier in PEG 200 led to direct contact between the steel balls under the high tribo-stress, which promoted not only high friction but also severe wear and scuffing of materials. Probably the severe wear and high scuffing increased with time and made the materials more uneven, consequently, the friction increased with time. In both ammonium and imidazolium ionic liquids, the alkyl chain structure was changed to study their effect on tribo-characteristics. There was a significant reduction in the friction coefficient for both ammonium and imidazolium ionic liquids blended samples compared to that of PEG 200. DOMPA-BScB ionic liquid showed a comparatively higher friction coefficient than the corresponding TBA-BScB and TOA-BScB ionic liquids (Fig. 4a). In tribology, the viscosity index (VI) and friction reducing additives play a crucial role in reducing the friction between contacting surfaces. In general, the viscosity of lubricant decreases with a increase of temperature and at high temperature the lubricant becomes too thin and unable to force the two contacting surfaces apart, resulting in severe wear. Hence, for good lubricants the viscosity should not be reduced significantly at high temperatures, which means that the VI should be high. As is shown in Table 2, the VI of PEG 200 was improved by the addition of TBA-BScB and TOA-BScB ionic liquids, whereas

Table 2 Physico-chemical properties of lubricants used for tribological evaluation

Lubricant	Kinematic viscosity/ $mm^2\ s^{-1}$ At 40 °C	At 100 °C	Viscosity index	Pour point/ °C	Density/ $g\ ml^{-1}$
PEG 200	22.4	4.1	70	−27	1.13
2% TBA-BScB	23.38	4.33	85	−45	1.13
2% TOA-BScB	23.46	4.34	85	−45	1.13
2% DOMPA-BScB	23.77	4.13	50	−45	1.14
2% EMIN-BScB	23.94	4.34	79	−51	1.13
2% BMIM-BScB	23.08	4.26	80	−48	1.13

DOMPA-BScB ionic liquid reduced the VI. This reveals that the low VI of DOMPA-BScB blended PEG 200 at high temperature (75 °C), might be unable to support the load, hence there is more chance of metal-to-metal contact. Therefore, DOMPA-BScB ionic liquids have a higher friction coefficient (Fig. 4a and 5b) and wear scar diameter compared to those of TBA-BScB and TOA-BScB. It was also noted that after a couple of minutes, DOMPA-BScB molecules were able to reduce the friction, however, friction was still higher than that for the TBA and TOA cations based ionic liquids.

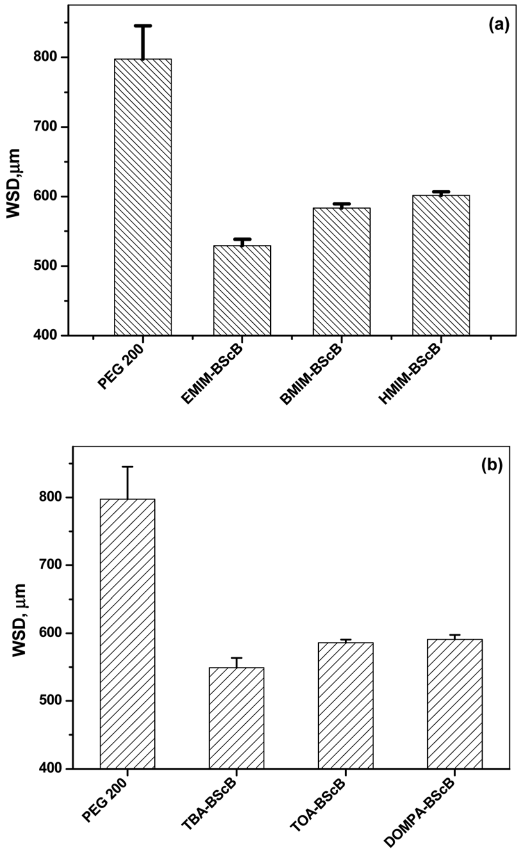
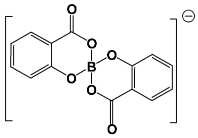
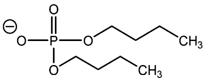
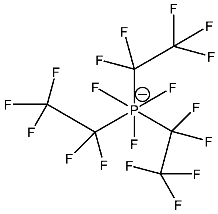


Fig. 5 WSD of (a) imidazolium ionic liquids (EMIM-BScB, BMIM-BScB and HMIM-BScB) and (b) ammonium ionic liquids (TBA-BScB, TOA-BScB and DOMPA-BScB) lubricated steel balls. A 2% blend of each ionic liquids in PEG 200 is used as lubricant. Load: 392 N, rotating speed: 1200 rpm, temperature: 75 °C, test duration: 1 hour. WSD values are based on measurement of worn area on three different balls and the provided error bars are the standard deviation of these values.

Likewise, imidazolium ionic liquids (EMIM-BScB, BMIM-BScB, HMIM-BScB) having variation in associated alkyl chain length ($C_n = 2$, 4 and 6), show a considerable reduction in friction compared to PEG 200 (Fig. 4b). Importantly, it was noted that the friction coefficient gradually reduced with time. Fig. 5a shows the WSD for PEG 200 and alkylmethylimidazolium-BScB ionic liquids blended with PEG 200. An increase in the alkyl chain length associated with the imidazolium ring, increases the WSD. An EMIM-BScB ionic liquid having the shortest chain length shows ~33% reduction in WSD of PEG 200, whereas HMIM-BScB ionic liquid with the longest chain length shows ~24% reduction. These results follow an opposite trend to the results obtained for of imidazolium tetrafluoroborate ionic liquids, where the highest friction and wear were found for the shortest alkyl chain ionic liquid, EMIM-BF_4, owing to the corrosive events under the tribo-stressed area.[7] Here, alkylmethylimidazolium-BScB ionic liquids are halogen-free and possess high interactions associated with the bulk size of the BScB anion, which provides hydrophobic and reduced polar character. And such a phenomenon, further increases with an increase of the chain length of associated imidazolium cations. As a whole, the interaction of these ionic liquids on tribo-surfaces could subside with an increase of the chain length. Therefore, EMIM-BScB ionic liquid, possessing maximum polar character among this series shows more interaction with contacting surfaces and forms the tribo-film, which protects metal-to-metal contact and provides very good anti-wear properties compared to the BMIM-BScB and HMIM-BScB. The gradual reduction in friction coefficient with increasing contact time (Fig. 4b), further revealing the reduced polar character of alkylmethylimidazolium-BScB ionic liquids. These ionic liquids with reduced polar character take a longer time to form a tribo-film, and probably the degree of such tribo-film formation increases with increasing tribo-contact time, hence there is a gradual reduction in friction. Another plausible reason could be wearing of the steel balls to some extent even in the presence of ionic liquid. This worn material from steel balls (primarily Fe and Cr) makes the structure complex with ionic liquids, which function as a complex tribo-film on the steel surfaces. However, such a mechanism is slow compared to direct interaction of ionic liquids on the contact surfaces. As a result, the friction coefficient gradually reduces with time as is shown in Fig. 4. The tetraalkylammonium-BScB ionic liquids follow an interesting trend for WSD with a change of associated alkyl chain length (Fig. 5b). TBA-BScB ionic liquids possess very good packing and exist in a semi-solid form at room temperature. Probably, the good packing of TBA-BScB ionic liquids results in a solid like tribo-film and significantly reduces the WSD. Whereas, a further increase of alkyl chain length associated with the ammonium ionic liquid results in steric hindrance and the ionic liquids are found to be viscous liquids. We presume that the steric hindrance due to long alkyl chain length is unable to provide a good quality tribo-film, hence the WSD is a little high compared to that of TBA-BScB.

Table 3 Influence of anion structure of ionic liquids on the friction coefficient and WSD[a]

Lubricant	Chemical structure of anion	Avg. friction coefficient	WSD/μm
PEG 200	—	0.123 ± 0.014	798 ± 48
2% BMIM-BScB		0.042 ± 0.007	583 ± 6
2% BMIM-DBP		0.116 ± 0.004	478 ± 19
2% BMIM-FAP		0.147 ± 0.007	746 ± 15

[a] Load: 392 N, speed: 1200 rpm, test time: 1 hour.

To examine the effect of halogen and phosphorus based ionic liquid on lubrication properties, two different ionic liquids; BMIM-DBP and BMIM-FAP were selected and their lubrication properties were compared with BMIM-BScB. These ionic liquids possess different anions and their chemical structures are shown in Table 3. The friction coefficient and WSD for BMIM-DBP, BMIM-FAP and BMIM-BScB ionic liquids blended with PEG 200 are also presented in Table 3. The BMIM-DBP shows little reduction in friction coefficient compared to PEG 200, however, a significant improvement in anti-wear property is revealed. This could be due to the formation of a phosphate tribo-film on the contact surfaces, which provides excellent anti-wear properties under tribo-stress.[11,18,30] However, phosphorus based additives are known to be toxic in nature and are hazardous to the environment, hence there is growing interest in replacing the phosphorus with an environmentally-friendly element. Halogen containing ionic liquids are known to be sensitive to moisture and may produce acids (hydrogen halides) under tribological conditions, which can damage engineering surfaces. Fluorine rich BMIM-FAP ionic liquid shows no significant wear reduction but high friction compared to that of PEG 200. The presence of fluorine in the FAP anion might lead to tribo-corrosive events, therefore, high friction and no significant improvement in anti-wear properties. In-contrast, BMIM-BScB reveals significant reduction in both friction and wear owing to the formation of ionic liquid tribo-film having lubricous boron chemistry and a lack of tribo-corrosive elements.

Fig. 6 shows the FESEM images of the worn surface of steel balls lubricated with PEG 200 and ionic liquids blended samples at a load of 392 N. The WSD of all the steel balls lubricated with ionic liquids blended samples were notably smaller than with PEG 200 (Fig. 5). The worn area lubricated with PEG 200 shows severe plastic deformation with scuffing damage on the steel surface; illustrating the metal-to-metal contact because of poor lubrication. As shown in Fig. 6c–n, the wear scars of the steel balls lubricated with 2% ionic liquids (DOMPA-BScB, TOA-BScB, TBA-BScB, EMIM-BScB, BMIM-BScB and HMIM-BScB) were comparatively smoother with shallow friction scratches, and severe scuffing damage was greatly alleviated in the presence of ionic liquids. The shallow scratches and grooves on the worn area and reduction of WSD indicate undoubtedly the role of ionic liquids as anti-wear and anti-scuffing additives.

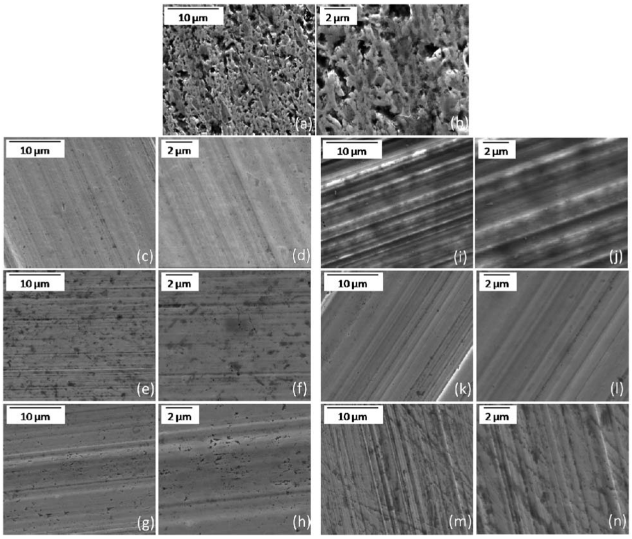


Fig. 6 FESEM images of the worn surfaces of steel balls lubricated with (a and b) PEG 200, (c and d) DOMPA-BScB blended with PEG 200, (e and f) TOA-BScB blended with PEG 200, (g and h) TBA-BScB blended with PEG 200, (i and j) EMIM-BScB blended with PEG 200, (k and l) BMIM-BScB blended with PEG 200, and (m and n) HMIM-BScB blended with PEG 200. Load: 392 N, rotating speed: 1200 rpm, temperature: 75 °C, tribo-test duration: one hour, concentration of ionic liquid: 2% w/v.

Table 4 Elemental composition on the worn area of lubricated steel balls under a load of 392 N

Lubricant	Fe%	Cr%	C%	O%	N%
PEG 200	72.45	1.42	12.00	14.13	—
2% DOMPA-BScB	74.49	1.60	11.26	7.64	5.00
2% TBA-BScB	74.33	1.48	12.76	6.83	4.60
2% EMIM-BScB	69.33	1.24	20.64	4.09	4.70
2% HMIM-BScB	69.61	1.93	13.06	8.83	6.56

Furthermore, EDX analysis of worn surfaces was carried out to examine the surface composition after tribo-tests. Because of the instrument detection limit, we couldn't detect boron on the worn area, though this is an important constituent element of BScB anion; hence, the role of ionic liquids in tribo-film formation was confirmed by the presence of nitrogen, which is a main constituent element of imidazolium and ammonium

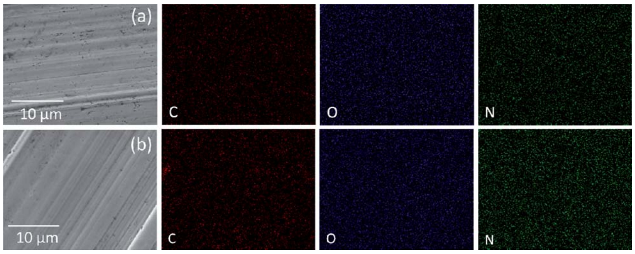


Fig. 7 FESEM micrograms and corresponding element (carbon, oxygen and nitrogen) maps of the worn surface of steel ball lubricated with (a) TBA-BScB and (b) BMIM-BScB ionic liquids blended PEG 200.

cations associated with BScB anion. Table 4 shows the elemental composition of the worn surfaces of steel balls lubricated with PEG 200 and BScB ionic liquids blended samples. The absence of nitrogen on the worn surface area of the steel ball lubricated with PEG 200, reveals the absence of ionic liquids, and the resulting very high friction and severe wear. However, a 2% dose of imidazolium and ammonium ionic liquids was good enough to prepare the tribo-film on the worn area as revealed by the presence of nitrogen (4.6 to 6.6%). The tribo-film composed of ionic liquids, not only reduced friction, but also prevented direct contact of the steel balls, resulting in significant reduction in wear. The FESEM micrographs and corresponding element maps of the worn surface of the steel ball after tribo-test with TBA-BScB and BMIM-BScB ionic liquids blended samples, illustrates the uniform distribution of nitrogen (Fig. 7), which is an integral part of imidazolium and ammonium based ionic liquids, revealing the formation of tribo-film composed of ionic liquids. Although, the exact mechanism of the role of these ionic liquids in reduction of friction and wear is expected to be very complex because of boron's chemistry. In general, boron compounds are known to be lubricious materials because of their remarkable tribochemical and mechanical properties.[31–33] Recently, it was found that under high pressure boron has a partial negative charge,[34] which may facilitate it's interaction with metallic surfaces under boundary lubrication conditions and forms a tribo-film. The very hard nature of the boron[35] tribo-film probably protects the contacting surfaces and provides the anti-wear and anti-scuffing properties. As a whole imidazolium and ammonium BScB ionic liquids not only enable the marked reduction of both friction and wear, but also protect the tribo-surfaces from the corrosive events, which makes the lubricant system green and energy efficient.

Conclusion

Bis(salicylato)borate anion based imidazolium and ammonium ionic liquids, which are free from halogen, phosphorous and sulphur, have been designed and investigated as potential lubricant additives for PEG 200. Ammonium-BScB and imidazolium-BScB ionic liquids were prepared by metathesis of lithium bis(salicylato)borate with ammonium and imidazolium halides, respectively and then characterized by NMR and FTIR. These ionic liquids are found to be hydrophobic in nature and possess good miscibility with PEG 200, which is very important for their efficient performance. BScB ionic liquids showed very high viscosities at room temperature, associated with high polarity, high London dispersive forces, high rigidity, bulk size and ring structure of bis(salicylato)borate anion, which is further increased with an increase of the alkyl chain length attached to the imidazolium ring. The BScB ionic liquids as additives in PEG 200 exhibited excellent friction-reduction and anti-wear properties. The WSD for imidazolium-BScB ionic liquids were found to increase with an increase of the alkyl chain length of imidazolium cations. This could be due to a reduction of their polar character as a result of an increase of the van der Waals interactions and such phenomena slow down the tribo-film formation. The microstructural examination of the worn surfaces of steel balls lubricated with PEG 200 and BScB ionic liquids revealed the anti-wear and anti-scuffing properties of these ionic liquids owing to the boron based chemistry of the tribo-film composed of BScB ionic liquids, as confirmed by their elemental analyses. The high viscosities, hydrophobic nature, good miscibility with lube base stock and outstanding tribological properties of these halogen-, phosphorus- and sulfur-free bis(salicylato)borate anion based ionic liquids suggest their potential as environment friendly lubricant additives.

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