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Fatty acid ionic liquids as environmentally friendly lubricants for low friction and wear†

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Vegetable oils are environmentally-friendly, sustainable and rich source of fatty acids, and have been used as lubricants since ancient times. The carboxylic group of fatty acids interacts with metal surface and forms the tribo-chemical thin film of low shear strength under the boundary lubrication, which reduces the friction and the wear. Herein, four fatty acids having variable chain length and unsaturated sites are selected as anionic precursors to prepare the tetrabutylammonium-fatty acid ionic liquids. The preparation of these ionic liquids is confirmed by FTIR and NMR (^{1}H and ^{13}C) analyses. The chain length and degree of unsaturation in the fatty acid anions control the viscosity, melting temperature, crystallization temperature and latent heat of fatty acid ionic liquids. These ionic liquids as lubricants exhibited significantly lower friction (18–50%) compared to polyol ester lube base oil. Further, the degree of friction reduction is largely influenced by the structure of the constituent fatty acid anion. The oleate anion showed the best tribo-performance among all fatty acid ionic liquids being studied. The elemental mapping of worn surfaces revealed the formation of fatty acid ionic liquids constituted a tribo-chemical thin film. Being halogen-free and abundantly available sources of fatty acid precursors, these ionic liquids promise immense potential for tribological applications, where the friction and environment are of prime importance.

Introduction

Ionic liquids, sterically hindered salts of an organic cation and organic/inorganic anion, exhibit good conductivity, non-volatility, non-flammability, wide liquid-range, high chemical and thermal stability, broad electrochemical window, inherent polarity *etc.* and have been proved as promising candidates for various applications such as catalysis, synthesis, drug-delivery, energy devices, chemical extraction, nuclear fuel reprocessing *etc.*[1–4] The potential of ionic liquids for lubrication application was introduced by Ye *et al.*, demonstrating friction-reducing, antiwear performance and load-carrying capacity of 1-alkyl-3-hexylimidazolium tetrafluoroborate ionic liquids.[5] Over the last decade, several studies have been made addressing the friction and the wear characteristics of ionic liquids as lubricants, lubricant additives and thin films for various solid surfaces including iron, aluminum, ceramic, and silicon.[6–9] The inherent polarity of ionic liquids is believed to facilitate their interaction with tribo-interfaces and avoids direct contact between the interacting surfaces. Furthermore, the molecular flexibility of ionic liquids by varying the constituent cation/anion not only controls the viscosity and thermal properties of ionic liquids but also makes them promising lubricious materials for various solid surfaces. To date, most of tribological studies have been made using the conventional ionic liquids, which exhibit halogens in simple/complex form; particularly, tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), trifluoromethansulfonate (OTf^-), bis(trifluoromethylsulfonyl) imide (NTf_2^-), trifluorotris(pentafluoroethyl)phosphate (FAP^-) anions.[6–13] These ionic liquids are considered to be hazardous for the environment and facilitate the corrosive events.[14,15] The halogen-constituted hydrophilic ionic liquids are prone to be hydrolyzed in the presence of water molecules and generate the acid halides, which corrode the tribo-interfaces.[16,17] Further, the disposal of halogenated ionic liquids has been a great concern and hold back their applications for solving the lubrication problems. Thus, environmentally-friendly and halogen-free ionic liquids are gaining large interest for the tribological applications. Recently, Antzutkin *et al.* studied the tribo-physical properties of chelated orthoborate ionic liquids. These ionic liquids as lubricants exhibited considerably lower friction and wear under boundary lubrication as compared to fully formulated engine oils.[18] The chelated orthoborate ionic liquids as additive to polyethylene glycol further revealed remarkable friction-reducing and antiwear properties by forming a tribo-chemical thin film on the steel surfaces.[19,20] Liu *et al.* have prepared and evaluated the lubrication properties of amino acids anion-based halogen-free ionic liquids. These ionic

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liquids as lubricants provided superior tribo-performance compared to synthetic lube base oil polyalphaolefin and conventional ionic liquid (1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide). The enhanced tribo-characteristics were attributed to the formation of physically adsorbed layers of amino acids ionic liquids on the contact surfaces under the tribo-stress.[21] Although, these ionic liquids are halogen-free, however, high cost of precursors and multi-step synthesis procedure limit their potential to the lubricant applications.

Vegetable oils, the triglycerides esters of various saturated and unsaturated fatty acids, are abundantly available in the nature and are considered as renewable and alternative lubricants.[22] These fatty acids and their esters exhibit inherent lubricious properties to form the tribo-chemical thin film on the metal surfaces under the tribo-stress. The tribo-chemical thin film of fatty acids provides low shearing and prevents direct contact between the interacting surfaces.[23,24] Taking the advantage of (a) wonderful tribo-chemistry of fatty acids and (b) their abundant availability from renewable resources (vegetable oils), fatty acid anions-based ionic liquids could be sustainable and economic alternate to the conventional ionic liquids for the tribological applications. The protic ammonium carboxylate ionic liquids as lubricants for the copper surface exhibited improved friction and wear properties compared to polyalphaolefins and were attributed to the formation of stable boundary thin film.[25] Qu *et al.* have revealed that carboxylate ionic liquids as lubricant additives to polyalphaolefins synthetic lube base oil provides superior tribological properties compared to that of sulfonate anion-based ionic liquids. It was attributed to formation of carboxylate anion-based antiwear thin film, which reduces both friction and wear.[26] Herein, tetrabutylammonium ionic liquids having fatty acid anions (caproate, caprylate, oleate and linoleate) with variable chain length and unsaturation are synthesized and then probed their thermal properties and viscosity. The tribo-characteristics of these ionic liquids as lubricants are explored using steel tribo-pairs and demonstrated the friction and wear characteristics as function of chain length and degree of unsaturation in the constituted fatty acid anions.

Experimental section

Materials

Tetrabutylammonium bromide (TBA-Br; 99%, Loba Chemie), caproic acid (99.5%, Sigma Aldrich), caprylic acid (99%, Loba Chemie), oleic acid (Extra pure, Loba Chemie) and linoleic acid (97%, Alfa Aesar) are used without further purification for synthesis of fatty acid ionic liquids. Pentaerythritol tetraoleate (polyol), purchased from M/s. Mohini Organic Pvt. Ltd. India is used as synthetic lube base oil.

Synthesis of fatty acid ionic liquids

All ionic liquids are synthesized by a facile and scalable metathesis reaction between the TBA-Br (cationic precursor) and sodium salts of fatty acids (anionic precursors). The sodium salt of each fatty acid is prepared by mixing the respective fatty acid with an aqueous solution of equimolar amount of NaOH at 60 °C for 3 hours. In the subsequent step, TBA-Br (0.2 M) is added to an aqueous solution of sodium salt of fatty acid (0.2 M) and uninterruptedly stirred for overnight. The developed product as ionic liquid is extracted in dichloromethane (DCM) and washed several times with distilled water to remove the non-reactant content and impurities. In the final step, DCM is distilled under the reduced pressure and ionic liquid is dried in the vacuum at 80 °C for 48 hours. Total four ionic liquids (Fig. 1): tetrabutylammonium caproate (TBA-C_6), tetrabutylammonium caprylate (TBA-C_8), tetrabutylammonium oleate (TBA-$C_{18\text{-}1}$) and tetrabutylammonium linoleate (TBA-$C_{18\text{-}2}$) are synthesized. Further, the preparation of each ionic liquid is confirmed by their FTIR and NMR analyses.

Characterization of ionic liquids

Synthesis and chemical structure of each ionic liquid are confirmed by FTIR and NMR (^1H and, ^{13}C) analyses. The FTIR spectra of ionic liquids are collected using Thermo-Nicolet 8700 Research spectrometer at a resolution of 4 cm^{-1}. A uniform thin film of each ionic liquid is prepared on the KBr pallet to collect the FTIR spectrum. The NMR (^1H and ^{13}C) analyses of ionic liquids are carried out using a Bruker Av III 500 MHz spectrometer. The NMR was operated at 500.13 and 125.78 MHz resonance frequencies for ^1H and ^{13}C NMR, respectively, using a 5 mm broad band probe. The 30% (w/V) sample of each ionic

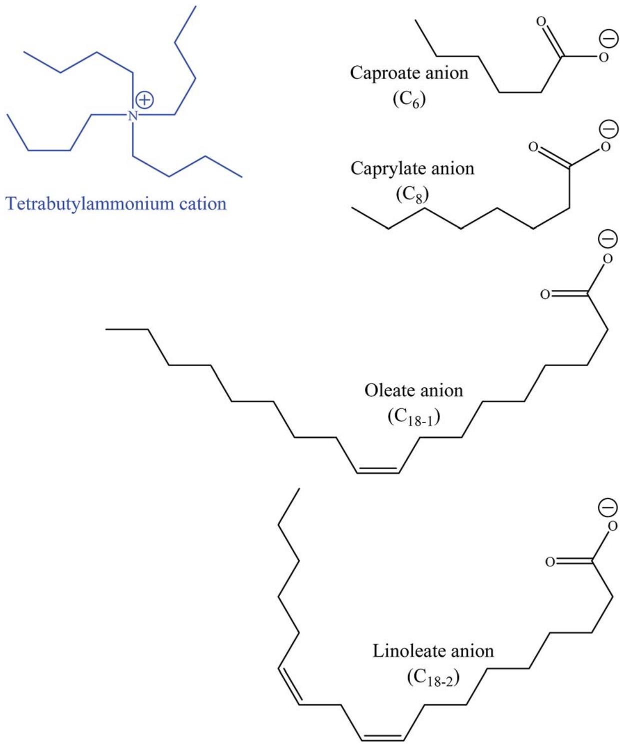


Fig. 1 Chemical structure of tetrabutylammonium (TBA) cation and fatty acid anions: caproate (C_6), caprylate (C_8), oleate ($C_{18\text{-}1}$) and linoleate ($C_{18\text{-}2}$).

liquid is prepared in the $CDCl_3$ for NMR analysis. The thermal properties of fatty acid ionic liquids including melting and crystallization points and latent heats during melting and crystallization events are measured by using a Differential Scanning Calorimeter (DSC Q200, TA Instruments). The heating and cooling thermal cycles are performed in the range of −60 to 120 °C at thermal rate of 5 °C min^{-1} under the flow of nitrogen (50 mL min^{-1}). The indium is used to calibrate the temperature reading. The latent heats of melting and crystallization are determined by calculating the integrated area of concerned peaks. Further, the thermal decomposition profile of each ionic liquid is collected using Diamond (Perkin-Elmer) thermal analyzer under the flow of nitrogen (50 mL min^{-1}) at thermal rate of 10 °C min^{-1}. The viscosity of all ionic liquids as a function of temperature are measured on Stabinger viscometer (Anton Paar, model SVM3000).

Tribo-evaluation of ionic liquids

The tribological properties of these ionic liquids for steel tribo-pair are measured using four-ball tribo-tester (Ducom, India). In a typical tribo-test, one steel ball is rotated over three stationary balls establishing the rotating point contact. The each test is run for one hour duration with rotational speed of 1200 rpm under the load of 392 N. The temperature of sample pot having ionic liquid as lube sample is maintained as 75 °C throughout the test. The worn areas of three stationary balls are used to examine the antiwear properties of fatty acid ionic liquids. The polyol lube base oil is used as reference lubricant for a comparative study. The morphological features of worn surfaces of steel balls are probed by field emission scanning electron microscopy (FESEM, FEI Quanta 200F). In order to understand the nature of tribo-chemical thin film deposited on the worn area, the elemental distribution on the worn surfaces is examined by Energy Dispersive X-ray spectroscopy (EDX) coupled to the FESEM.

Results and discussion

Tetrabutylammonium ionic liquids having four variable fatty acid anions *viz.* caproate (C_6), caprylate (C_8), oleate ($C_{18\text{-}1}$) and linoleate ($C_{18\text{-}2}$) are synthesized by following a facile and scalable metathesis reaction. The preparation of each ionic liquid is confirmed by FTIR and NMR analyses. Fig. 2 depicts FTIR spectra of TBA-C_8 and TBA-$C_{18\text{-}1}$ fatty acid ionic liquids. The FTIR spectra of other ionic liquids are shown as Fig. S1 (ESI).† The broad and strong vibrational peaks in the range of 3000–2800 cm^{-1} are attributed to asymmetric and symmetric C–H stretches of methylene and methyl units in the alkyl chains of ionic liquids. The butyl chains of TBA cation and variable alkyl/alkenyl chains of anions are contributing for the C–H stretches. Further, the vibrational modes in the range of 1480–1350 cm^{-1} are assigned to bending modes of methylene and methyl units in the TBA-fatty acid ionic liquids. The presence of unsaturation in TBA-$C_{18\text{-}1}$ and TBA-$C_{18\text{-}2}$ ionic liquids is deduced from vibrational mode in the range of at 3008–3004 cm^{-1} owing to =C–H stretching. The presence of fatty acid anions in these ionic liquids is confirmed by characteristic vibrations owing to the carboxylate group. The peaks in the range of 1762–1730, 1625–1635, and 1475–1460 cm^{-1} are attributed to the C=O, COO asymmetric and symmetric stretches, respectively and revealed the presence of carboxylate group in the TBA-fatty acid ionic liquids.

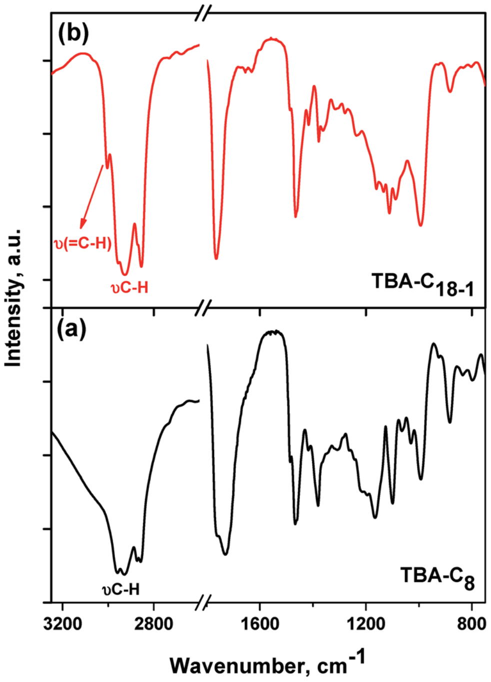


Fig. 2 FTIR spectra of (a) TBA-C_8 and (b) TBA-$C_{18\text{-}1}$ ionic liquids.

The molecular structures of fatty acid ionic liquids are further confirmed by ^1H and ^{13}C NMR analyses. The chemical shifts of ^1H NMR are extracted in the Table S1 (ESI†) and the corresponding protons in each ionic liquid are highlighted in the Fig. S2 (ESI).† The protons associated to terminal methyl groups in the TBA cation and the fatty acid anions exhibit chemical shifts in the range of 0.75–1.01 ppm and the corresponding carbons (^{13}C NMR, Fig. S3–S6, ESI†) appeared at ∼13–14 ppm. The cationic centre in tetrabutylammonium attracts electron cloud of adjacent methylene units, as a result ^1H NMR of corresponding protons show downfield shifts at ∼3.24–3.37 ppm with ^{13}C NMR shifts at ∼58–59 ppm. Whereas the methylene units of fatty acid anions adjacent to carboxylate anionic centre experienced upfield shifts of proton and carbon NMR signals at ∼2.23–3.37 and ∼34 ppm, respectively. The carbon in carboxylic group of fatty acid anions shows extreme upfield shift because of two adjacent electronegative oxygen atoms and experiences deshielded ^{13}C NMR shift at ∼172–177 ppm. The chemical shifts of methylene units in the carboxylate anion influenced by presence of electronegative atoms in the carboxylate group. Consequently, deshielding effect gradually reduces with increasing distance of methylene units from the carboxylate centre and exhibits chemical shifts of ^1H and ^{13}C peaks at upfield position of ∼1.17–2.08 and ∼15–30 ppm, respectively. The unsaturation site/s and in oleate (TBA-$C_{18\text{-}1}$) and linoleate (TBA-$C_{18\text{-}1}$) anions influences the shift of proton and carbon NMR due to free movement of pi-electrons and provides deshielded shifts. As a result, protons of double bonded and neighbouring carbon exhibit chemical shifts at ∼5.22–5.42 and ∼2.61–2.81 ppm, respectively. While, correspondingly carbon NMR signal appeared at ∼129 and ∼29 ppm, respectively. These featured chemical shifts associated to constituted cation and anions confirmed the preparation of fatty acid ionic liquids.

The electrostatic interaction between the constituted ions and other interactive forces such as van der Waals interaction, inductive forces, hydrogen-linkage *etc.* control the physico-chemical properties of ionic liquids.[27] The presence of alkyl groups, unsaturation sites, aromatic and cyclic moieties along with polarity and size of constituted ions determines both the electrostatic and the interactive forces in the ionic liquids. The variable alkyl chain length and degree of unsaturation in the fatty acid anions primarily control the viscosity of TBA-fatty acid ionic liquids. The van der Waals interaction between the methylene units of fatty acid anions increases the interactive forces, as a result viscosity of these ionic liquids increases with increasing the chain length. The TBA-C_8 ionic liquid exhibited higher viscosity than TBA-C_6 and was attributed to increasing van der Waals interaction between the higher number of methylene units in the caprylate anion of TBA-C_8 ionic liquid (Fig. 3). Further gradual increase of methylene units leads to gel–solid phase of resultant ionic liquids, which are not favourable as lubricant for the tribological application. The introduction of unsaturation in the fatty acid anion leads to bending of alkyl chain at sp^2 site and disturbed the packing orientation by diminishing the van der Waals interaction between the associated methylene units. As a result, TBA-$C_{18\text{-}1}$ ionic liquid exhibits liquid phase structure. An increasing of unsaturation sites further increases the steric constraint and significantly reduces the van der Waals interaction. Therefore, TBA-$C_{18\text{-}2}$ ionic liquid having two unsaturation sites exhibited significantly lower viscosity than the TBA-$C_{18\text{-}1}$ ionic liquid (Fig. 3) and was attributed to their packing orientation. Further, the van der Waals interactions in fatty acid ionic liquids are gradually reduces with increasing temperature (thermal energy), as a result viscosity of fatty acid ionic liquids decreased significantly.

Thermal properties such as phase transition and latent heat flow during melting and crystallization of fatty acid ionic liquids are deduced from their DSC patterns. Fig. 4 shows DSC patterns of TBA-C_8 and TBA-C_6 as representative fatty acid ionic liquids. The TBA-C_8 ionic liquid melts at 1.3 °C during the heating cycle and crystallizes at −9.4 °C during the cooling cycle. Table 1 lists the melting point (T_m), crystallization point (T_c) and latent heats of fatty acid ionic liquids. It is revealed that both T_m and T_c increases with increasing the chain length of fatty acid ionic liquid.[28,29] This is attributed to higher van der Waals interaction between the increasing numbers of methylene units in the fatty acid anion, as a result TBA-C_8 ionic liquid exhibit higher latent heats of melting and crystallization compared to that of TBA-C_6 ionic liquid (Table 1). The oleate anion ($C_{18\text{-}1}$) have significantly higher number of methylene units than caprylate (C_8) anion, however, both T_m and T_c for TBA-$C_{18\text{-}1}$ ionic liquid are comparatively low. This was attributed to the presence of unsaturation site in the oleate anion, which distort the orientation of methylene units and generates sterically hindered structure, as a result reduced van der Waals interaction diminishes the packing structure of TBA-$C_{18\text{-}1}$ ionic liquid. Further increasing number of unsaturation sites in the fatty acid anion reduces phase transition temperatures and latent heats as shown in the Table 1. The thermal decomposition patterns of fatty acid ionic liquids are measured by thermo-

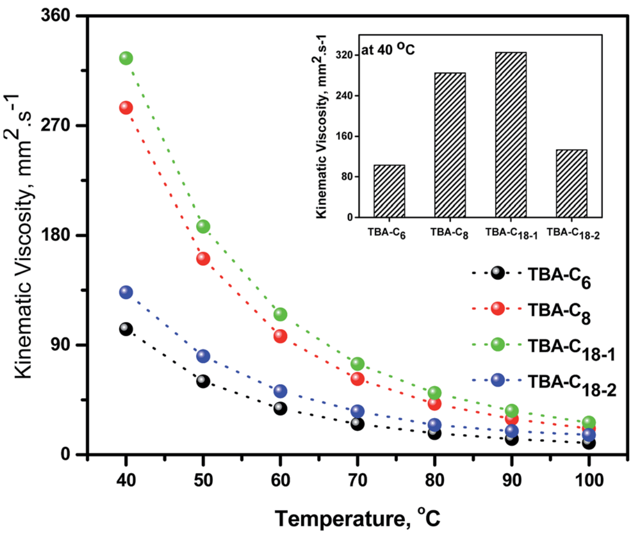


Fig. 3 Viscosity of fatty acid ionic liquids as a function of temperature. Inset graph shows kinematic viscosity of these ionic liquids at 40 °C.

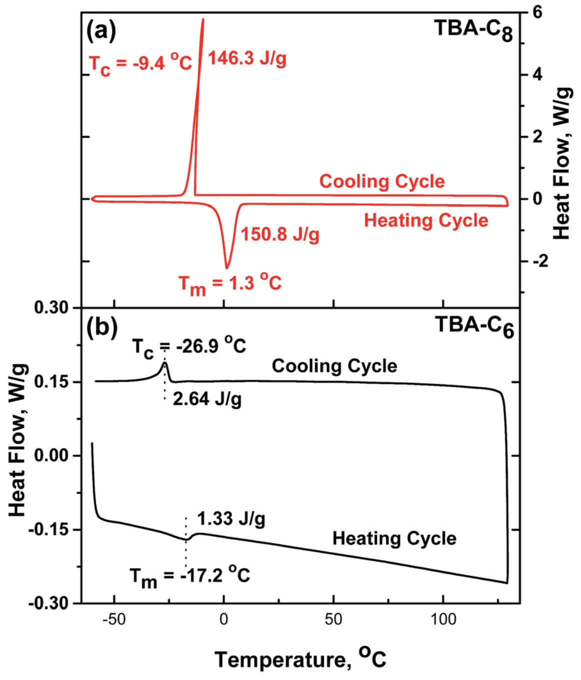
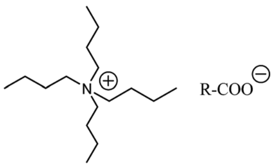


Fig. 4 Differential scanning calorimetric patterns of (a) TBA-C_8 and (b) TBA-C_6 as representative fatty acid ionic liquids.

Table 1 The structures and thermal properties of fatty acid ionic liquids[a]



		Melting feature		Crystalline feature		
Ionic liquids	R, anion group	T_m, °C	Heat flow, J g^{-1}	T_c, °C	Heat flow, J g^{-1}	T_{d50}, °C
TBA-C_6	CH_3–$(CH_2)_4$–, caproate	−17.2	1.4	−27.0	2.6	222.3
TBA-C_8	CH_3–$(CH_2)_6$–, caprylate	1.3	150.8	−9.4	146.3	248.9
TBA-$C_{18\text{-}1}$	CH_3–$(CH_2)_7$–CH=CH–$(CH_2)_7$–, oleate	−15.3	51.0	−26.2	45.4	268.4
TBA-$C_{18\text{-}2}$	CH_3–$(CH_2)_4$–CH=CH–CH_2–CH=CH–$(CH_2)_7$–, linoleate	−31.3	14.9	−50.0	13.6	262.7

[a] T_{d50}: the temperature, where 50% of ionic liquid thermally decomposed.

gravimetric analysis. These ionic liquids are found to be thermally stable up to 190 °C and then gradually decomposed with increasing of temperature as shown in Fig. 5. The longer chain length of constituted fatty acid anions provides higher thermal stability (Table 1) to the resultant ionic liquids and it could be attributed to their organized structure driven by increasing van der Waals interaction. The observed trend is found to be opposite of imidazolium ionic liquids, where the thermal decomposition temperature reduces with increasing of substituted alkyl chain length.[30,31] The increasing number of unsaturation site in fatty acid anions further reduce the decomposition temperature and was attributed to poorer packing orientation in TBA-$C_{18\text{-}2}$ compared to TBA-$C_{18\text{-}1}$ ionic liquid.

Tribological properties of fatty acid ionic liquids in terms of friction and wear are examined under the rolling contact between the steel balls. The polyol ester was used as reference lube oil for a comparison purpose. Fig. 6 illustrated the coefficient of friction and wear scar diameter (WSD) of fatty acid ionic liquids and polyol ester under the load of 392 N at a rotating speed of 1200 rpm for one hour duration. The polyol lube base oil, a biodegradable pentaerythritol ester consisting of four oleate chains, exhibited ~0.086 coefficient of friction and

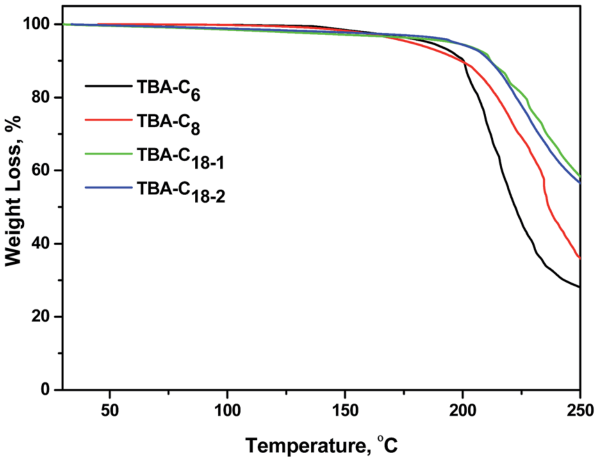


Fig. 5 Thermal decomposition patterns of TBA-C_6, TBA-C_8, TBA-$C_{18\text{-}1}$ and TBA-$C_{18\text{-}2}$ ionic liquids at thermal rate of 10 °C min^{-1} under the nitrogen flow.

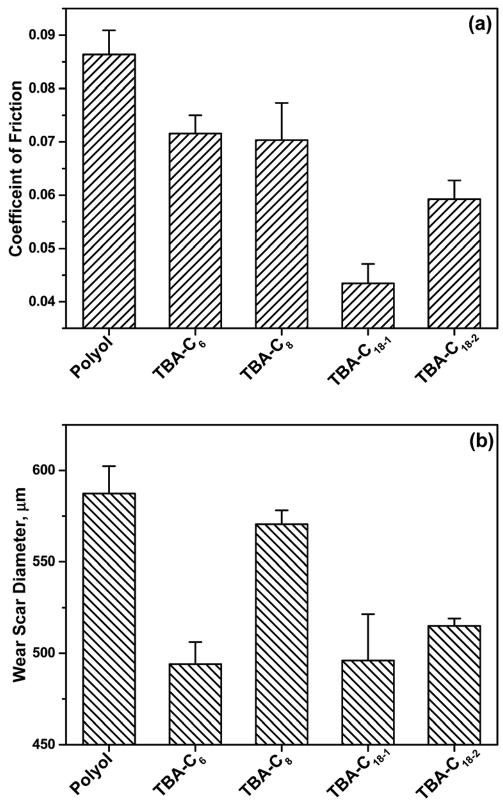


Fig. 6 (a) Coefficient of friction and (b) wear scar diameter of fatty acid ionic liquids and polyol ester (as a reference lube base oil) under the rolling contact between steel balls. Load: 392 N, speed: 1200 rpm, temperature: 75 °C, test duration: 1 hour.

~590 μm WSD. The fatty acid ionic liquids as lubricants showed significantly lower coefficient of friction (18–50%) compared to the polyol ester (Fig. 6a) under identical experimental conditions. The TBA-C_6, TBA-C_8, TBA-$C_{18\text{-}1}$ and TBA-$C_{18\text{-}2}$ ionic liquids exhibited 18, 20, 50 and 31% lower coefficient of friction compared to that of polyol ester. Recently, Espinosa *et al.* demonstrated the lubrication properties of bis(2-hydroxy) ammonium oleate ionic liquid for copper tribo-pair.[25] The bis(2-hydroxy)ammonium oleate ionic liquid as lubricant showed low friction for initial sliding distance and then stabilized to 0.14, which is even higher than the coefficient of friction for non-polar synthetic lubricant PAO 6. The high coefficient of friction could be attributed to presence of hydroxyl groups and short alkyl groups in the ammonium cation.

The polyol ester exhibited intrinsic lubricious nature owing to presence of oleate moiety in the ester form. In spite of that fatty acid ionic liquids showed lower friction than polyol ester. The TBA-C_6 and TBA-C_8 exhibited coefficient of friction in the same range, however, a larger deviation of friction was noted with TBA-C_8 ionic liquid. This effect is also reflected in the wear characteristic. Further increasing the chain length of fatty acid anion provides gel-to-solid like structure, hence couldn't execute the tribo-tests with longer alkyl chain fatty acid ionic liquids. However, introduction of unsaturation site/s in the fatty acid anions (oleate and linoleate in TBA-$C_{18\text{-}1}$ and TBA-$C_{18\text{-}2}$ ionic liquids, respectively) leads to steric constraint in the alkyl chain and changes the physical state of ionic liquids from solid to liquids by diminishing the van der Waals interaction between the associated methylene units. Hence, TBA-$C_{18\text{-}1}$ and TBA-$C_{18\text{-}2}$ ionic liquids could be used as lubricants. The TBA-$C_{18\text{-}1}$ ionic liquid having oleate anion with one unsaturation site showed lowest coefficient of friction among all ionic liquids (Fig. 7) and was attributed to the formation of stable tribo-chemical thin film on the steel interfaces induced by tribo-stress. Both coefficient of friction and WSD further increases with increasing of unsaturation site in the ionic liquids, as a result TBA-$C_{18\text{-}2}$ ionic liquid showed comparatively higher friction and wear.

Fig. 8 show the FESEM images of worn area on steel balls lubricated with polyol ester and fatty acid ionic liquids. The polyol ester-lubricated steel ball showed larger wear scar with deep scratches. Ionic liquids with inherent polarity interact with the tribo-interfaces and form a thin film of low shear strength, which not only protect the contact surface against the wear at some extent but also reduces the friction significantly. As a result, steel balls lubricated with fatty acid ionic liquids showed comparatively lower wear scar (Fig. 8b–e). Furthermore, the elemental distribution images on the worn surfaces of steel balls lubricated with fatty acid ionic liquids are collected to understand the nature of tribo-chemical thin film. The carbon, oxygen and nitrogen are key constituent elements of fatty acid ionic liquids. Herein, nitrogen is selected as a characteristic element and found to be uniformly distributed on the worn surfaces of steel balls (Fig. 9) lubricated with fatty acid ionic

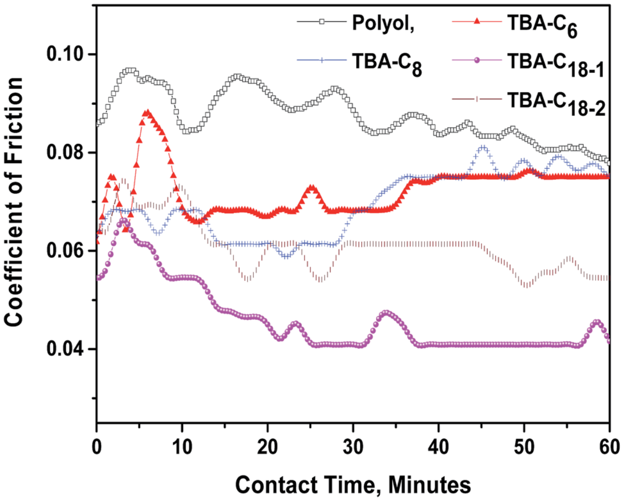


Fig. 7 The evolution of coefficient of friction with contact time for fatty acid ionic liquids and polyol ester (as a reference lube base oil) under the rolling contact between steel balls. Load: 392 N, speed: 1200 rpm, temperature: 75 °C, test duration: 1 hour.

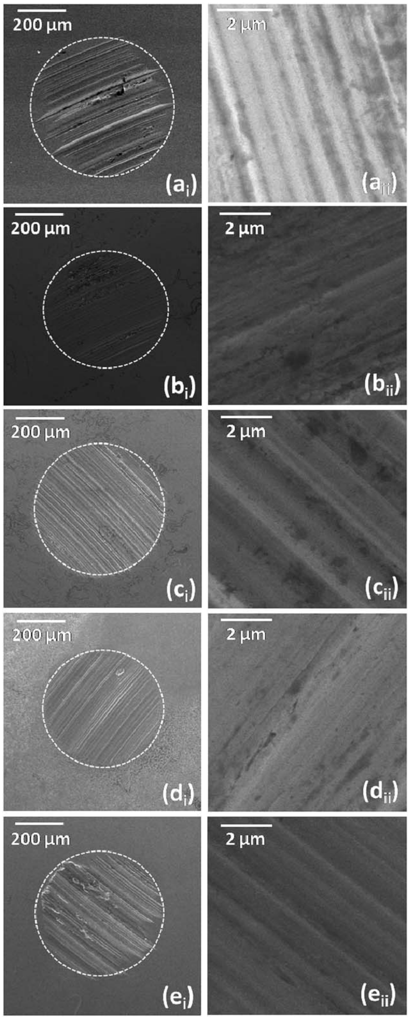


Fig. 8 FESEM images of the worn surfaces of steel balls lubricated with (a_{i-ii}) polyol ester, (b_{i-ii}) TBA-C_6, (c_{i-ii}) TBA-C_8 and (d_{i-ii}) TBA-$C_{18\text{-}1}$ and (e_{i-ii}) TBA-$C_{18\text{-}2}$ ionic liquids. Load: 392 N, speed: 1200 rpm, temperature: 75 °C, test duration: 1 hour.

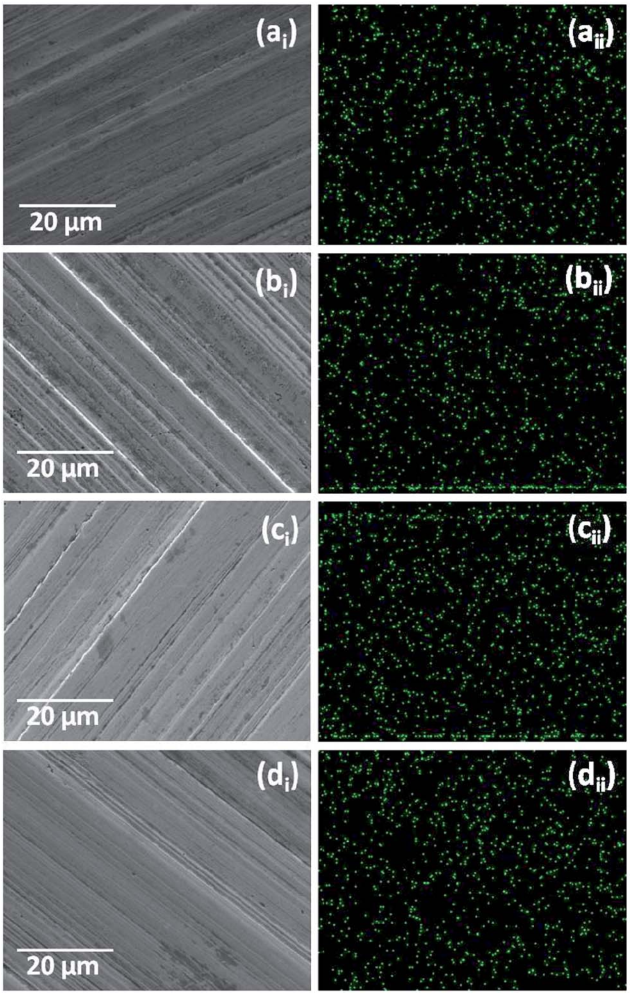


Fig. 9 FESEM images and correspondingly distribution of nitrogen on the worn surfaces of steel balls lubricated with (a_i–a_{ii}) TBA-C_6, (b_i–b_{ii}) TBA-C_8, (c_i–c_{ii}) TBA-$C_{18\text{-}1}$ and (d_i–d_{ii}) TBA-$C_{18\text{-}2}$ ionic liquids. Nitrogen (ammonium cation) is an integral part of TBA-fatty acid ionic liquids and suggesting the participation of these ionic liquids in tribo-chemical thin film formation.

liquids. These images suggested the formation of fatty acid ionic liquids constituted tribo-chemical thin film on the worn surfaces. The polyol molecules is usually decomposed under the tribo-stress and generates the oleate units, which interact with steel surface under the tribo-stress and provides good tribological properties. Herein, fatty acid ionic liquids consisting of fatty acid anions are believed to promptly interact with steel tribo-interfaces and forms the good quality tribo-chemical thin film compare to that of with polyol ester. Therefore fatty acids ionic liquids exhibited significantly improved friction-reducing and antiwear properties compared to that of polyol ester lube base oil.

Conclusion

Lubricants, the indispensable materials for engineering surfaces, are gaining large attention because of their adverse effect to the environment and depletion of hydrocarbon resources. As a result, renewable and eco-friendly lubricants are showing immense interest for fundamental understanding to applications perspective. The fatty acids-enriched vegetable oils and animal fats are well-established lubricants since ancient time. The fatty acids interact with steel surface under the tribo-stress and prepare the thin film of low shear-strength, which reduces the friction and protect the surface against the undesirable wear. Herein, fatty acids as renewable precursors having variable chain length and degree of unsaturation are selected to prepare fatty acid ionic liquids. The syntheses of TBA-fatty acids ionic liquids are confirmed by FTIR and NMR analyses. The viscosity of these ionic liquids increases with increasing the chain length of fatty acid anions and was attributed to increasing van der Waals interaction between the associated methylene units. The introduction of unsaturation sites in fatty acid anions significantly diminished the van der Waals interaction owing to steric constraint and reduced the viscosity. The structural parameters of fatty acid anions further influence the thermal properties (T_m, T_c, T_{d50} and latent heats) of these ionic liquids. The fatty acid ionic liquids as lubricants provide 18–50% reduction in coefficient of friction compared to that of polyol ester lube base oil. The inherent polar nature of fatty acid anions facilitates their interaction promptly with steel surface under the boundary lubrication and forms the stable tribo-chemical thin film of ionic liquids. The FESEM and nitrogen mapping (Fig. 9) of worn surfaces further confirmed the deposition of tribo-chemical thin film of fatty acid ionic liquids, which reduces both the friction and the wear. The TBA-$C_{18\text{-}1}$ and TBA-$C_{18\text{-}2}$ ionic liquids exhibited comparatively better tribo-performance than TBA-C_6 and TBA-C_8 ionic liquids and was attributed to difference of their chain length. Further, degree of unsaturation in fatty acid anion found to control the lubrication characteristics. This study demonstrates that fatty acid ionic liquids could be excellent alternative to the conventional halogenated ionic liquids. Further, significantly low cost, environmentally-friendly nature, renewable and sustainable resources of fatty acid precursors promise immense potential of these ionic liquids for various applications.

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