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Halogen-Free Bis(imidazolium)/Bis(ammonium)-Di[bis(salicylato)borate] Ionic Liquids As Energy-Efficient and Environmentally Friendly Lubricant Additives

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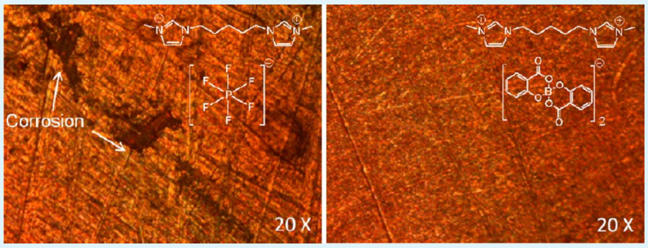
S *Supporting Information*



ABSTRACT: Bis(imidazolium)- and bis(ammonium)-di[bis(salicylato)borate] ionic liquids with variable alkyl chain and cyclic ring structures, were synthesized and then evaluated them as potential lubricant additives. The copper strip test results revealed noncorrosive properties of these ionic liquids. Introduction of halogen content in bis(imidazolium) ionic liquid by replacement of bis(salicylato)borate (BScB) anion with hexafluorophosphate (PF_6^-), severely corroded the copper strip. Thermogravimetric results showed that bis(imidazolium) ionic liquids exhibited higher thermal stability than bis(ammonium) ionic liquids owing to compact structure provided by imidazolium rings, higher intermolecular interactions, smaller free volume and low steric hindrance. The lubrication properties of these ionic liquids as additives to synthetic lubricant poly(ethylene) glycol (PEG 200) were evaluated for steel balls. Results showed that bis(ammonium)- and bis(imidazolium)-$(BScB)_2$ ionic liquids as additives significantly reduced both friction coefficient and wear of PEG 200. The structure of cations, particularly the variation in substituted alkyl chain length monitored the degree of reduction in friction and wear. The excellent lubrication properties were attributed to the formation of adsorbed tribo-thin film and tribochemical product during the tribo-contact. Being halogen-, phosphorus-, and sulfur-free, these ionic liquids (a) protects contact surfaces from tribo-corrosive events, (b) reduces the friction and wear, and (c) keep environment green and clean.

KEYWORDS: *ionic liquids, bis(ammonium) and bis(imidazolium) cations, di[bis(salicylato)borate] anion, friction, wear*

INTRODUCTION

Ionic liquids are composed of organic cations and weakly coordinating organic/inorganic anions. Owing to low symmetry and bulkier size of constituent ions, their charges are usually delocalized that reduces the electrostatic interaction between them and impede their close packing in a regular crystalline order, as a result, most of ionic liquids are liquids at room-temperature.[1] Ionic liquids exhibit remarkable and tunable physicochemical characteristics such as negligible vapor pressure, nonflammability, wide electrochemical window, high thermal stability, broad liquid range, and excellent conductivity, which promises their potential for large range of applications like batteries, chemical reactions and processes, active pharmaceutical ingredients, cellulose processing, solar cells, organic compounds extractions, lubricants, etc.[2−9] Ionic liquids as neat lubricants and as additives in various lube base oils provide superior performance for different engineering surfaces. The flexible molecular structure and inherent polar nature of ionic liquids as lubricant additives facilitate their interaction with engineering surfaces and forms the thin film of low shear strength, which not only avoids the direct contact between the mating surfaces but also reduces the friction and wear.[10,11] The first report by, Ye et al. in 2001, revealed the potential of ionic liquid as versatile lubricant for various engineering surfaces.[12] Since, then several studies have been made on different types of ionic liquids, applying them as lubricants and lubricant additives.[10−16] Prior to these studies on lubrication properties of ionic liquids as additives, liquid zinc salt of O,O-dialkyl hydrogen phosphorodithioates have been applied as lubricant additives during 1960s. However, the ionic liquid term was not well-known during those days.[17] In lubricant industry, zinc dithiophosphates (ZDDPs) are considered to be most successful additives owing to their antiwear, oxidation inhibition, extreme-pressure and friction-reducing properties.[18] Over the last two decades, several studies have been made to replace the use of ZDDP as lubricant additive because of its toxicity to aquatic wildlife, adverse effects to human-health and poisoning of automotive exhaust gas catalyst components.[19,20]

In recent years, a "green tag" of ionic liquids has been challenged because of their toxicity and hazardous effect to aquatic organism and terrestrial ecosystem.[21,22] The most of ionic liquids been studied as lubricant additives, possess halogen either as whole or part of anions like X^- (F^-, Cl^-, Br^-, or I^-), $(PF_6)^-$, $(BF_4)^-$, $(AlCl_4)^-$, $(CF_3SO_3)^-$,

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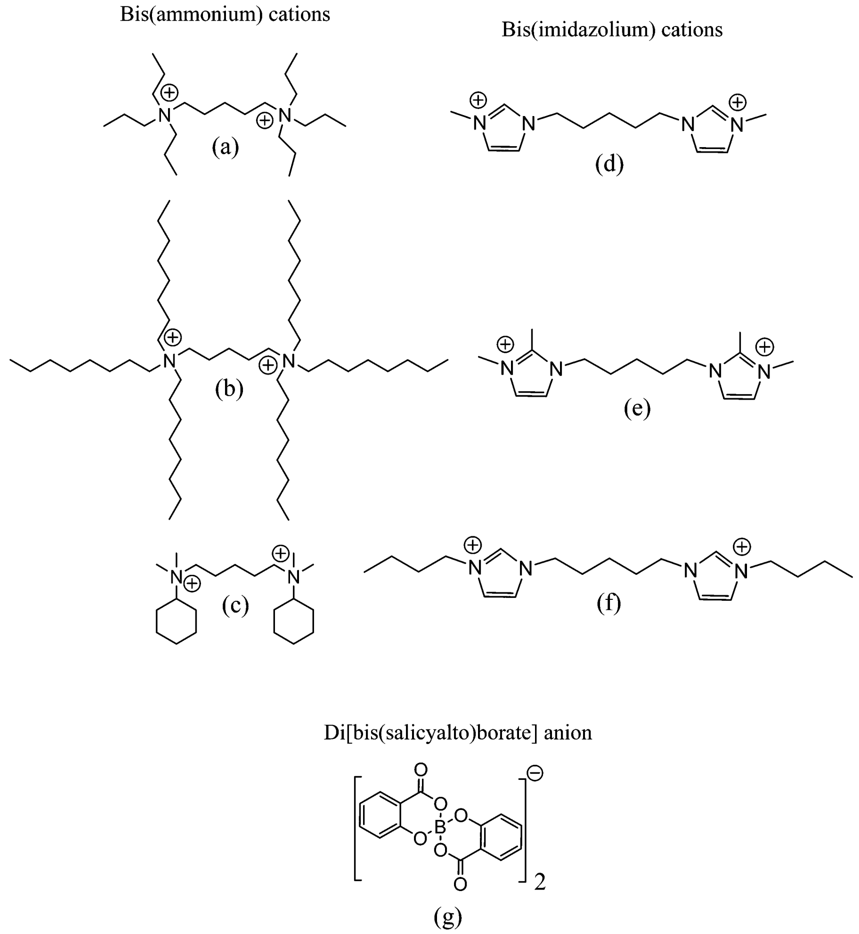

Figure 1. Chemical structure of bis(ammonium) cations (a) N3335, (b) N8885, (c) N11Cy65, bis(imidazolium) cations, (d) MIm5, (e) MMIm5, (f) BIm5, and (g) di[bis(salicylato)borate] anion.

$[(CF_3SO_2)_2N]^-$, $PF_3(CF_3)_3^-$, and so on.[8,9,13] The use of halogenated ionic liquids have raised serious concern for both the environment and the lubrication application perspective. The hydrolysis of moisture sensitive halogen-containing ionic liquids $[X^-, (PF_6)^-, (BF_4)^-, (AlCl_4)^-]$ evolve toxic and corrosive gases (HF, HCl etc.). These gases contaminate the environment and corrode the engineering surfaces under tribological conditions.[23−25] Caporali et al. have found that halogenated anion such as $[(CF_3SO_2)_2N]^-$ corrodes the AZ91D alloy.[26] Furthermore, the high cost of halogens, particularly, fluorine based precursors makes these ionic liquids expensive and that restricts their potential for lubrication applications. Concurrently, phosphorus and sulfur containing ionic liquids have been explored as lubricant additives to the mineral oil and synthetic lubricants.[27−29] However, because of the toxic and hazardous effect of phosphorus and sulfur, there is growing interest to replace these elements by environment benign composition. Besides that, the disposal/degradation of halogen, phosphorus, and sulfur constituted ionic liquids has becomes a matter of serious concern because of ever increasing strict regulations toward the environment.

Recently, dicyanamide $[N(CN)_2]^-$, tricyanomethanide $[C(CN)_3]^-$, and tetracyanoborate $[B(CN)_4]^-$ anions-based ionic liquids were explored as halogen-, phosphorus-, and sulfur-free ionic liquids for tribological applications.[30,31] The $[N(CN)_2]^-$ and $[C(CN)_3]^-$ ionic liquids showed good lubricity for sintered ceramics and hard coating (DLC) owing to formation of nitrogen compounds constituted thin films on the sliding surfaces. The ionic liquids derived from different amino acids were studied as green fluid lubricants for tribological applications.[32] The lubricating properties of amino acids ionic liquids were attributed to the formation of physically adsorbed layers on the contact interfaces. Recently, chelated orthoborate anions based ionic liquids having imidazolium/ammonium/pyrrolidinium cations were studied as lubricant additives to poly(ethylene) glycol (PEG). These ionic liquids provided low friction and wear compared to the neat PEG.[33,34] The development of a new family of protic ionic liquids based on carboxylate anions, which can be prepared by facile approaches,[35,36] have shown improved lubrication properties. Bermudez et al. revealed ultralow friction with bis(2-hydroxyethylammonium) succinate ionic liquid boundary film at the water-lubricated sapphire-steel interface.[37] The adipate and salicylate anion-based ionic liquids exhibited reduced friction and wear compared to nonpolar synthetic lubricant PAO6 and aprotic ionic liquid HMI-$(CF_3SO_2)_2N$. The lower friction and wear properties by adipate and salicylate ionic liquids were attributed to the formation of stable boundary thin film on the copper substrate.[38]

Dicationic ionic liquids have been established as a highly stable ionic liquids for high-temperature and thin-film lubrication applications because of their excellent thermal stability ranges, which generally exceeded those of monocationic counterparts.[39−43] The dicationic ionic liquids with $[(CF_3SO_2)_2N]^-$ anion revealed good tribological properties at higher temperature (300 °C), and meeting the criteria for high-temperature applications.[44] Bis(imidazolium) ionic liquids with different anions such as $[(CF_3SO_2)_2N^-]_2$, $(PF_6^-)_2$, $(BF_4^-)_2$ as lubricant additives could effectively reduced both the friction and wear of sliding pairs.[45] Among these anions, $(PF_6^-)_2$ showed least reduction in friction and wear compared to that of lube base. Till date, all dicationic ionic liquids, been studied for lubrication applications contain halogen/phosphorus/sulfur, which are no more acceptable because of their toxic and hazardous effect to the environment and corrosiveness to engineering interfaces.

In this article, we reports synthesis, characterization, and then tribo-evaluation of bis(ammonium)- and bis(imidazolium)-di[bis(salicylato)borate] ionic liquids. Bis(ammonium) and bis(imidazolium) ionic liquids with variable alkyl substitutions were evaluated for corrosion, friction-reducing, and antiwear properties. The influence of cationic structure and concentration of ionic liquids in the lube base oil are discussed in detail to understand the role of ionic liquids for improved tribophysical properties. Being halogen-, phosphorus-, and sulfur-free, these ionic liquids offers an environmentally friendly and green alternative to the conventional halogenated ionic liquids for the lubrication applications.

■ EXPERIMENTAL SECTION

Chemicals. Methylimidazole (99%, Sigma-Aldrich), butylimidazole (98%, Sigma-Aldrich), 1,2-dimethylimidazole (98%, Sigma-Aldrich), tripropylamine (>98%, Sigma-Aldrich), trioctylamine (98%, Sigma-Aldrich), *N,N*-dimethylcyclohexylamine (99%, Sigma-Aldrich), 1,5-dibromopentane (97%, Sigma-Aldrich), boric acid (99.5%, Loba Chemie), lithium carbonate (99.9%, Sigma-Aldrich), and salicylic acid (99.8%, Merck) were used as precursors to synthesize the ionic liquids. All other chemicals and solvents used in this work were of AR/GR grades. The poly(ethylene glycol) (PEG 200, Molecular weight: 190−210) procured from Sigma was used as a synthetic lube base oil.

Synthesis and NMR Characterization of Ionic Liquids. A total of six ionic liquids based on bis(ammonium) and bis(imidazolium) cations with variable alkyl chain substitution were synthesized. The bis(salicylato)borate anion was selected in this study to replace the halogen-, phosphorus-, and sulfur-containing conventional anions.

Synthesis of Bis(ammonium)-di[bis(salicylato)borate] Ionic Liquids. Under this category three ionic liquids with variable alkyl chains and cyclic ring substituted cations were synthesized. The molecular structures of these ionic liquids (a) pentane-1,5-diyl-bis(tripropylammonium) di[bis(slicylato)borate]: N3335-$(BScB)_2$, (b) pentane-1,5-diyl-bis(trioctylammonium) di[bis(slicylato)borate]: N8885-$(BScB)_2$, (c) pentane-1,5-diyl-bis-(dimethylcyclohexylammonium) di[bis(slicylato)borate]: N11Cy65-$(BScB)_2$ are presented in Figure 1. In a typical procedure, first the anion precursor, lithium salt of bis(salicylato)borate, was prepared by mixing salicylic acid (2.762g, 20 mmol) in an aqueous solution of lithium carbonate (0.368g, 5 mmol) and boric acid (0.619g, 10 mmol). The cation precursor, pentane-1,5-diyl-bis(tripropylammonium) dibromide, was prepared by the reaction of tripropylamine and 1,5-dibromopentane (2:1 molar ratio) at 60 °C under uninterrupted stirring. In the subsequent step, pentane-1,5-diyl-bis-(tripropylammonium) dibromide (5.36g, 10 mmol) was added to anionic precursor solution and heated the reaction mixture for 2 h. An organic layer composed of N3335-$(BScB)_2$ ionic liquid formed in the reaction product, was extracted using dichloromethane (DCM). The washing of N3335-$(BScB)_2$ with pure water was carried out until no more bromide ions were detected in the water. After washing of ionic liquids, a drop of collected water was mixed with solution of diluted nitric acid and silver bromide for bromide ion detection. The white turbid appearance owing to preparation of silver nitrate indicates the presence of bromide ion. This exercise was repeated until, no white turbidity was appeared in the water. Finally, dichloromethane was removed by vacuum distillation and the extracted product was dried in a vacuum oven at 80 °C temperature under reduced pressure. Likewise, N8885-$(BScB)_2$ and N11Cy65-$(BScB)_2$ ionic liquids were synthesized by using trioctylamine and dimethylcyclohexylamine, respectively, instead of tripropylamine, for the respective cationic precursors. The rest of the procedure remained the same for synthesis of these ionic liquids. The preparation and structure of these ionic liquids [N3335-$(BScB)_2$, N8885-$(BScB)_2$, and N11Cy65-$(BScB)_2$] were confirmed by ^1H and ^{13}C NMR spectroscopy.

N3335-$(BScB)_2$. ^1H NMR ($CDCl_3$, ppm): δ 0.7−0.9 (m, 18H, $N(CH_2)_2C\underline{H}_3$), 1.3−1.4 (q, 2H, $N(CH_2)_2C\underline{H}_2(CH_2)_2$), 1.5−1.8 (m, 16H, $NCH_2C\underline{H}_2CH_3$ & $NCH_2C\underline{H}_2CH_2C\underline{H}_2CH_3$), 2.7−3.1 (m, 16H, $NC\underline{H}_2$), 6,8−6.9 (m, 8H, C_6H_4), 7,29−7.3−7.4 (m, 4H, C_6H_4), 7.85−7.95 (dd, 4H, C_6H_4). ^{13}C NMR (ppm): 165.79, 159.44, 135.01, 129.66, 119.29, 119.18, 115.17, 60.31, 60.20, 58.76, 54,12, 20.90, 16.81, 15.41, 15.35, 10.92, 10.55. Yield: 92%

N8885-$(BScB)_2$. ^1H NMR ($CDCl_3$, ppm): δ 0.8−0.98 (t, 18H, $CH_2C\underline{H}_3$), 0.98−1,34 (m, 62H, $N(CH_2)_2(C\underline{H}_2)_5CH_3$ & $N(CH_2)_2C\underline{H}_2(CH_2)_2$), 1.4−1.74 (m, 16H, $NCH_2C\underline{H}_2$), 2.85−2.93, 2.93−3.03 and 3.03−3.12 (t, 16H, $NC\underline{H}_2$), 6.8−6.95 (m, 8H, C_6H_4), 7.35−7.45 (m, 4H, C_6H_4), 7.85−7.98 (dd, 4H, C_6H_4). ^{13}C NMR (ppm): 172.33, 165.93, 161.95, 159.48, 135.70, 134.96, 130.67, 129.68, 119.10, 118.58, 117.31, 115.11, 58.72, 52.44, 31.62, 29.05, 29.00, 26.54, 26.23, 26.17, 23.17, 22.59, 21.81, 20.88, 14.09. Yield: 81%

N11Cy65-$(BScB)_2$. ^1H NMR ($CDCl_3$, ppm): δ 1.25−1.35 (m, 6H, $CH_2(C\underline{H}_2)_3CH_2$), 1.62−1.81 (m, 20H, cyclohexane $C\underline{H}_2$), 2.64−2.65 (t, 4 H, $NC\underline{H}_2$), 2.83 and 2.96 (s, 12 H, NCH_3), 3.22−3.29 (m, 2H, NCH), 6.87−6.93 (m, 8H, C_6H_4), 7.38−7.42 (m, 4H, C_6H_4), 7.86−7.87 (dd, 4H, C_6H_4). ^{13}C NMR (ppm): 165.76, 159.46, 135.03, 129.61, 119.22, 118.66, 115.19, 48.34, 47.93, 33.21, 26.09, 25, 20, 25.03, 24.63, 21.31. Yield: 90%

Synthesis of bis(imidazolium) di[bis(salicylato)borate] ionic liquids: Under this category, three ionic liquids with variable alkyl chain substituted cations were synthesized. The molecular structure of these ionic liquids (a) 1,1′-(pentane-1,5-diyl)-bis(3-methylimidazolium) di[bis(salicylato)borate]: MIm5-$(BScB)_2$, (b) 1,1′-(pentane-1,5-diyl)-bis(2,3-dimethylimidazolium) di[bis(salicylato)borate]: MMIm5-$(BScB)_2$, and (c) 1,1′-(pentane-1,5-diyl)-bis(3-butylimidazolium) di-[bis(salicylato)borate]: BIm5-$(BScB)_2$ are presented in Figure 1. The MIm5-$(BScB)_2$, MMIm5-$(BScB)_2$, and BIm5-$(BScB)_2$ ionic liquids were synthesized following the N3335-$(BScB)_2$ preparation procedure using 1-methylimidazole, 1,2-dimethylimidazole, and 1-butylimidzole as cationic precurors, respectively, instead of tripropylamine. The rest of the procedure remained the same for synthesis of these ionic liquids. The structures of the prepared ionic liquids [MIm5-$(BScB)_2$, MMIm5-$(BScB)_2$, and BIm5-$(BScB)_2$] were characterized by ^1H and ^{13}C NMR spectroscopy.

MIm5-$(BScB)_2$. ^1H NMR ($CDCl_3$, ppm): δ 1.117 (q, 2H, $N(CH_2)_2C\underline{H}_2$), 1.63−1.66 (q, 4H, $NCH_2C\underline{H}_2$), 3.72 (s, 6H, NCH_3), 4.03−4.06 (t, 4H, NCH_2), 6.87−6.91 (m, 8H, C_6H_4), 6.92−6.95 (d, 2H, NCH), 7.39−7.394 (d, 2H, NCH), 7.4−7.42 (m, 4H, C_6H_4), 7.83−7.85 (dd, 4H, C_6H_4). ^{13}C NMR (ppm): 165.88, 159.35, 136.74, 135.19, 129.59, 122.88, 122.73, 119.32, 118.61, 114.99, 49.43, 36.15, 28.59, 21.90, 19.1. Yield: 93%

MMIm5-$(BScB)_2$. ^1H NMR ($CDCl_3$, ppm): δ 1.118−1.13 (q, 2H, $N(CH_2)_2C\underline{H}_2$), 1.56−1.61 (q, 4H, $NCH_2C\underline{H}_2$), 2.24 (s, 6H $C-CH_3$), 3.4 (s, 6H, NCH_3), 3.6−3.8 (t, 4H, NCH_2), 6.67−6.78 (m, 8H, C_6H_4), 6.83−6.88 (d, 2H, NCH), 7.35−7.38 (m, 4H, C_6H_4), 7.61−7.63(d, 2H, NCH), 7.83−7.85 (dd, 4H, C_6H_4). ^{13}C NMR (ppm): 165.54, 165,13, 143.55, 135.04, 129.52, 122.09, 121.23, 119.21, 118.48, 115.07, 114.98, 48.18, 35.07, 28.50, 9.47. Yield: 94%

BIm5-$(BScB)_2$. ^1H NMR ($CDCl_3$, ppm): δ 0.76−0.81 (t, 6H, $C\underline{H}_3$), 1.04−1.12 (q, 2H, $N(CH_2)_2C\underline{H}_2$), 1.13−1.2 (h, 4H, $C\underline{H}_2CH_3$), 1.6−1.68 (m, 8H, $NCH_2C\underline{H}_2$), 3.89−4.07 (t, 8H, NCH_2), 6.82−6.9 (m, 8H, C_6H_4), 7.05−7.08 (d, 2H, NCH), 7.37−7.41 (m, 4H, C_6H_4), 7.42−7.43(d, 2H, NCH), 7.8−7.9 (dd, 4H, C_6H_4). ^{13}C NMR (ppm): 165.67, 159.25, 135.65, 135.15, 129.61, 122.68, 121.80, 119.35, 118.45, 115.06, 49.59, 49.22, 31.66, 28.78, 22.12, 19.35, 13.30. Yield: 90%

Characterization of Ionic Liquids. Fourier transform infrared (FTIR) spectra of all ionic liquids were recorded using a Thermo-nicolet 8700 Research spectrophotometer with a resolution of 4 cm^{-1}.

Table 1. Physicochemical Properties of Lubricants Used for Tribological Evaluation

lubricant	kinematic viscosity (ASTM D445) at 40 °C ($mm^2\ s^{-1}$)	kinematic viscosity (ASTM D445) at 100 °C ($mm^2\ s^{-1}$)	viscosity index (ASTM D2270)	pour point (°C) (ASTM D97)	density ($g\ mL^{-1}$) (ASTM D4052)
Lube Base Oil					
PEG 200	22.4 ± 0.22	4.1 ± 0.09	70	−27	1.13 ± 0.01
2% (w/v) Bis-Ammonium Ionic Liquids Blends with PEG 200					
N3335-(BScB)$_2$	23.26 ± 0.21	4.27 ± 0.06	87	−45	1.13 ± 0.01
N8885-(BScB)$_2$	22.92 ± 0.18	4.20 ± 0.11	85	−45	1.12 ± 0.01
N11Cy65-(BScB)$_2$	23.44 ± 0.16	4.32 ± 0.09	83	−42	1.13 ± 0.01
2% (w/v) Bis-Imidazolium Ionic Liquids Blends with PEG 200					
MIm5-(BScB)$_2$	23.80 ± 0.14	4.30 ± 0.08	75	−48	1.13 ± 0.01
MMIm5-(BScB)$_2$	23.27 ± 0.19	4.34 ± 0.06	93	−42	1.13 ± 0.01
BIm5-(BScB)$_2$	23.55 ± 0.11	4.42 ± 0.09	97	−45	1.13 ± 0.01

Table 2. Infrared Vibration Frequencies of Ionic Liquids with Their Vibrational Assignments

bis(ammonium) cations			bis(imidazolium) cations			
N3335-(BScB)$_2$	N8885-(BScB)$_2$	N11Cy65-(BScB)$_2$	MIm5-(BScB)$_2$	MMIm-(BScB)$_2$	BIm5-(BScB)$_2$	vibrational assignment
3062w, 3041s	3065w, 3041s	3064s, 3042s	3150s, 3112m, 3043w	3143s, 3143s, 3062m, 3041b	3142s, 3107s, 3081b, 3043w	ν (C−H), aromatic groups
2973s, 2941s, 2882s	2954s, 2927s, 2857b	2942s, 2864s	2954s, 2867s, 2872s	2942b, 2869s	2961s, 2935s, 2874s	ν_a & ν_s (C−H), CH_2/CH_3 groups
1685b	1686b	1675s	1686b	1683s	1682b	ν (C=O)
1608s	1610s	1608s	1609s	1607s	1609s	ν_a (COO)
1577s	1577s	1578m				ν (C=C), aromatic
			1577w	1536m	1577s	ν (C−N/C-C), imidazolium) ring, ν (C=C), aromatic
1466s	1467b	1466s	1466s	1466s	1466s	δ (C−H, CH_2) groups
1267s, 1244s	1269s, 1242s	1268s, 1243s	1267s, 1244b	1267s, 1242s	1267s, 1243s	ν_s (COO), split peaks
1200−900	1200−900	1200−900	1200−900	1200−900	1200−900	ν_a (B−O)/ν (C−O)
850s	850s	848s	850s	849s	850s	δ (C−H), aromatic
762s, 698s	760s, 698s	763s, 698s	766s, 698s	764s, 698s	764s, 698s	ν_s (B−O)

Each sample was thoroughly mixed with KBr and then prepared the pellets for their FTIR measurements. The nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectroscopy of all ionic liquids were carried out using a 500 NMR Spectrometer operating at 500 Hz using $CDCl_3$ as a solvent. Thermal stability of these ionic liquids was examined using a thermal analyzer (Diamond, PerkinElmer). The temperature was programmed from 25 to 450 °C with thermal rate of 10 °C/min under a flow of nitrogen gas. The % weight loss as a function of temperature was monitored in the thermogravimetric analyzer. All synthesized ionic liquids were thoroughly mixed with the PEG 200 by simple stirring and these blends were found to be very stable. The physicochemical properties including viscosities at 40 and 100 °C, viscosity index, pour point, density of PEG 200 and ionic liquids blended PEG 200 samples were measured (Table 1) as per the ASTM D445, ASTM D2270, ASTM D97, and ASTM D4052 standard test methods, respectively. The corrosion properties of these ionic liquids were measured by copper strip test. A freshly polished and cleaned bright finished copper strip was immersed in a vial containing ionic liquid sample. The temperature of vial was raised to 100 °C using an oil bath. After 3 h, copper strip was taken out and washed thoroughly to remove sample traces. The corrosion events in the form of pits were examined by optical microscopy of copper strips.

Friction and wear Tests. The lubrication properties in terms of the friction coefficient and the wear scar diameter (WSD) for PEG 200 and ionic liquids blended PEG 200 samples were examined by using the four-ball tribotester. All synthesized ionic liquids exhibited excellent miscibility in synthetic lube base PEG. Furthermore, efforts were made to blend these ionic liquids in PAO and mineral lube base (N-150 and N-500) oils; however, because of poor and short-term miscibility, all lubrication tests were conducted with their blends in PEG 200. In a typical tribo-experiment, a steel ball (ϕ = 12.7 mm, material: AISI 52100, hardness: 64−66 Rc and surface finish: grade 25 EP) under the applied load was rotated against three stationary steel balls, clamped in the holder. During tribo-tests, the four balls were covered with a lube sample, which was used for the friction and wear evaluation. All tests were carried out as per the ASTM D 4172 standard test method under a load of 392 N at a rotating speed of 1200 rpm for 1 h and temperature of sample housing was maintained 75 °C throughout the experiment. Morphological features of worn surfaces and the elemental distribution in the tribo thin film deposited on the worn area of steel balls, lubricated with different samples, were examined using the FESEM and energy dispersive X-ray spectroscopy (EDX), respectively on an FEI Quanta 200.

RESULTS & DISCUSSION

Bis(ammonium)- and bis(imidazolium)-di[bis(salicyalto)-borate] ionic liquids were synthesized by metathesis of pentane-1,5-diyl-bis(trialkylammonium) dibromide and 1,1′-(pentane-1,5-diyl)-bis(alkylimidazolium) dibromide with lithium bis(salicylato)borate, in 1:2 molar ratio, respectively. The 1,5-dibromopentane linker was used to bridges the ammonium and the imidazolium cations into bis(ammonium) and bis(imidazolium) precursors, respectively. A total of six ionic liquids, three under each category, having variable alkyl chain length were prepared. The preparation of these ionic liquids was confirmed by their NMR (^{1}H and ^{13}C) and FTIR analyses.

The characteristic peaks extracted from the FTIR spectra of synthesized bis(ammonium)-(BScB)$_2$ and bis(imidazolium)-(BScB)$_2$ ionic liquids are compared in Table 2 along with the vibrational assignment. The strong vibrations in the range of

3000−2800 cm^{-1} attributed to the C−H stretches of methylene and methyl groups, revealing the presence of alkyl groups in bis(ammonium) and bis(imidazolium) ionic liquids.[46] The other characteristics vibration bands in the range of 3066−3039 cm^{-1}, attributed to aromatic C−H stretches, confirming the presence of aromatic ring in the $(BScB)_2$ anion. Furthermore, appearance of new vibrational peaks in the range of 3180−3035 cm^{-1} in the bis(imidazolium) ionic liquids, were assigned to C−H stretches of bis(imidazolium) rings. The other vibrational signatures in the range of 1686−1675, 1610−1607, and 1269−1242 cm^{-1}, were attributed to νC=O stretch (C=O functional group), ν_aCOO and ν_sCOO stretches of carboxylate group, respectively. The ν_sCOO vibration was splitted into two sharp peaks at ∼1268 and ∼1242 cm^{-1}, revealing the complex structure of carboxylate group in the BScB anion.[47] The broad and strong vibrations in the range of 1200−900 cm^{-1} were assigned to the ν_a(B−O) in tetrahedral boron complexes. The two strong vibrational bends centered at 764 and 698 cm^{-1} were attributed to the ν_s(B−O) stretches of $(BScB)_2$ anion. These vibrational characteristics along with their NMR characterization, confirmed the preparation of bis(ammonium) and bis(imidazolium)-$(BScB)_2$ ionic liquids. The FTIR spectra of these ionic liquids are provided as Figure S1 (see the Supporting Information).

Thermal decomposition properties of all ionic liquids were examined by measuring the weight loss as a function of temperature. Figure 2 shows the TGA curves for N3335-$(BScB)_2$, N8885-$(BScB)_2$, MIm5-$(BScB)_2$, and MMIm-$(BScB)_2$ ionic liquids. The thermal stability of ionic liquids is usually monitored by their structure and packing orientation. Figure 2 explicitly demonstrate that the bis(imidazolium) ionic liquids exhibited higher thermal stability than bis(ammonium) ionic liquids. The observed higher thermal stability of bis(imidazolium) ionic liquids was attributed to the compact structure of imidazolium ring, higher intermolecular interactions, smaller free volume and low steric hindrance.[48] It was observed that bis(ammonium) ionic liquids thermally decomposed by 10% of total mass in the range of 240−270 °C, whereas the decomposition temperature range for bis(imidazolium) ionic liquids could stretched to 300−370 °C (Table 3). Increasing the substituted alkyl chain length decreased the thermal stability for both bis(imidazolium) and bis(ammonium) series ionic liquids. This was associated with the steric hindrance by long alkyl chains, larger free volume, reduced columbic interactions, etc. It is believed that positive inductive effect due to long alkyl chain increased the stability of cation, and such an effect becomes larger with increasing of alkyl chain length. As a result, the thermal stability of ionic liquids reduced significantly.[49] Therefore, N8885-$(BScB)_2$ exhibited lower thermal stability than the N3335-$(BScB)_2$ as shown in Table 3. The bis(imidazolium)-$(BScB)_2$ ionic liquids exhibited the excellent thermal stability with decomposition temperature of ∼400 °C, which is higher than the conventional monocationic ionic liquids. The observed higher thermal stability of dicationic ionic liquids was attributed to the larger charge and intermolecular interactions, their higher molecular weight, smaller free volume and high shear viscosity.[39] The high thermal stability of both bis(imidazolium) and bis(ammonium) ionic liquids promises their potential for lubrication applications.

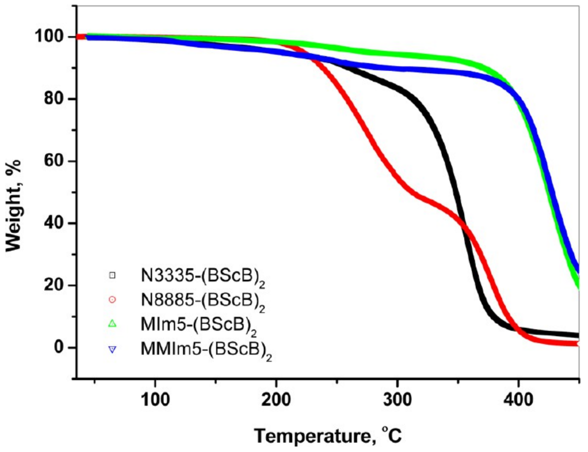

Figure 2. TGA patterns of bis(ammonium) [N3335-$(BScB)_2$, N8885-$(BScB)_2$], and bis(imidazolium) [MIm5-$(BScB)_2$, MMIm5-$(BScB)_2$] ionic liquids. Thermal rate: 10 °C/min under nitrogen flow.

Table 3. Thermal Loss of Ionic Liquids As Deduced Form Thermogravimetric Analysis of Respective Ionic Liquid

	TGA temperature for % weight loss, °C			
ionic liquids	10%	20%	30%	50%
	Bis(ammonium) Ionic Liquids			
N3335-BScB	260	313	331	344
N8885-BScB	238	258	273	312
N11Cy65-BScB	269	314	346	370
	Bis(imidazolium) Ionic Liquids			
MIm5-BScB	371	399	410	426
MMIm5-BScB	299	399	412	427

The tribo-physical properties of bis(ammonium)/bis(imidazolium)-$(BScB)_2$ ionic liquids as lubricant additives were studied using PEG 200 as a synthetic lube base oil. These ionic liquids are thoroughly miscible with PEG 200 by simple stirring. An addition of 2 wt % ionic liquids has significantly changed the physicochemical properties of PEG 200 as shown in Table 1. The kinematic viscosities at 40 and 100 °C for PEG 200 were slightly increased by addition of 2 wt % ionic liquids, attributed to the high viscosities of these ionic liquids, which is monitor by their complex structure.[50] The viscosity index of PEG was increased by 7−38% with these ionic liquids. This revealed that lowering of viscosity as a function of temperature were subsidized and could provided good lubrication properties at high temperature. Usually, lubricants gradually losses their flow properties by lowering the temperature, and becomes semisolid at a particular temperature, which is known as a pour point. In lubrication applications, the flow properties of lubricant should be maintained at low temperature for their optimized performance. PEG 200 became semisolid at −27 °C and found that an addition of 2 wt % of bis(ammonium)-/bis(imidazolium)-$(BScB)_2$ ionic liquids could extent the pour points to −42 to −48 °C. As a result, these ionic liquids could be used for low-temperature/cryogenic lubrication applications.

The copper strip corrosion tests were carried out for evaluating the corrosion characteristics of the synthesized di[bis(salicylato)borate] anion based ionic liquids, which are halogen-, phosphorus-, and sulfur-free. The N3335-$(BScB)_2$, N8885-$(BScB)_2$, MIm5-$(BScB)_2$, and MMIm5-$(BScB)_2$ ionic liquids were selected for corrosion study. The 1,1′-(pentane-1,5-diyl)-bis(methylimidazolium) di(hexafluorophosphate) [MIm5-$(PF_6)_2$] ionic liquid constituting halogen and phospho-

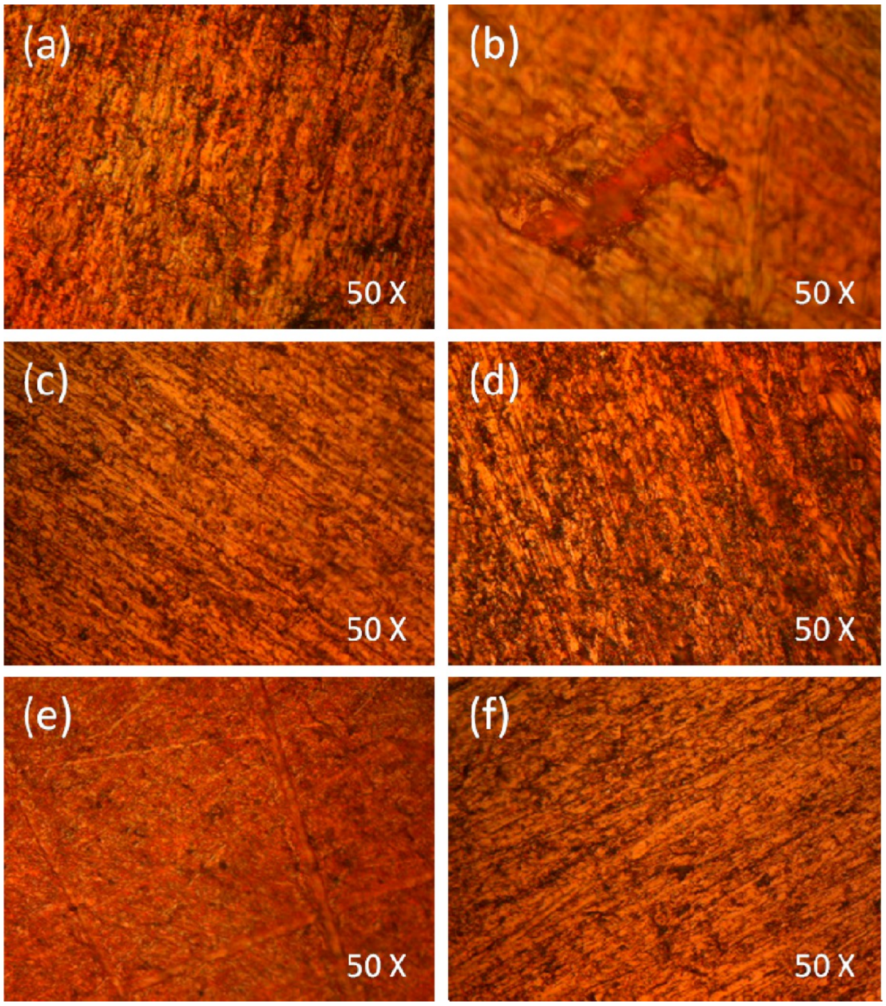

Figure 3. Optical images of copper strips exposed to (a) PEG 200 and 2 wt % of (b) MIm5-$(PF_6)_2$, (c) N3335-$(BScB)_2$, (d) N8885-$(BScB)_2$, (e) MIm5-$(BScB)_2$, (f) MMIm5-$(BScB)_2$ ionic liquids in PEG 200 for 3 h at 100 °C.

rus elements was examine for the comparison. A freshly polished bright luster copper strip was immersed in a vial containing 2 wt % of each ionic liquid in the PEG 200 at 100 °C for 3 h. After the washing, the surface features of each copper strip were evaluated by optical microscope. Figure 3 shows the optical images of the copper strips exposed to PEG 200, 2 wt % blends of each ionic liquid. The copper strip exposed to MIm5-$(PF_6)_2$ was significantly corroded and developed plenty of corrosion pits as shown in Figure 3b. However, the surface features of copper strips, exposed to N3335-$(BScB)_2$, N8885-$(BScB)_2$, MIm5-$(BScB)_2$, and MMIm5-$(BScB)_2$ ionic liquids were found to remain intact without any degradation of the copper surface. This revealed that both the bis(ammonium)- and bis(imidazolium)-$(BScB)_2$ ionic liquids, which are halogen-, phosphorus-, and sulfur-free, do not corrode the copper strips. Considering the noncorrosive properties, these ionic liquids could be used as additives for the lubricant applications.

The lubrication properties of the bis(ammonium) and bis(imidazolium)-$(BScB)_2$ ionic liquids as lubricant additives to PEG 200 were explored for the steel−steel contact. Figure 4 show the changes in average friction coefficient and wear scar diameter (WSD) as a function of MIm5-$(BScB)_2$ dose in the PEG 200. Both the friction coefficient and the WSD were gradually reduced with increasing dose of MIm5-$(BScB)_2$ to PEG 200 and no further significant changes were observed beyond the 2 wt %. Thus, 2 wt % dose has been considered as an optimum concentration for further tribo-studies of different ionic liquids. These results indicated that the MIm5-$(BScB)_2$ ionic liquid as lubricant additive significantly improved the friction-reducing and antiwear properties of the PEG 200.

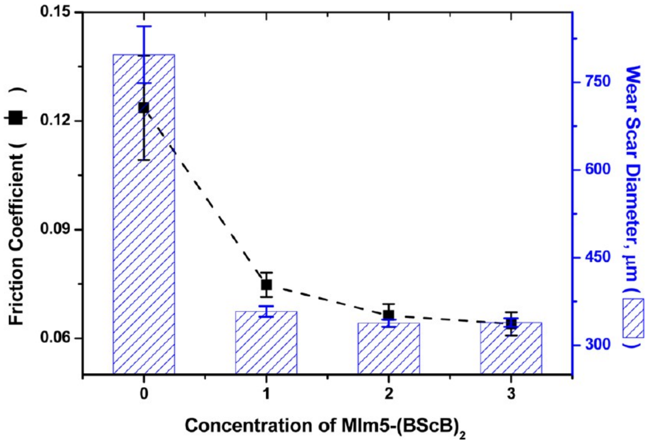

Figure 4. Changes in friction coefficient and WSD for the PEG 200 as a function of increasing dose of MIm5-$(BScB)_2$ ionic liquid. Load, 392 N; rotating speed, 1200 rpm; temperature, 75 °C; test duration, 1 h.

Figure 5 compare the changes in friction coefficient as a function of contact time for the steel balls lubricated by 2 wt % of bis(ammonium)- and bis(imidazolium)-$(BScB)_2$ ionic liquids in PEG 200. The steel balls lubricated by PEG 200 shows gradually increased friction over the time. In contrast, bis(ammonium) ionic liquids [N3335-$(BScB)_2$, N8885-$(BScB)_2$, N11Cy65-$(BScB)_2$] exhibited lower and relatively stable friction (Figure 5a). The high friction with unstable trend for PEG 200 was attributed to the direct contact between the steel balls and this was further supported by the severe wear and scuffing of the materials on the worn area. A 2 wt % dose of bis(ammonium)-$(BScB)_2$ ionic liquids in PEG 200 significantly reduced both the friction and wear of steel balls (Figures 5a and 6). The little differences in friction and WSD for these ionic liquids as shown in Figures 5a and 6, were attributed to their cationic structure. The N8885-$(BScB)_2$ ionic liquid exhibited better friction-reducing properties than N3335-$(BScB)_2$ and N11Cy65-$(BScB)_2$ ionic liquids. The inherent polarity of these ionic liquids is believed to provide strong adsorption to the contact interfaces and form the tribo-thin film, which provided effective separation to the contact interfaces, consequently, reduction of both the friction coefficient and wear. The long alkyl chains of N8885-$(BScB)_2$ ionic liquid in the tribo-thin film not only reduced the shear strength but also improved the antiwear properties. The N3335-$(BScB)_2$ and N11Cy65-$(BScB)_2$ ionic liquids exhibited marginal higher friction attributed to the shorter alkyl chains and cyclic ring, respectively.

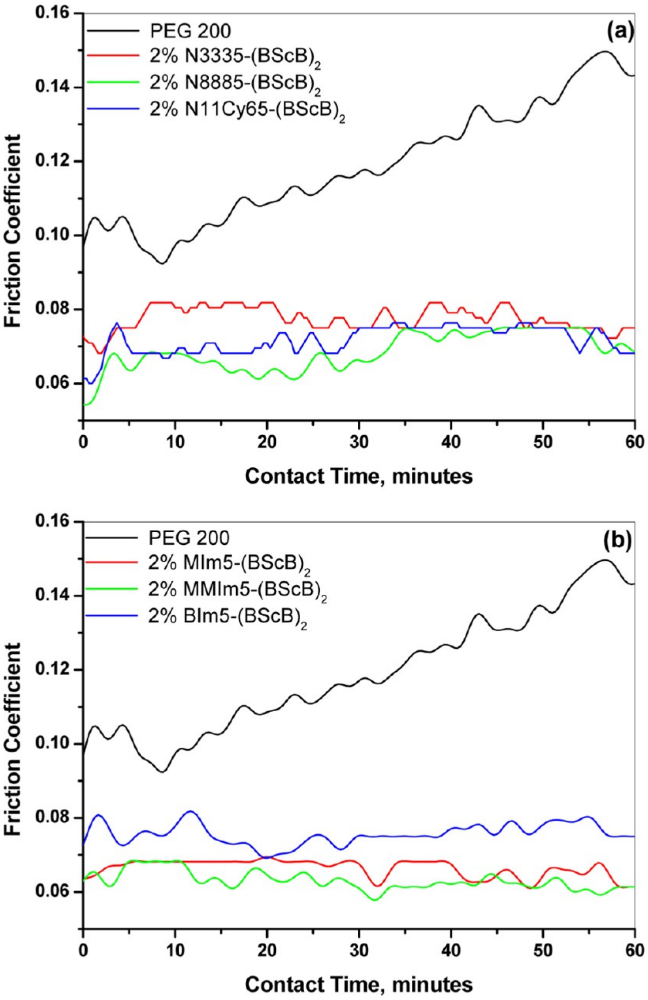

Figure 5. Evolution of friction coefficient with time for 2 wt % of (a) bis(ammonium) [N3335-$(BScB)_2$, N8885-$(BScB)_2$, N11Cy65-$(BScB)_2$] and (b) bis(imidazolium) [MIm5-$(BScB)_2$, MMIm5-$(BScB)_2$, BIm5-$(BScB)_2$] ionic liquids in PEG 200. Load, 392 N; rotating speed, 1200 rpm; temperature, 75 °C; test duration, 1 h.

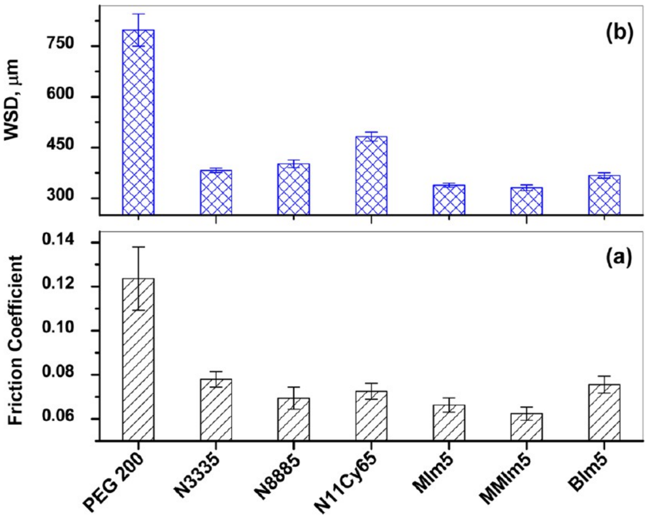

Figure 6. Comparison of (a) friction coefficient and (b) WSD of steel balls lubricated with 2 wt % of dicationic ionic liquids in the PEG 200. Load, 392 N; rotating speed, 1200 rpm; temperature, 75 °C; test duration, 1 h.

Similarly, bis(imidazolium)-$(BScB)_2$ ionic liquids as lubricant additives to PEG 200 have significantly reduced both friction coefficient and WSD for the steel balls as shown in Figures 5b and 6. A 2 wt % of MIm5-$(BScB)_2$ ionic liquid having single methyl group showed 46 and 56% reduction in friction coefficient and wear, respectively. An introduction of one more methyl group at C2 position of imidazolium ring in the MMIm5-$(BScB)_2$ ionic liquid, further marginally improved the lubrication properties by reducing friction coefficient and wear 49 and 59%, respectively. Recently, Liu et al. have revealed that the hydrogen at C2 position of imidazolium ring is acidic in nature and can interact with the polar solvent, as a result the participation of imidazolium ring in the boundary thin film formation were reduced.[51] The replacement of hydrogen by inert methyl group at C2 position provided more stability and facilitated the role of bis(imidazolium) in tribo-thin film formation, hence exhibited better friction-reducing and antiwear properties. Furthermore, an increasing of alkyl chain length BIm5-$(BScB)_2$ provided comparatively higher friction coefficient and the wear. Bermudez et al. have demonstrated that an increase in the alkyl chain length in imidazolium ring of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ionic liquids increased the wear rate. The bulkier size of the cation and anion reduced the molecular polarity and surface tension, which were found to be responsible for this behavior.[52] In contrast, imidazolium ionic liquids with smaller anion such tetrafluoroborate (BF_4^-) as lubricant exhibited higher friction and wear rate for the shortest alkyl chains, owing to the severe tribo-corrosion process taken place by the EMIM-BF_4.[53] Herein, the tribo-corrosive events are ruled out, since bis(imidazolium)-$(BScB)_2$ ionic liquids are halogen-free. Hence, it is believed that the interaction/adsorption of BIm5-$(BScB)_2$ ionic liquid on the tribo-interfaces were subsidized

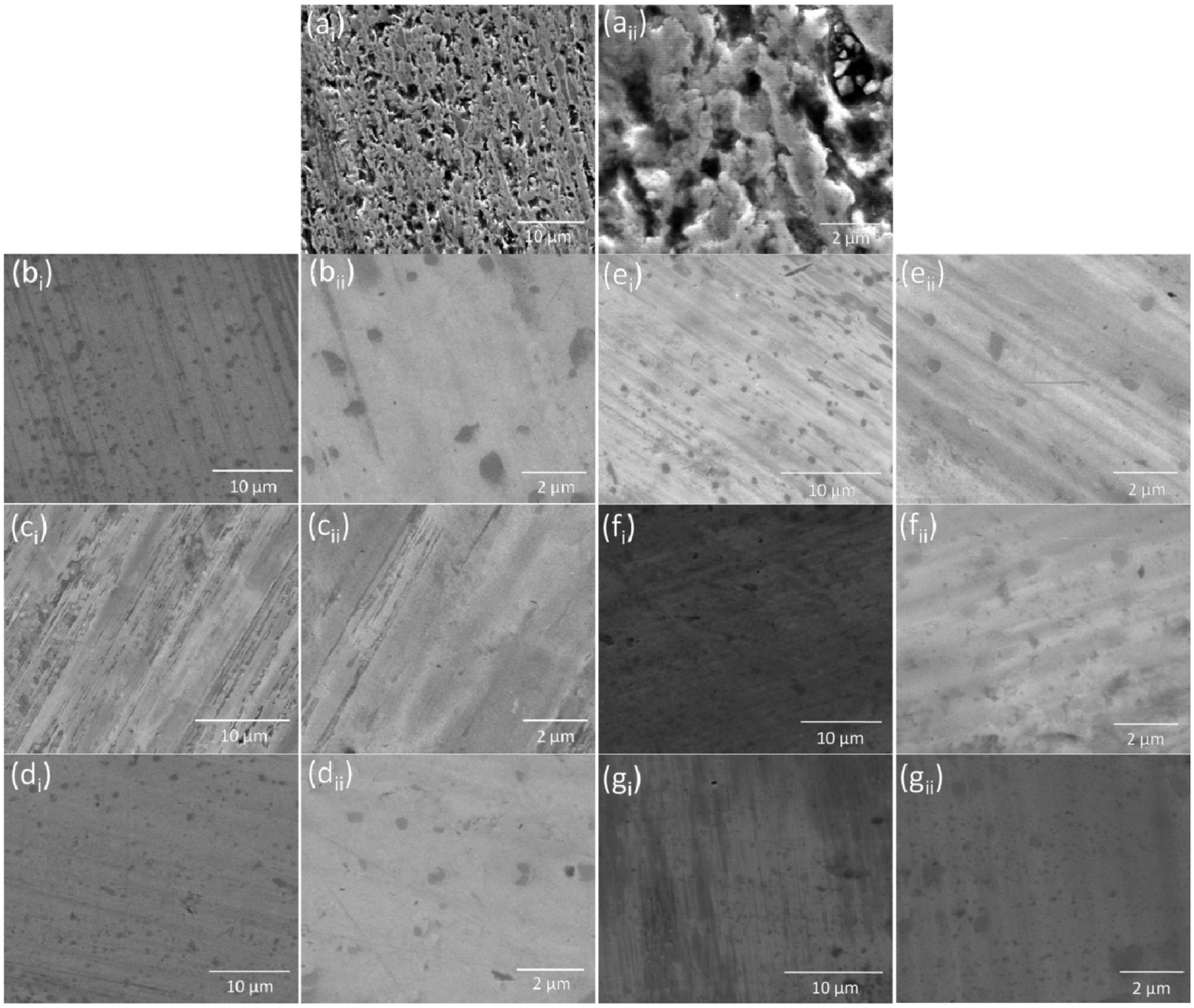

Figure 7. FESEM images of the worn surfaces of steel balls lubricated with (a_i, a_{ii}) PEG 200 and 2 wt % (b_i, b_{ii}) N3335-$(BScB)_2$, (c_i, c_{ii}) N8885-$(BScB)_2$, (d_i, d_{ii}) N11Cy65-$(BScB)_2$, (e_i, e_{ii}) MIm5-$(BScB)_2$, (f_i, f_{ii}) MMIm5-$(BScB)_2$, and (g_i, g_{ii}) BIm5-$(BScB)_2$ ionic liquids in PEG 200. Load, 392 N; rotating speed, 1200 rpm; temperature, 75 °C; tribo-test duration, 1 h.

owing to its reduced polar character. Therefore, BIm5-$(BScB)_2$ provided higher friction and wear compared to the shorter alkyl chain substituted bi(imidazolium)-$(BScB)_2$ ionic liquids.

Figure 7 displays the FESEM images of worn surfaces of steel balls lubricated by PEG 200 and 2 wt % bis(ammonium)/bis(imidazolium)-$(BScB)_2$ ionic liquids in the PEG 200. The worn area lubricated by PEG 200 showed severe plastic deformation with scuffing-associated adhesive wear on the steel surface, revealing the direct contact between the steel balls under the rolling contact. However, the wear scars of steel balls, lubricated with 2 wt % bis(ammonium)/bis(imidazolium)-$(BScB)_2$ in PEG 200 were much smoother with shallow friction scratches, and the severe scuffing damages were greatly reduced, indicating a significantly improved antiwear properties owing to these ionic liquids as additives to the PEG 200. Furthermore, the energy-dispersive X-ray spectroscopic (EDX) analyses on the worn surfaces of steel balls were carried out for probing the qualitative chemical estimation of tribo-interfaces. The FESEM micrographs and corresponding distribution of carbon, nitrogen, and oxygen on the worn area of steel balls lubricated with MIm5-$(BScB)_2$ and N3335-$(BScB)_2$ ionic liquids (Figure 8), illustrate their uniform distribution. Boron and nitrogen are characteristics elements of both ionic liquids. However, the instrument detection limit could not detect boron on the worn area, hence, the role of ionic liquids in tribo-chemical thin film formation was deduced by nitrogen distribution. The uniform distribution of nitrogen on the worn areas of steel balls, revealed the formation of tribo-chemical thin film composed of ionic liquids and/or tribochemical product of ionic liquids, whereas the PEG 200 lubricated worn surface showed carbon, oxygen, iron, and chromium distribution and no signal for the nitrogen. It is worth mentioning here that in general, the detection depth of EDX is ∼2 μm; however, the developed tribo-chemical thin films by tribo-chemical product of ionic liquid with steel surfaces and adsorption of ionic liquids are usually less than 50−100 nm. Hence, the collected elemental distribution mapping results, through EDX, is a qualitative idea and revealed the role of ionic liquids in tribo-chemical thin film formation rather than providing the exact mechanism.

The exact mechanism and role of ionic liquid in tribo-chemical thin film formation is believed to be complex because of inherent polarity of ionic liquids and rich boron chemistry under the tribo-stress. It is known that the rubbing of iron (steel) surfaces under the tribo-stress, induced the positive charge,[54] where the anionic part of ionic liquid, di[bis-(salicylato)borate] could be adsorbed. The counter cations bis(ammonium)/bis(imidazolium) may then be adsorbed

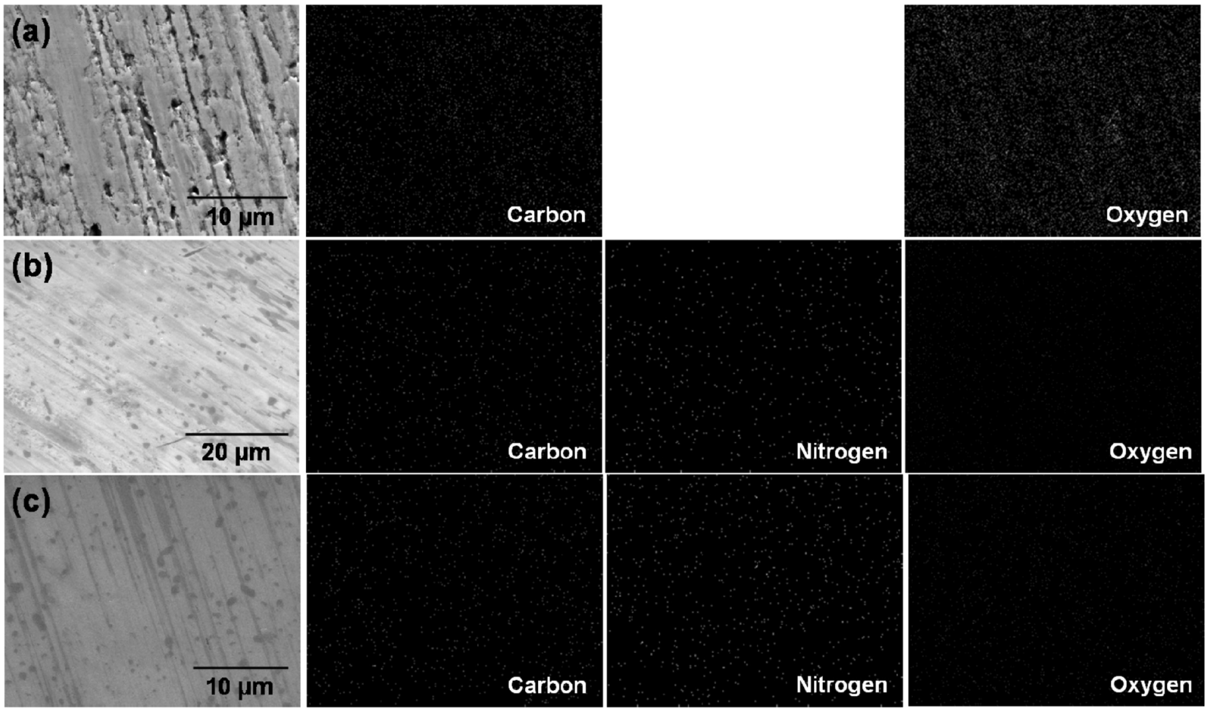

Figure 8. FESEM micrographs and corresponding element mapping on the worn areas of steel balls lubricated with (a) PEG 200, (b) 2 wt % of MIm5-$(BScB)_2$, and (c) 2 wt % of N3335-$(BScB)_2$ ionic liquids in PEG 200. The distribution of carbon, nitrogen, and oxygen on the worn areas of steel balls revealed the formation of ionic liquids composed tribo-thin film. However, a surface of steel ball lubricated with PEG 200 has no nitrogen.

through electrostatic attractions and generate the physicochemically adsorbed tribo-thin film. This mechanism is further supported by the layering structure of ionic liquids confined between the two surfaces, which are very smooth.[55] However, without precise experimental evidence, it is very difficult to conclude such mechanism for rough steel surfaces. Alternatively, under harsh tribo-conditions, ionic liquids may react with steel surface and worn particles/debris of steel owing to rich chemistry of boron compounds and form a thin film of tribo-chemical products, which improved the antiwear properties by protecting direct contact between the steel balls. The significant reduction in friction and wear along with remarkable noncorrosive properties by halogen-, phosphorus-, and sulfur-free bis(ammonium)-/bis(imidazolium)-$(BScB)_2$ ionic liquids makes the lubricant system green and energy efficient.

■ CONCLUSIONS

Bis(ammonium)- and bis(imidazolium)-$(BScB)_2$ ionic liquids were synthesized by metathesis of pentane-1,5-diyl-bis-(trialkylammonium) dibromide and 1,1′-(pentane-1,5-diyl)-(bis-alkylimidazolium) dibromide with lithium salt of bis-(salicylato)borate, respectively. A total of six ionic liquids [N3335-$(BScB)_2$, N8885-$(BScB)_2$, N11C65-$(BScB)_2$, and MIm5-$(BScB)_2$, MMIm5-$(BScB)_2$, BIm5-$(BScB)_2$], three under each category with variable alkyl chain length and cyclic ring, were prepared and then characterized by NMR and FTIR analyses. These ionic liquids as lubricant additives (2 wt %) to PEG 200 improved the viscosities and pour point of PEG 200. Thermal decomposition results revealed that the bis-(imidazolium) ionic liquids possess higher thermal stability than the bis(ammonium) ionic liquids. The observed higher thermal stability was attributed to the compact structure of imidazolium ring, higher intermolecular interactions, smaller free volume and low steric hindrance. Prior to tribo-evaluation, the corrosion properties of these ionic liquids were examined by copper strip test. Both bis(ammonium) and bis-(imidazolium) ionic liquids showed noncorrosive properties, which was attributed to nonexistence of corrosion driven elements such as halogen, phosphorus and sulfur in these ionic liquids. Furthermore, it was observed that the bis(imidazolium) ionic liquid having hexafluorophosphate anion severely corroded the copper strip facilitated by fluoride ions. The addition of 2 wt % bis(ammonium)/bis(imidazolium)-$(BScB)_2$ ionic liquids in PEG 200, remarkably improved the friction-reducing and antiwear properties. Elemental mapping on the worn areas revealed the formation of tribo-chemical thin film composed of ionic liquids. The excellent lubrication properties were attributed to the tribo-chemical thin film, generated owing to inherent polarity of ionic liquids and the tribochemical product by rich boron chemistry. The results imply that halogen-, phosphorus-, and sulfur-free ionic liquids as lubricant additives conserve the energy by reducing friction, prevents the material loss by improving antiwear and noncorrosive properties, and are safer to the environment.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

FTIR, NMR (^{1}H & ^{13}C) spectra of synthesized ionic liquids. This material is available free of charge via Internet at http://pubs.acs.org.

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