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ORIGINAL ARTICLE

Synthesis of ricinoleate anion based ionic liquids and their application as green lubricating oil additives

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Abstract Ricinoleate anion based ionic liquids (ILs) were synthesized from four different nitrogen containing cationic counterparts such as tetrabutylammonium, tetrapropylammonium, cetyltrimethylammonium, imidazolium. Tribological performance of synthesized ILs were evaluated using four ball tribo tester by blending with two lubricant base oils namely epoxy2-ethylhexyl esters of karanja fatty acids (EKE) and dioctyl sebacate (DOS). Antiwear behaviour was explored by varying different factors including concentration, applied load and rotation speed. It was found that the synthesized ILs in base oil significantly reduced the wear scar diameter by 17–25% at 0.8 wt% and a remarkable reduction in wear scar diameter was observed for all the tested applied load (40 to 80 kg) and rotation speed (1200 to 1742 rpm). Further, the load carrying capacity of base oil was improved by 25–43% at 1.25 wt% of IL dosage. The imidazolium cation containing IL outperform tribological performance among all the ILs being studied. The morphology of worn surface after the wear tests and deposition of elementals on the worn surface lubricated with neat base oil and IL blended base oil was studied by scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX).

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1. Introduction

Preventing energy loss and prolonging machine service life are the major challenges for the transportation and industrial machine [1,2]. Wear and friction are the prime factors to diminish the performance of machine, accelerate material degradation and machine failure [3,4]. Mineral oil, animal and vegetable fat/oil derived fluids are serving as chief source for lubricants to counter wear and friction. Neat lubricating

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oil alone could not protect the tribo-surfaces operating under extreme conditions (high pressure, load and temperature), certain amount of additive package play a significant role in enhancing the lubrication properties. Surface protectors like antiwear and extreme pressure additives, performance enhancers like viscosity improvers and pour point depressants and lubricant protectors such as antioxidants are required to add in optimised quantity [5]. Conventional additives such as ZDDP (Zinc dialkyldithiophosphate), MoDTC (molybdenum dithiocarbamate) and other heavy metal based compounds have been serving as additives to the lubricants due to their multifunctional behaviour [6,7]. According to the environmental concern using this kind of materials as additives can pollute the natural resources such as air, water and soil moreover, an adverse effect on human health by emitting toxic materials to the environment [8,9]. Hence, there is an urgent demand for invention of new ecofriendly and potential additives for applications in the area of lubrication. In this context, ionic liquids have been emerged as an effective additives to improve the tribological properties of lubricating oils.

Ionic liquids (ILs) are molten salts containing organic or inorganic cations and anions with lower boiling point than water [10–13]. Their unique features such as high thermal stability, broad liquid range, low vapour pressure and non-flammability promise their potential for broad range of applications like solvents for organic synthesis, electrolytes in batteries, solar cells, and lubricants etc [14–19]. The ILs composed with ammonium, phosphonium, pyrrolidinium and imidazolium cations along with tetrafluoroborate, tosylate, halide and hexafluorophosphate anions were evaluated as lubricants and their interaction with metal surfaces was studied [18,20–23]. These studies proved that the ILs act as neat lubricants and also as additives to the base oils. Due to inherent polarity, ILs strongly adsorb on metal surfaces to form tribochemical film, which enhance antiwear and antifrication performance [24–28]. Nevertheless, there is a limitation for using ILs as neat lubricants due to high cost and multistep reaction procedure involved in their synthesis compared to traditional base oils [11,29,30]. However, minimum weight percent of ILs in mineral oil and other synthetic oils performed better than the neat base oil [31–33].

Currently, most of the ionic liquid additives using for the tribological applications were synthesized with anions such as halide [F⁻, Cl⁻, Br⁻ or I⁻], phosphate and sulphate, these ILs liberate high amount of toxic components to the environment. Stolte et al., investigated the ecotoxicity and biodegradability of ionic liquids such as pyrrolidinium and quaternary ammonium based cations combined with CH₃O₄S⁻, CH₃O₃S⁻ and (CF₃SO₂)₂N⁻ as counter ions. The anion (CF₃SO₂)₂N⁻ being highly resistant to biodegradation so cannot be considered for applications with potentially high environmental exposure [34]. Conventional IL additives containing halide, sulphate and PF₆ anions are replacing with environmentally benign components like fatty acids and amino acids. Biodegradable and bio compatible behaviour of amino acid and fatty acid anions are alternatives for the hazardous anions [35]. Khatri et al., reported the synthesis of tetramethylguanidinium ionic liquids with various fatty acid anions for steel/steel contact in grade I mineral oil. Significant reduction in friction and wear was observed with long alkyl chain constituted ILs [36]. Fatty acids are desirable in boundary lubrication for their tendency to adhere to tribo-surfaces due to

their polar carboxyl group and form a strong monolayer tribofilm that is efficient in minimizing wear and friction by decreasing the surface asperity [37]. The present work describes the synthesis of environmentally friendly ricinoleate anion based ILs containing various cations and evaluation of their tribological performance by blending in base oil EKE and DOS. The impact of cation structure and concentration of IL in base oil was investigated in detail to estimate the efficiency of synthesized ILs. Ionic liquids in different concentrations were blended in base oil to explore the effect of concentration on tribological performance as well as to estimate the optimum IL dose. Tribological test results were compared with commercial additives. The post wear tests were conducted in order to estimate the surface asperity and elemental composition by SEM and EDX analysis.

2. Experimental

2.1. Materials

Sodium ricinoleate was purchased from TCI chemicals (Tokyo, Japan), tetra butyl ammonium bromide (TBA-Br), tetra propyl ammonium bromide (TPA-Br), cetyl trimethyl ammonium bromide (CTA-Br) and butyl hexyl imidazolium bromide (BHI-Br) were purchased from Sigma Aldrich (St. Louis, USA). Highest grade purity of solvents were purchased from SD Fine Chemicals (Mumbai, India).

2.2. Synthetic procedure

Ricinoleate anion-based ionic liquids having four different cations were synthesized by a facile metathesis reaction as per the earlier reported procedure [38]. The reaction proceeds in a single step by stirring equimolar ratio of both bromide salt and sodium ricinoleate in water for 18 h. The reaction mixture was extracted by using dichloromethane (DCM) followed by washing with distilled water to remove excess sodium ricinoleate and sodium bromide. Solvent was removed under reduced pressure and the obtained ionic liquids were dried for 48 h at 80 °C. The synthesized four ionic liquids tetrabutylammonium (Z)-12-hydroxyoctadec-9-enoate (TBA-RA), tetrapropylammonium (Z)-12-hydroxyoctadec-9-enoate (TPA-RA), N,N,N-trimethylhexadecan-1-ammonium (Z)-12-hydroxyoctadec-9-enoate (CTB-RA), 1-butyl-3-hexyl-1H-imidazol-3-ium (Z)-12-hydroxyoctadec-9-enoate (BHI-RA) were characterised by NMR and FT-IR spectroscopy.

2.3. Synthesis of tetrabutylammonium (Z)-12-hydroxyoctadec-9-enoate (TBA-RA)

Quantities of substrates taken: Sodium ricinoleate (1 g, 0.0031 mol), TBA-Br (1 g, 0.0031 mol), yield obtained 90% (1.46 g). ¹H NMR (CDCl₃, ppm): δ 5.55 (m, —CH=CH—), 5.38 (m, —CH=CH—), 3.61 (m, 1H, —CHOH), 3.31 (m, 8H, —CH₂N), 2.26 (t, 2H, —H₂CCOO), 2.18 (t, 2H, —CH₂—C=C—), 2.04 (t, 2H, —CH₂—C=C—), 1.65 (m, 8H, 4xCH₂), 1.58 (m, 2H, —CH₂), 1.43 (m, 2H, —CH₂), 1.33 (m, 12H, 6xCH₂), 1.28 (m, 12H, 6x-CH₂), 1.01 (m, 12H, 4x-CH₃), 0.88 (t, 3H, CH₃). ¹³C NMR (CDCl₃, ppm): δ 178.8, 133.2, 124.9, 71.3, 58.8, 36.6, 35.8, 31.7, 29.7, 25.5, 22.7,

19.6, 13.8. IR (CHCl₃, cm⁻¹): 3330, 3004, 2929, 2867, 1713, 1571, 1470, 1248, 749.

2.4. Synthesis of tetrapropylammonium (Z)-12-hydroxyoctadec-9-enoate (TPA-RA)

Quantities of substrates taken: Sodium ricinoleate (1 g, 0.0031 mol), TPA-Br (1 g, 0.0037 mol), yield obtained 86% (1.24 g). ¹H NMR (CDCl₃, ppm): δ 5.54 (m, —CH=CH—), 5.38 (m, —CH=CH—), 3.60 (m, 1H, —CHOH), 3.27 (m, 8H, —CH₂N), 2.20 (t, 2H, —H₂CCOO), 2.19 (t, 2H, —CH₂—C=C—), 2.02 (t, 2H, —CH₂—C=C—), 1.73 (m, 8H, 4xCH₂), 1.56 (m, 2H, —CH₂), 1.44 (m, 2H, —CH₂), 1.33 (m, 4H, 2xCH₂), 1.27 (m, 12H, 6x-CH₂), 1.03 (m, 12H, 4x-CH₃), 0.87 (t, 3H, CH₃). ¹³C NMR (CDCl₃, ppm): δ 177.3, 132.4, 125.1, 71.3, 58.6, 36.6, 31.8, 35.2, 29.6, 25.5, 22.7, 15.7, 14.1, 13.5. IR (CHCl₃, cm⁻¹): 3346, 3005, 2922, 2854, 1709, 1554, 1451, 1151, 731.

2.5. Synthesis of N,N-trimethylhexadecan-1-aminium (Z)-12-hydroxyoctadec-9-enoate (CTB-RA)

Quantities of substrates taken: Sodium ricinoleate (1 g, 0.0031 mol), CTA-Br (1 g, 0.0027 mol), yield obtained 88% (1.54 g). ¹H NMR (CDCl₃, ppm): δ 5.53 (m, —CH=CH—), 5.37 (m, —CH=CH—), 3.60 (m, 1H, —CHOH), 3.39 (t, 2H, —CH₂N), 3.32 (s, 9H, —CH₃), 2.48 (t, 2H, —H₂CCOO), 2.15 (m, 2H, —CH₂—C=C—), 2.02 (t, 2H, —CH₂—C=C—), 1.72 (m, 8H, 4xCH₂), 1.55 (m, 2H, —CH₂), 1.44 (m, 2H, —CH₂), 1.34 (m, 4H, 2xCH₂), 1.26 (m, 36H, 18x-CH₂), 0.88 (t, 3H, —CH₃). ¹³C NMR (CDCl₃, ppm): δ 180.4, 133.0, 125.5, 71.2, 66.9, 53.4, 37.6, 35.6, 31.8, 29.7, 25.1, 22.5, 14.1. IR (CHCl₃, cm⁻¹): 3356, 3008, 2924, 2853, 1760, 1556, 1463, 1218, 773.

2.6. Synthesis of 1-butyl-3-hexyl-1H-imidazol-3-ium (Z)-12-hydroxyoctadec-9-enoate (BHI-RA)

Quantities of substrates taken: Sodium ricinoleate (1 g, 0.0031 mol), BHI-Br (1 g, 0.0034 mol), yield obtained 84% (1.28 g). ¹H NMR (CDCl₃, ppm): δ 7.28 (s, 1H), 7.18 (d, 2H), 5.52 (m, —CH=CH—), 5.40 (m, —CH=CH—), 5.31 (t, 2H, —CH₂N⁺), 4.34 (t, 2H, —CH₂N), 3.59 (m, 1H, —CHOH), 2.38 (t, 2H, —H₂CCOO), 2.21 (m, 4H, —CH₂—C=C—), 2.01 (m, 4H, 4x-CH₂), 1.57 (m, 2H, —CH₂), 1.40 (m, 2H, —CH₂), 1.30 (m, 4H, 2xCH₂), 1.26 (m, 18H, 9xCH₂), 1.0 (m, 8H, 4x-CH₂), 0.88 (t, 3H, CH₃). ¹³C NMR (CDCl₃, ppm): δ 180.1, 138.2, 133.1, 125.9, 121.4, 71.5, 53.4, 49.3, 37.8, 31.8, 29.9, 25.5, 22.7, 13.8, 13.4. IR (CHCl₃, cm⁻¹): 3355, 3136, 3003, 2957, 2856, 1760, 1698, 1557, 1463, 1215, 755.

2.7. Characterization

The synthesized ionic liquids were characterized by ¹H and ¹³C NMR spectra on Varian 300 and 75 MHz, respectively using trimethylsilane (TMS) as internal standard. FTIR spectra were recorded on Perkin-Elmer Fourier transform (FT-IR) spectrum in chloroform solvent.

2.8. Tribological tests

Synthesized ionic liquids were analyzed for their tribological performance using four-ball tribotester (Stanhope-Seta, UK) by blending with base fluid varying concentration from 0.2 to 1.5 wt%. The antiwear behaviour was examined as per the method ASTM D 4172 at 40 kg load and 1200 rpm for 60 min at 60–70 °C at different additive concentrations. At the end of each test, the lower three balls were washed with hexane and ether and air dried for 15 min. The scar diameter on lower balls was measured with Mitutoyo toolmaker's microscope and the average of three measurements was taken as mean wear scar diameter (MWD). The load carrying capacity of ionic liquids blended base oil was analyzed as per the method IP 239 at 1475 rpm and time duration 60 sec. The analysis was carried out twice and the average of two values was reported.

2.9. Surface characterization

Carl Zeiss (model no EVO18, Germany) scanning electron microscope (SEM) was used to study the morphology of worn surface lubricated with base oil and base oil containing ionic liquid. The elemental composition on worn surface was identified by energy dispersive X-ray spectroscopy (EDX).

2.10. Thermal properties

Differential scanning calorimeter (DSC) was used to measure the thermal properties such as melting and crystallization temperatures of synthesized ionic liquids (DSC Q-100 thermal analyzer from TA instruments). Typically, 5 ± 0.5 mg of tested sample was weighed in a sealed aluminum pan and placed in the equipment chamber under continuous nitrogen flow 50 mL/min. Both the heating and cooling cycles were performed at –100 to 100 °C at the heating rate of 5 °C/min. The melting and crystallization temperatures were determined by calculating the integrated area of concerned peaks. Thermal degradation temperature of ionic liquids was determined by thermo gravimetric analysis (TGA) using TA Q500 (TA Instruments, Inc., New Castle, DE, USA). Typically, 4–5 mg of sample was placed in α-Al₂O₃ crucible under continuous nitrogen flow 60 mL/min at the heating rate of 10 °C/min from room temperature to 500 °C.

3. Results and discussion

3.1. Synthesis and characterization

Ricinoleic acid ((9Z, 12R)-12-hydroxy-9-octadecenoic acid) is the most abundant fatty acid present in castor oil and it provides better lubricity performance due to the presence of hydroxy functionality [39,40]. Four ricinoleate anion based ILs with different types of bromine salts (TBA-Br, TPA-Br, CTB-Br and BHI-Br) were synthesized by conducting metathesis reaction between sodium ricinoleate and bromide salts using a green synthetic route and the chemical structures of synthesized ILs was given in Fig. 1. The synthesized ILs were characterised by ¹H, ¹³C NMR and FTIR spectroscopy. The characteristic peak appeared at 3330–3356 cm⁻¹ in the FTIR

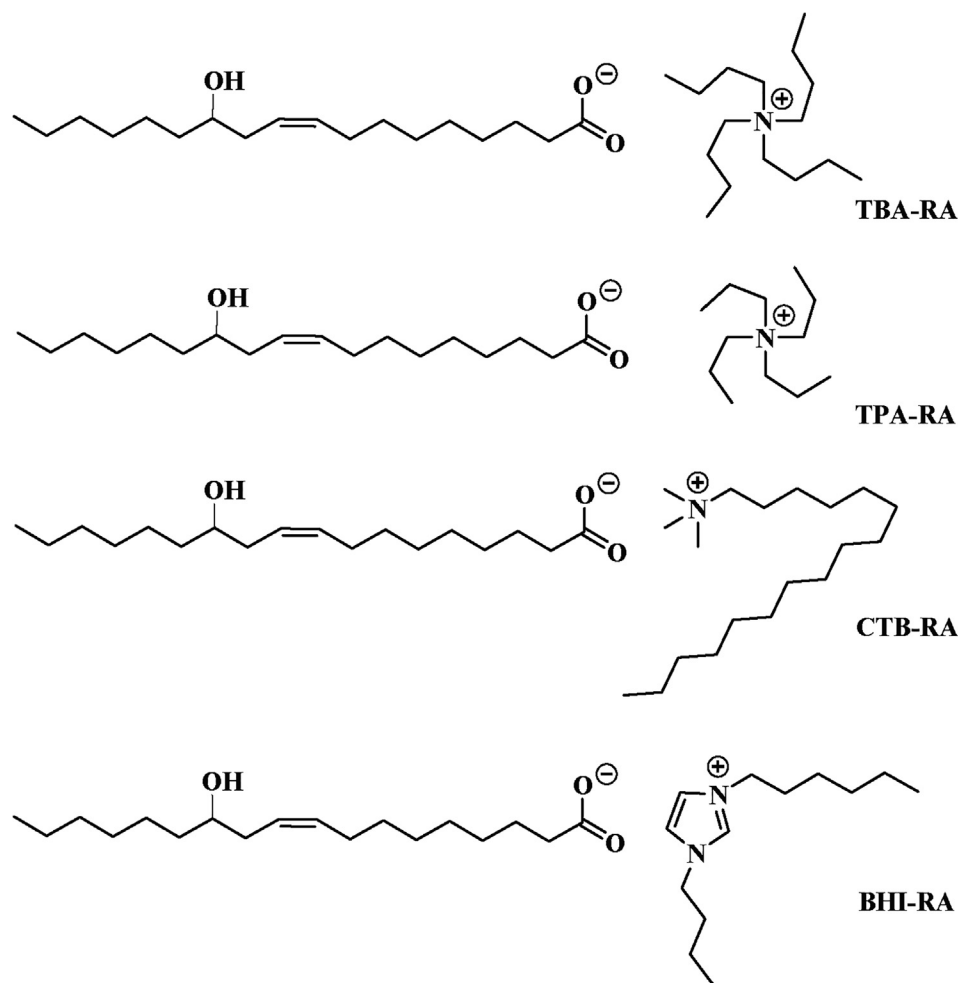


Fig. 1 Chemical structures of synthesized ionic liquids.

spectrum (Fig. 2) was due to hydroxy functional group. The signals observed at $3008\text{--}3004\text{ cm}^{-1}$ were due to unsaturation and the peaks appeared in the range of $1713\text{--}1698\text{ cm}^{-1}$ and $1470\text{--}1451\text{ cm}^{-1}$ correspond to $\text{C}=\text{O}$, COO^- stretching vibrations respectively which confirm the presence of carboxylate group. Strong vibrational bands appeared at $2929\text{--}2854\text{ cm}^{-1}$ corresponding to asymmetric and symmetric C–H frequencies of the alkyl chain. The peaks present at $1470\text{--}1386\text{ cm}^{-1}$ were attributed to the methylene and methyl bending modes in the cationic alkyl chains.

The peaks observed at $0.87\text{--}0.88\text{ ppm}$ in ^1H NMR and $13.4\text{--}14.1\text{ ppm}$ in C^{13} NMR spectra ascribed to terminal methyl protons and corresponding carbons of fatty acid anion. The methylene groups in long alkyl chain of fatty acid anion exhibited proton and carbon peaks in the range of $1.26\text{--}1.73$ and $15.7\text{--}31.8\text{ ppm}$ respectively. The methylene protons adjacent to the electronegative carboxylic group (COO^-) showed downfield signals near $2.20\text{--}2.48\text{ ppm}$ in ^1H NMR as triplet peak. Moreover, the signals observed at $178.8\text{--}183.3\text{ ppm}$ and $35.8\text{--}37.8\text{ ppm}$ in C^{13} spectra were due to COO^- and neighbouring CH_2 carbons respectively. The unsaturated protons and the protons adjacent to unsaturation showed chemical shifts at $5.36\text{--}5.55$, $2.01\text{--}2.21\text{ ppm}$ and their carbon signals appeared at $124.9\text{--}125.9$ and $29.6\text{--}29.9\text{ ppm}$ respectively. The

more prominent peaks appeared at $7.18\text{--}7.28\text{ ppm}$ and $\sim 121\text{ ppm}$ in ^1H and C^{13} spectra indicated the presence of aromatic protons and carbons of BHI-RA ionic liquid. The protons adjacent to the cationic centred nitrogen suffer from severe deshielding effect, these proton signals appeared at $3.27\text{--}3.39\text{ ppm}$. Further moving away from the nitrogen centre the chemical shift values shifted to upfield [38].

3.2. Thermal properties

Thermal properties such as melting and crystallisation behaviour during the phase transition of the synthesized ionic liquids were determined by DSC thermo grams. The results obtained from the test is summarised in Fig. 3 and Table 1. Fig. 3 shows the DSC patterns of ionic liquids CTB-RA and BHI-RA. The CTB-RA exhibited melting point at $2.6\text{ }^\circ\text{C}$ during the heating cycle and crystallizes at $-7.8\text{ }^\circ\text{C}$ during the cooling cycle. Table 1 summarises the melting point (T_m), crystallization point (T_c) of fatty acid based ILs. It is indicating that the significant differences in their T_m and T_c were observed. The difference in their T_m and T_c might be due to the difference in their cationic structure. Imidazolium cation containing IL showed lower T_m and T_c temperatures than all the quaternary ammonium salts. This is ascribed to the lower

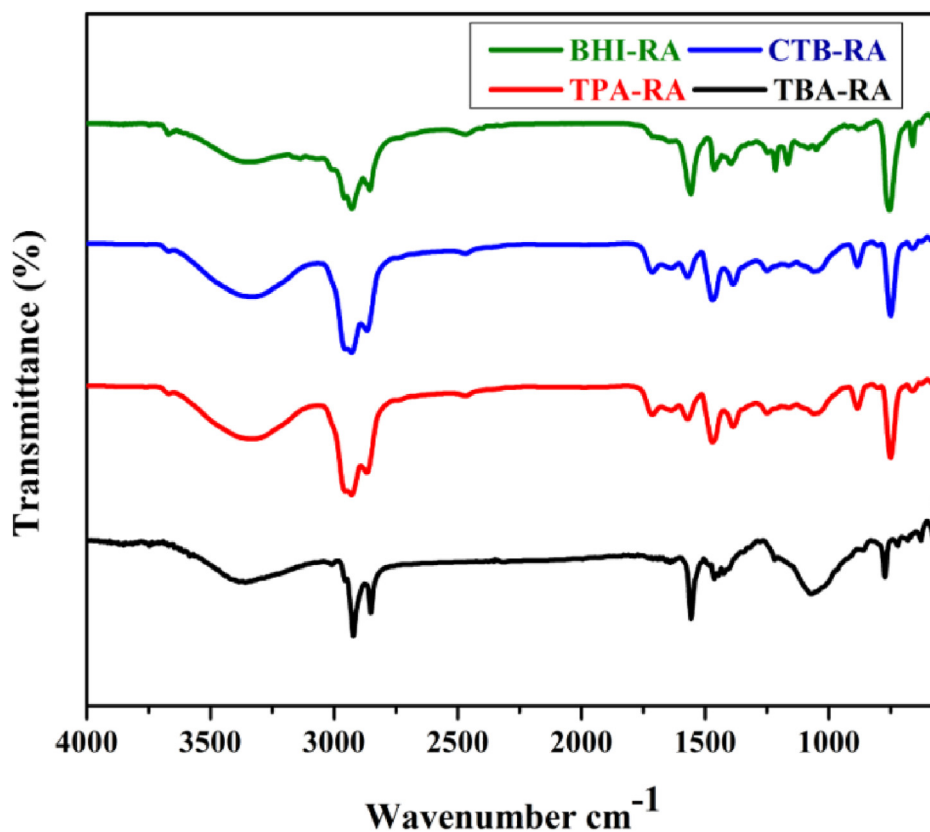


Fig. 2 FT-IR spectra of synthesized ionic liquids.

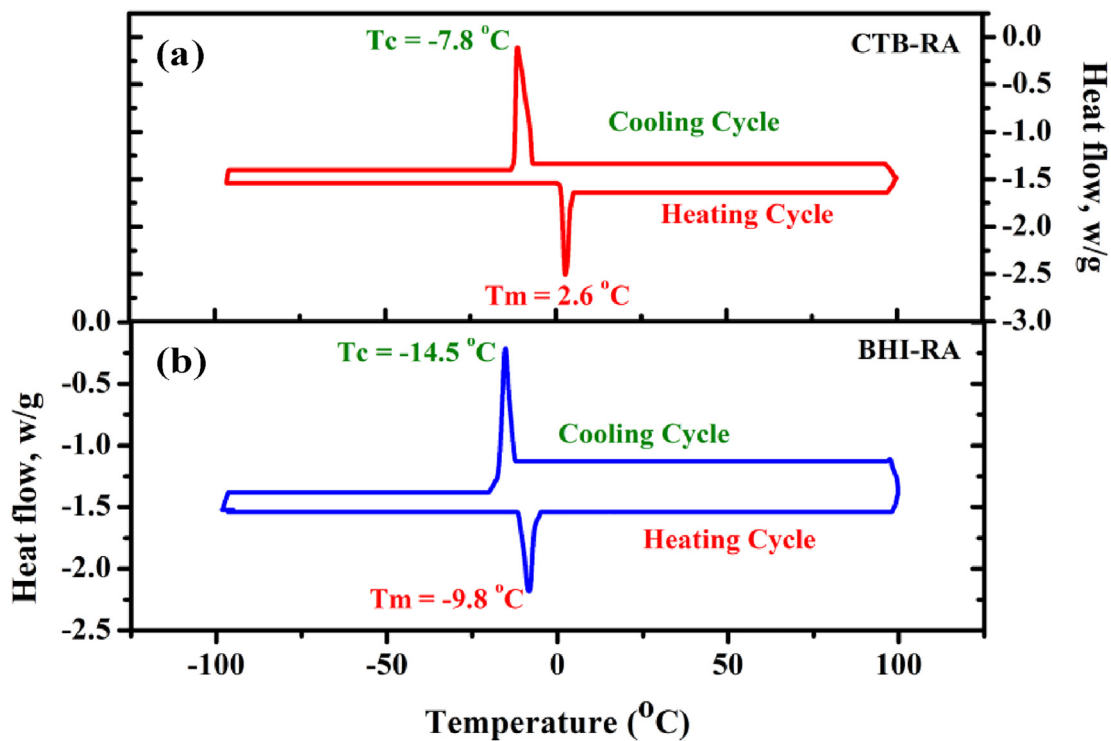


Fig. 3 Differential scanning calorimetric thermo grams of (a) CTB-RA and (b) BHI-RA.

Table 1 Thermal properties of synthesized ionic liquids.

Ionic liquids	R [⊕] Cation group	R [⊕]		
		T _m °C	T _c °C	T _{d(onset)} °C
TBA-RA	Tetra butyl ammonium	0.9	-8.5	197
TPA-RA	Tetra propyl ammonium	-1.8	-11.4	225
CTB-RA	Cetyl trimethyl ammonium	2.6	-7.8	203
BHI-RA	Butyl hexyl imodazolium	-9.8	-14.5	258

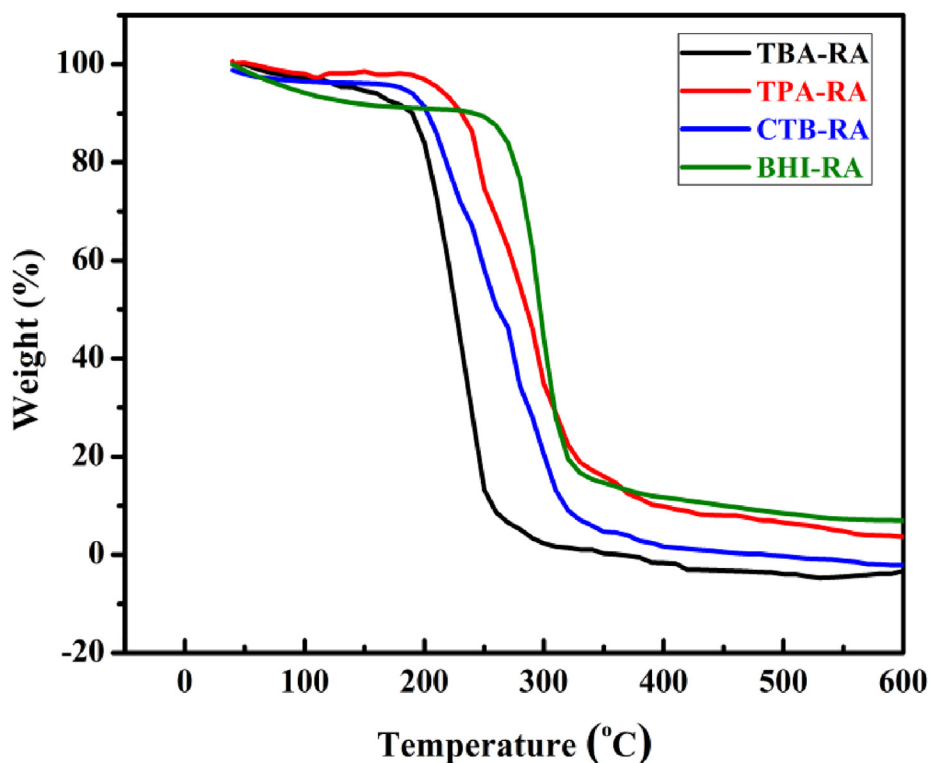
Vander Waals interaction of imidazolium cation due to sterically hindered structure. McFarlane et al., stated that the alkyl-imidazolium ions geometric packing constrained the planar imidazolium ring moreover, it has dangling alkyl chains combined with the delocalization of the charge over the N–C–N moiety in the ring, with all of them serving to decrease the ion–ion interactions and lower the melting point [41]. The higher T_m and T_c observed for CTB-RA due to high Vander Waals interaction between methylene groups, as increasing the number of methylene groups increases Vander Waals interaction, which leads to higher T_m and T_c.

Thermogravimetric analysis was carried out to find the thermal stability of synthesized ILs by determining the weight loss temperature. Fig. 4 shows the thermal decomposition patterns of the ILs under nitrogen atmosphere. Thermal stability was measured in terms of onset decomposition temperature, (T_{d(onset)}) and maximum weight loss temperature (T_{d(max)}). Results showed that the fatty acid chain length has significant

effect on thermal degradation temperature of ILs. Exclusively, the longer alkyl chain fatty acid anion containing ILs decomposed at higher temperature due to increasing Vander Waals interaction [42]. The synthesized ILs were stable up to 196 °C further, increase in temperature ILs gradually decomposed in the temperature range of 197–258 °C. The variation caused due to difference in their constituted ion structure and interactive forces [43,44]. Especially, imidazolium ions provide better stability due to compact ring structure and high inter molecular interactions [45]. All the four ILs exhibited high thermal stability hence, these ILs are potential lubricant additives for base oil operating at high temperature.

3.3. Antiwear performance

A series of wear tests were conducted by varying the IL concentration (0.2 to 1.2 wt%) on two different base oils EKE

**Fig. 4** TGA curves of ionic liquids under nitrogen atmosphere.

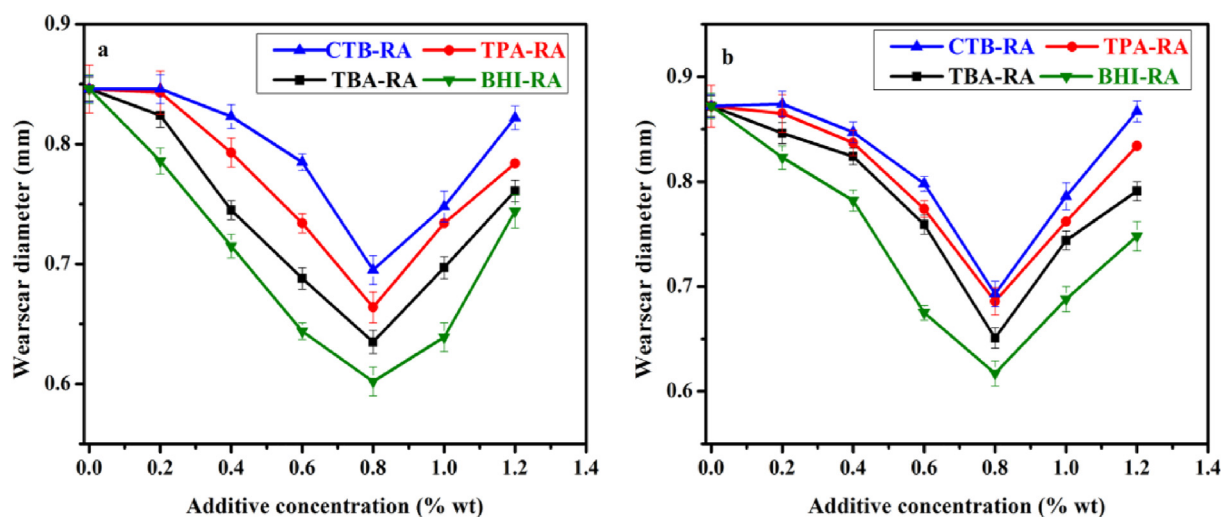


Fig. 5 Variation of wear scar diameter with different concentrations of additives in base oil (a) EKE and (b) DOS.

and DOS in order to determine the effect of concentration on antiwear behavior. Fig. 5(a and b) illustrates the variation in wear scar diameter (WSD) with IL concentration. From the figure, there observed decrease in WSD by increasing the concentration from 0.2 to 0.8 wt%. At 0.8 wt% all the four synthesized ILs showed excellent antiwear performance in two base oils. Further, no significant reduction in WSD was observed by increasing the IL concentration to 1.0 and 1.2 wt% thus, 0.8 wt% was considered as optimized concentration. Higher wear scar observed above the optimized concentration might be due to the adsorption of excess amount of additive on the metal surface, which leads to coagulation and causes severe damage to the tribofilm by increase in frictional force [46]. Fig. 5 indicating that all the synthesized ILs showed lower WSD in both base oils at all the tested concentrations than neat base oil. At optimized concentration BHI-RA exhibited maximum reduction in WSD on both base oils. WSD of base oil EKE reduced from 0.846 to 0.602 mm and 0.872 to 0.617 mm in the case of DOS. The presence of CTB-RA, TPA-RA, TBA-RA and BHI-RA on base oil EKE significantly reduced the WSD by 17, 21, 25 and 28% respectively whereas, 38% reduction in WSD was observed with commercially available antiwear additive Lubrizol 1359. Overall, the order of antiwear behavior is as follows: BHI-RA > TBA-RA > TPA-RA > CTB-RA. Remarkable variation in antiwear behaviour among the four ILs indicates that the WSD depend on composition of IL. The antiwear behaviour of BHI-RA is slightly better than others, which could be due to the presence of heterocyclic imidazole ring. Variation in antiwear performance of TBA-RA and TPA-RA could be attributed to the alkyl chain length difference on quaternary ammonium ion. According to Gusain et al., longer alkyl chain containing quaternary ammonium ILs provide better lubrication performance than shorter chains [47].

The effect of applied load on WSD was also studied in order to estimate the performance of synthesized ILs at different loads. The tests were conducted by varying the load from 40 to 80 kg at optimized IL concentration (0.8 wt%) and rotation speed (1200 rpm) and the results were presented in Fig. 6. It clearly illustrates that at the initial load (40 kg) WSD of the surface lubricated with two neat base oils was very high

whereas, surface lubricated with IL blended base oils exhibited lower WSD. Further, increasing the load from 40 to 80 kg and recorded the WSD at each test, results observed that the WSD of surface lubricated with neat base oil was higher than the surface lubricated with IL treated base oils. Higher WSD observed by the surface lubricated with neat base oils and base oil blended ILs at higher load may be due to decrease in the thickness of tribofilm between rubbing surfaces [48].

The effect of rotation speed on WSD was also studied at optimized additive concentration (0.8 wt%) and load (40 kg) by varying the rotation speed from 1200 to 1742 rpm and the results were given in Fig. 7. From the figure, minimum WSD was observed by the surface lubricated with base oils and base oils blended with ILs at 1200 rpm meanwhile, raising the rotation speed from 1200 rpm to 1742 rpm, there observed increase in WSD. However, comparing to the neat base oils IL blended base oils showed lower WSD at higher rotation speed. Higher WSD observed at higher rotation speed in both cases is due to break out of tribofilm by increasing entrainment force [49]. Above experimental results indicate that the synthesized ILs were good tribo active additives to reduce the WSD of tested base oils even at higher load and rotation speed.

3.4. Extreme pressure performance

The extreme pressure (EP) behaviour of the synthesized ILs were analyzed in two base oils and the results were shown in Fig. 8. It can be seen that the weld point of two base oils improved with addition of synthesized ILs. The base oils EKE and DOS exhibited weld points 160 and 120 kg respectively, further the addition of ILs resulted significant enhancement in weld points may be due to the development of effective tribofilm on the lubricated surface. Fig. 8 compares the weld points of base oils with different IL concentration from 0.25 wt% to 1.5 wt%. While increasing the concentration from 0.25 to 1.25 wt% increase in weld point of the base oil was observed. Further, increasing the concentration to 1.5 wt% resulted decrease in weld point, thus 1.25 wt% was taken as optimized additive concentration. At this particular concentration all the synthesized ILs were greatly effective

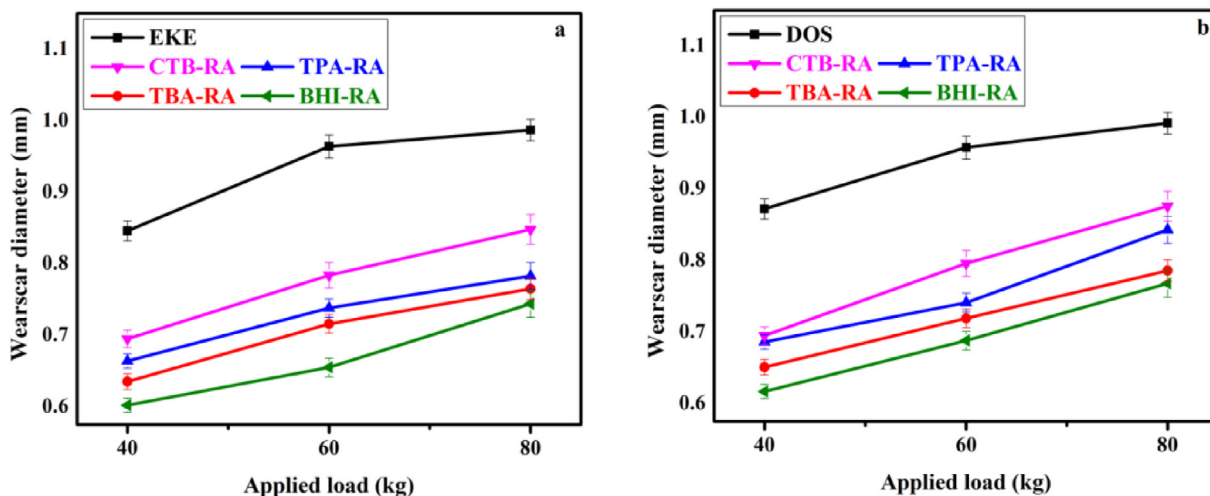


Fig. 6 Variation of wear scar diameter with different loads.

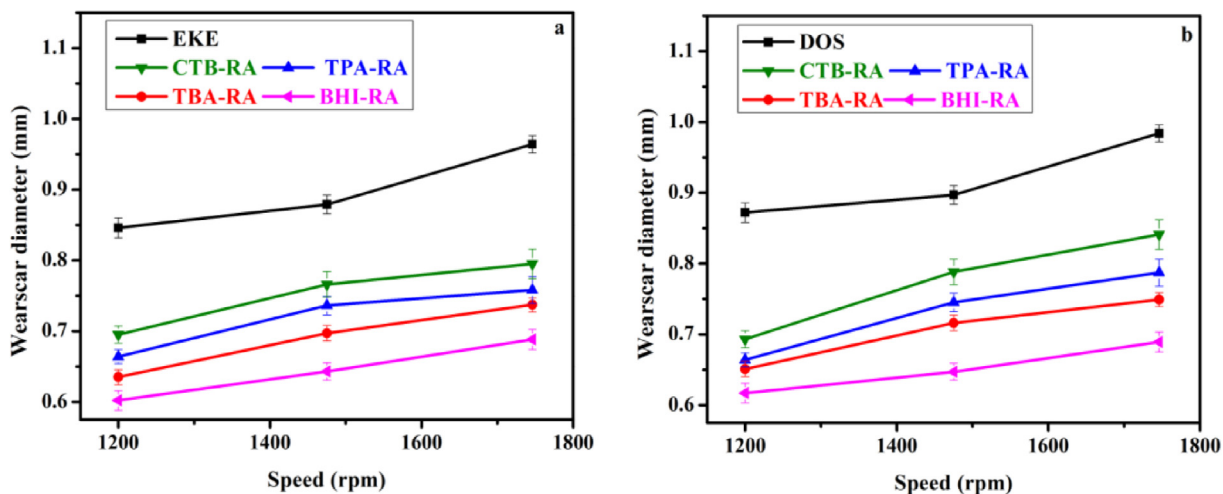


Fig. 7 Variation of wear scar diameter with different rotation speed (rpm).

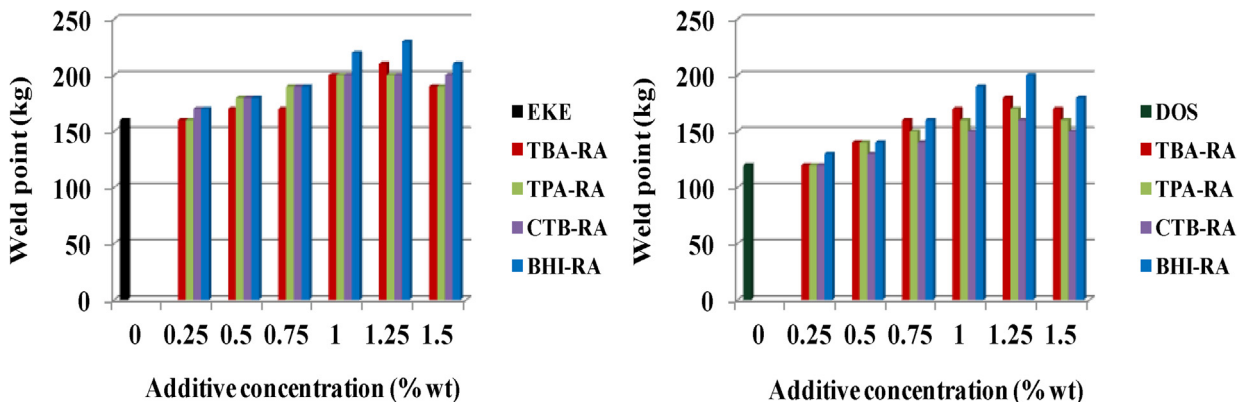


Fig. 8 Weld points at different concentration of additives in base oil EKE and DOS.

tive in improving the weld point of the two base oils. The ILS BHI-RA, TBA-RA, TPA-RA and CTB-RA enhanced the weld point by 43, 31, 25 and 25% respectively in base oil

EKE. Among all the ionic liquids BHI-RA exhibited superior extreme pressure performance in both base oils. Yang et al., reported that the nitrogen containing heterocyclic compounds

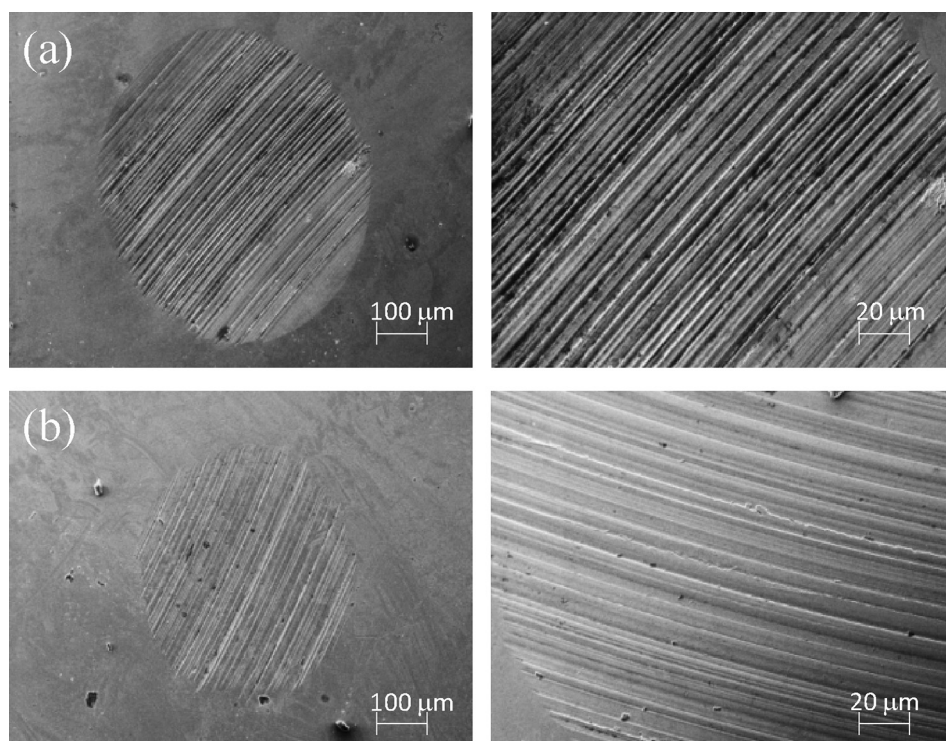


Fig. 9 SEM images of the worn surface lubricated with (a) EKE and (b) EKE containing 0.8 wt% of BHI-RA.

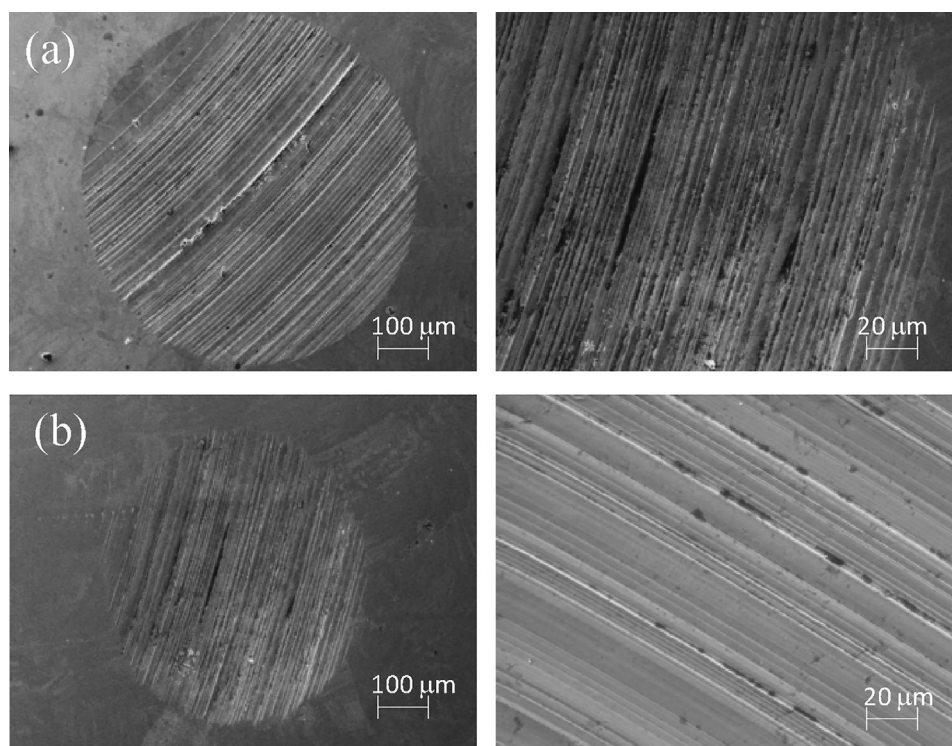


Fig. 10 SEM images of the worn surface lubricated with (a) DOS and (b) DOS containing 0.8 wt% of BHI-RA.

are capable to develop strong tribofilms under extreme pressure conditions [50]. The weld points obtained with all the synthesized ILs were compared with commercially available

EP additive dibenzyl disulfide (DBDS), results indicate that the synthesized ILs exhibited either comparable or better EP performance to DBDS.

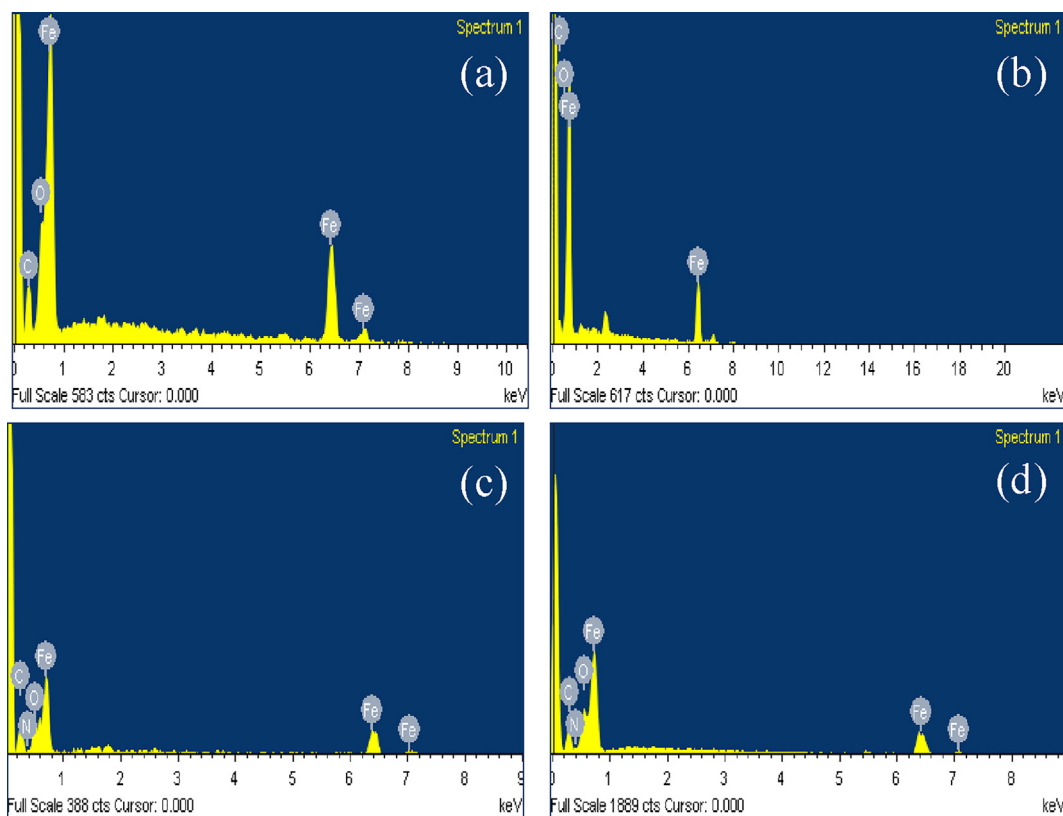


Fig. 11 EDX analysis of the worn surfaces lubricated with (a) EKE, (b) DOS, (c) EKE containing 0.8 wt% of BHI-RA and (d) DOS containing 0.8 wt% of BHI-RA.

3.5. Surface morphology

SEM analysis was carried to study the worn surface morphology of steel balls after the wear tests. Fig. 9(a, b) and Fig. 10(a, b) shows the morphology of worn surface of steel balls lubricated with base oil EKE and EKE containing IL (BHI-RA), base oil DOS and DOS containing IL (BHI-RA) respectively. It can be observed that the base oil lubricated surface was quite rough with wide scratches and deep furrowed wear tracks which are signs of mordant wear. Whereas, the surface lubricated with base oil containing IL was smooth with few scratches and wear tracks, which well corresponds to the efficient antiwear behaviour of IL. These results show that a stable tribofilm formed with ILs to prevent the direct contact between interacting surfaces [51]. Fig. 11(a, b) shows the EDX spectrum of worn surface lubricated with base oil EKE, DOS and base oil blended with BHI-RA (Fig. 11(c, d)). It can be seen that the surface lubricated by neat base oil EKE and DOS showed iron, carbon and oxygen signals whereas, surface lubricated by IL blended base oil showed additional nitrogen signal. These findings further suggest that the incorporation of nitrogen on the surface provide better protection against severe wear damage.

4. Conclusion

Four novel ricinoleate anion-based ionic liquids were synthesized by metathesis between sodium ricinoleate and bro-

mid salts and characterized by NMR and FTIR spectroscopy. Synthesized ionic liquids possess high thermal degradation temperature. At optimum concentration the fatty acid constituted ILs greatly reduced the wear scar diameter and improved the weld point of both base oils. The results obtained from the tribological tests confirmed that there is a significant effect of the cation on tribological performance of ionic liquids. The ionic liquids BHI-RA and TBA-RA exhibited better tribological performance compared to TPA-RA and CTB-RA under boundary lubrication conditions. Elemental analysis and worn surface morphology studies further confirmed the deposition of tribofilm by ricinoleate constituted ionic liquid. This study illustrates that fatty acid constituted ILs are potential lubricating oil additives to minimize or replace the use of environmentally hazardous ILs.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jscs.2020.08.003>.

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