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RESEARCH PAPER

Synthesis of Novel Imidazolium Based Ionic Liquids for Use as Multifunctional Green Additives in Gear Oils

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Abstract: *In this work, the facile synthesis and identification of hexylmethylimidazolium bis(trifluoromethyl sulfonyl) amide ([HMIM]TFSA) and hexylmethylimidazolium triethyltrifluorophosphate ([HMIM]FAP) ionic liquids (ILs), as multifunctional and multipurpose gear oil additives, is introduced. The tribological tests indicated that both ([HMIM]TFSA) and ([HMIM]FAP) ILs demonstrate antiwear/extreme pressure properties (AW/EP) to the gear oils by preventing wear and scar of the lubricated system at low and high temperatures. [HMIM]TFSA provided superior performance in comparison to [HMIM] FAP. Because of the presence of heteroaromatic imidazole moiety in the ILs structure, the prepared ILs also imparted anti-corrosion, antioxidant, and anti-rust properties to the lubricant. All these observations confirmed that the ILs are single component multifunctional and multipurpose oil additives. Also, due to avoiding the use of toxic and harmful elements in the preparation of ILs make the fabricated oils potential candidates for green lubricants.*

Keywords: *Ionic liquids, Gear oil, Tribology, Multifunctional gear oil additive, Green Lubricant.*

1. INTRODUCTION

Choosing an appropriate lubricant for gearboxes reduces the rate of wear, operating temperature, and increases energy efficiency [1, 2]. Nowadays, gearbox designers consider viscosity, polarity, and oil absorption to the lubricated surfaces, because these properties are the main parameters affecting pressure tolerance (extreme pressure property) of lubricants. A lubricant with higher extreme pressure (EP) property induces less wear in the system, which results in more effective lubrication of machine parts [3].
Additives used in gear oil must impart extreme EP, anti-wear, friction reduction, anti-corrosion, and anti-rust properties, and prevent oil degradation [4, 5]. EP additives or pressure-resistance compounds are compounds which are added to the lubricating oils to prevent the damage caused by metal surfaces contact at high working temperature, or pressure. Indeed, the EP compound reacts with the metal surfaces and forms a film of metal salts, which acts as a solid lubricant. This type of lubrication is called boundary lubrication and occurs in the presence of sulfur, halogens, phosphorus, and carboxylic salts that are capable of chemically reacting with metals [6-8]. In boundary lubrication, the asperities come into close contact causing stick and break-off of some of them. When the viscosity of the lubricant and sliding speed are very low or the load is high, boundary lubrication occurs and liquids are substantially suppressed and form a solid-like adsorption film at contact points, which is capable of supporting a load and prevents serious breakdown. Therefore, the film formation capability determines the performance of boundary lubrication. Moreover, the local flash temperature is usually very high and induces a chemical reaction of either the lubricant or additive to form a tenacious film (boundary film) on a freshly generated metal surface, which also helps to prevent direct contact and severe wear of the sliding pair [9]. Consequently, the search for ideal EP additive has led organic chemists as well as mechanical engineers to make a rigorous contribution to this field and improve their research results for the use by car engineers. However, conventional EP additives are mainly sulfurized compounds containing phosphorous or halogens. It is well known that sulfur is corrosive toward metals and always there is a need to use anti-corrosion additives in EP containing oils to prevent corrosion. Also, these compounds produce highly toxic gases including SO_2 during combustion, which are not environmental friendly and in the case of halogens presumed to be ozone depleting. To address these problems and

challenges and to improve tribological properties, ionic liquids (ILs) have been introduced as reliable oil additives in the last two decades [10, 11]. In recent years, synthesis and investigation on tribological properties of ILs, as oil additives, have given rise to the publication of numerous reports from both academia and industry [12, 13]. ILs possess several interesting properties that distinguish them from regular liquids and make them highly effective lubricating materials [14, 15]. These significant properties are: (1) solubility of a wide range of both organic and inorganic materials are in ILs because they have high molecular polarity, which leads to increment in tribological properties of ILs; (2) they can be used as base oil or additives; (3) it is easy to fine-tune the properties of the ILs by changing the cations and anions, providing novel characteristics; (4) the estimated number of IL kinds is on the order of thousands, because there are a large number of cation and anion species currently available. Interestingly, each IL has its own properties and can be utilized according to a unique environment; (5) ILs are not volatile; (6) contamination problems inherent to regular synthetic lubricating oil can be successfully avoided. (7) ILs have outstanding thermal stability, for example, certain types of ILs can resist temperatures up to 300–400 ˚C, conversely, the decomposition of synthetic lubricants is always a key factor that limits their applications at high temperature conditions, and (8) ILs have high polarity, thus enabling them to form a very strong lubricating film and enhance boundary lubrication of surfaces. Combination of these unique features has qualified the ILs as ideal lubricants in terms of environmentally friendly or green lubricating materials criteria [16].

The most common anions examined in the tribology studies are BF4- and PF6, but they suffer from their low hydrolytic stability and high tendency to produce corrosive HF [17-19]. Therefore, these anions lead to deep corrosion of the gears and system under lubrication, which restricts ILs application as oil additives. Indeed, low hydrolytic stability restricts the application of IL lubricants in the presence of water due to the loss of their performance. This restriction is especially important in gear oil, because there are situations in which oils come into close contact with water [20].

To address the above concerns, we report the synthesis of two ILs, namely hexyl methyl imidazolium bis (trifluoromethylsulfonyl) amide ([HMIM] TFSA) and hexylmethylimidazolium triethyltrifluorophosphate ([HMIM]FAP) for the first time. The anions of the prepared ILs are hydrolytically stable. Therefore, they provide better lubricating properties than ILs containing conventional anions such as BF4- and PF6- due to the prevention of corrosive HF production and consequent system failure. Furthermore, these ILs contain heteroaromatic imidazole moiety in their chemical structure, which also gives ILs antioxidant and anticorrosion properties [21, 22]. The effectiveness of the prepared ILs as additives in a gear-box oil was investigated systematically by tribological and surface analysis examinations.

2. EXPERIMENTAL

2.1. Instruments, Chemicals, and Reagents

All reagents including 1-methylimidazole, isopropyl alcohol, bis (trifluoromethylsulfonyl) amide, triethyl trifluorophosphate, 1,6-dibromo hexane, 1-methylimidazole, EtOAc, acetone, CH_3CN, and CH_2Cl_2 were purchased from commercially available sources including Sigma–Aldrich and Merck and used without further purification.

The characteristics of base oils are given in Table 1. The oil additives including EP package (HITEC 343), viscosity index polymer and pour point depressant, silicone antifoam were kindly provided by Pars Oil Company.

^{1}H NMR spectra were recorded in DMSO-d_6 on a 300 MHz Bruker spectrometer using TMS as the internal reference. IR spectra were recorded with a Shimadzu 8400s FT-IR spectrometer using potassium bromide pellets. The SEM and EDS analyses were done with a TESCAN VEGA3 model. Anton-Paar automatic viscometer (model SVM 3001) was used for viscosity, viscosity index, and density measurements according to ASTM D445, ASTM D2270, and ASTM D1298, respectively. Flashpoint measurements were performed using Herzog Pensky Martins tester according to ASTM D92. Pour point measurements were done using a semi-automatic ISL trademark (France) tester according to ASTM D97. TAN measurements were done using Metrohm semiautomatic TAN tester according to ASTM D664. Four ball measurements were

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performed according to ASTM D2596 using STANHOPE-SETA test rig. Mitotoyo TM microscope (×30 magnification) was used for observing and measuring the wear diameter of balls. Foaming tendencies were measured using SCVAVINI Tester according to ASTM D892. Timken OK loads were measured using Falex Timken Extreme Pressure Test Rig. Copper corrosion tests were done according to ASTM D130. Brookfield viscosity measurements were measured by the KOEHLER instruments according to ASTM 2893 standard. Thermo Scientific iCAP 7400 ICP-OES was used for elemental analysis according to ASTM D5185. The FZG gear tests were performed using Starma-MPS FZG test rig. Water separability measurements were done using SCVAVINI Tester (Baveno, Italy) according to ASTM D1401.

2.2. Methods

2.2.1. Synthesis of Double-Charged Cationic Imidazolium ILs

Scheme 1 shows the general synthesis procedure of the ILs. Generally, the double charged cationic imidazolium ILs were prepared in two general steps: First, the imidazolium cation was prepared, and then anion exchange was used to obtain the final products, as described in ref. [23]. The first prepared IL was 3,3'-(1,6-hexanediyl) bis (1-methyl-1H-imidazol-3-ium) triethyl trifluoro phos phate, which is abbreviated as IL3. The second prepared IL was 3,3'-(1,6-hexanediyl) bis (1-methyl-1H-imidazol-3-ium) bis (trifluoromethylsulfonyl) amide, which is abbreviated as IL4. The step-by-step procedure and FT-IR and identification data of the ILs are given below.

Table 1. The physical and chemical characteristics of the group III base oils used in the gear oil formulations.

Chemical and physical characteristics	Test method	Results	
		grade 4	grade 6
Density (15 ˚C)	ASTM D1298	0.8425	0.8465
Kinematic viscosity at 40 ˚C (mm^2/s)	ASTM D445	18.2	35.9
Kinematic viscosity at 100 ˚C (mm^2/s)	ASTM D445	4.1	6.3
Viscosity index	ASTM D 2270	130	127
TAN	ASTM D 664	0.01	0.04
Flash point (˚C)	ASTM D92	200	230
Pour point (˚C)	ASTM D97	-18	-15
Copper corrosion	ASTM D130	2b	2b
Carbon residue	ASTM D524	0.04	0.04

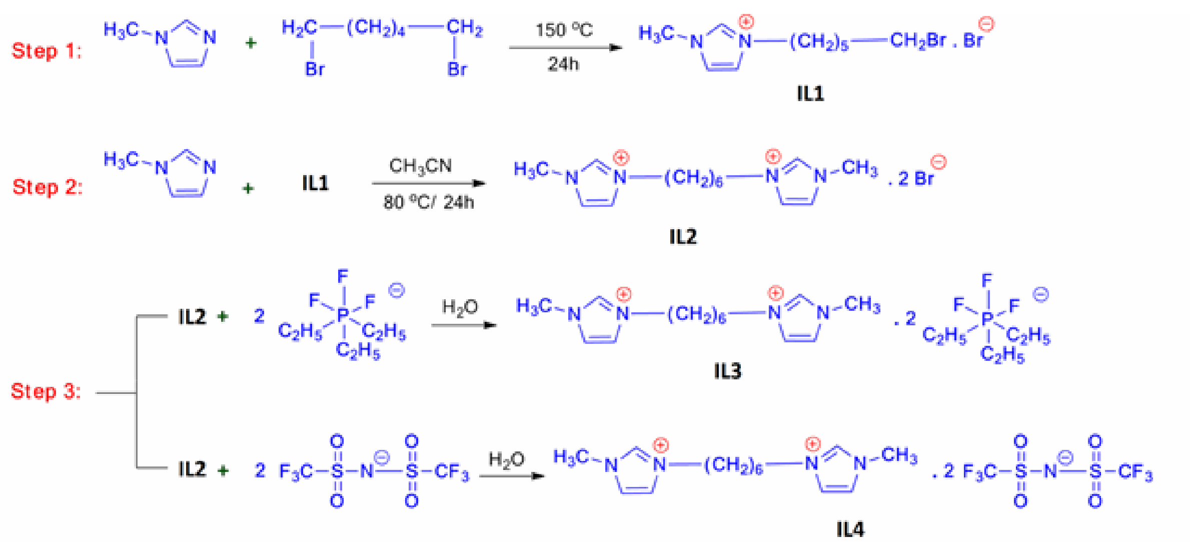

Fig. 1. The overall synthetic procedure for the preparation of IL3 and IL4.

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2.2.2. Synthesis of (3, 3'-(1,6-Hexanediyl) Bis (1-methyl-1H-imidazol-3-ium) Tri Ethyl Tri Fluoro Phosphate) ([HMIM]FAP, IL3)

1,6-Dibromohexane (76.0 mmol, 18.3 g) was charged into a 50.0 mL three-necked round-bottom flask. Afterward, 1-methylimidazole (17.0 mmol, 1.42 g) was added dropwise to the vessel. The reaction mixture was heated at 150 °C for 24 h under N_2 atmosphere and then cooled to room temperature. The resulting white sediment (product) was washed with EtOAc (7.0 mL). The solid product was then solved in isopropyl alcohol: acetone mixture (5.0:15.0 V/V, 20 mL) with stirring. The solution was filtered off and the filtrate was kept in a refrigerator for 24 h. Finally, the solvents were evaporated under reduced pressure to obtain yellowish-white liquid product (88% yield) [21]. This product is abbreviated as IL1. The identification data of the IL1 were as follows: ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.47 (s, 1H, N-CH-N), 7.88 (s, 1H, CH, imidazolium ring), 7.79 (s, 1H, CH, imidazolium ring), 4.32 (t, 2H, N-CH_2), 3.85 (s, 3H, CH_3), 3.65 (t, 2H, CH_2-Br), 2.27 (m, 2H, -CH_2) ppm. FT IR (KBr pellet, cm^{-1}): 3442 (imidazole ring), 3145 (CH aromatic), 2936 (CH alkane), 1572 (C=C aromatic), 1465 (CH alkane), 1309 (C-N aromatic), 1169 (CH_2X alkyl halide), 622 (C-Br alkyl halide).

Then, 1-methylimidazole (5.0 mmol, 0.41 g) and IL1 (4.0 mmol, 1.24 g) were added to CH_3CN (10.0 mL) and the obtained mixture was heated at 80 °C under N_2 atmosphere for 24 h. The obtained yellow solid was filtered off and washed with cold CH_3CN (3 x 5.0 mL). Finally, the solvent was evaporated under reduced pressure. The resulting ionic liquid was obtained in high purity (86% yield) [21] and is abbreviated as IL2. The identification data of the IL2 was as follows: ^{1}H NMR (300 MHz, D_2O): δ 9.03 (s, 1H, N-CH-N), 8.69 (s, 1H, N-CH-N), 7.72 (d, 1H, imidazolium ring), 7.52 (s, 1H, imidazolium ring), 7.42 (d, 1H, imidazolium ring), 7.37 (d, 1H, imidazolium ring), 7.05 (m, 1H, CH=CH), 5.72 (dd, 1H, CH_2), 5.34 (dd, 1H, CH_2), 4.24 (m, 4H, 2CH_2), 3.79 (s, 6H, CH_3), 2.45 (quintet, 2H, CH_2) ppm. FT IR (KBr pellet, cm^{-1}): 3392 (imidazole ring), 3041 (CH aromatic), 1651 (C=C alkene), 1573 (C=C aromatic), 1458 (CH alkane), 1310 (C-N aromatic), 752 (CH alkane).

Afterwards, IL2 (10.0 mmol, 4.21 g) and potassium triethyltrifluorophosphate (47.0 mmol, 8.22 g) were added to distilled water (10.0 mL) in a 50.0 mL round-bottom flask. The reaction mixture was vigorously stirred at ambient temperature for 24 h. The solvent was then removed by evaporation at 70 °C under reduced pressure. Then, the residue was dissolved in CH_2Cl_2 (4.0 mL) and anhydrous $MgSO_4$ (1.2 g) was added and the obtained mixture stirred for one h to remove the remaining water in the product. After filtering of the mixture, the volatile part of the filtrate was removed under reduced pressure at 30 °C for 2 h to afford a light yellow viscous liquid (3,3'-(1,6-hexanediyl) bis (1-methyl-1H-imidazol-3-ium) triethyltrifluorophosphate) ([HMIM]FAP) in 92% yield [21]. This IL was abbreviated as IL3 and was the first ionic liquid used in gear oil experiments. The identification data of the IL3 were as follows: FT-IR (KBr pellet, cm^{-1}): 3122 (imidazole ring), 3145 (C-H aromatic), 2936 (CH alkane), 1640 (CH alkane), 1572 (C=C aromatic), 1309 (C-N aromatic), 1194 (-FAP).

2.2.3. Synthesis of (3, 3'-(1,6-Hexanediyl) Bis (1-Methyl-1H-Imidazol-3-Ium) bis (Tri Fluoro Methyl Sulfonyl) Amide ([HMIM]TFSA, IL4)

The synthesis of the IL4 was carried out in the same way as described for IL3, except that potassium bis(trifluoromethylsulfonyl)amide (20 mmol, 5.52 g) was used instead of potassium triethyltrifluorophosphate in the last step of its synthesis. The obtained product was a yellow liquid in 90% yield and high purity [21].

The identification data of the IL4 was as follows: FT IR (KBr pellet, cm^{-1}): 3442 (imidazole ring), 3145 (CH aromatic), 2936 (CH alkane), 1572 (C=C aromatic), 1465 (CH alkane), 1309 (C-N aromatic), 1180 (-SO_2), 1269 (-CF_3). This IL was named as IL4 and was the second ionic liquid used in gear oils preparation.

2.3. Preparation of Multi-Grade Gearbox Oils

The prepared ILs were used for the preparation of two grades of gear oil, i.e., 75W80 and 75W90 (API category, GL-5). The oil components include base oil, silicone antifoaming additive (10 mg/kg), pour point depressant (polymethyl methacrylate polymer), AW/EP package additive, and viscosity index improver polymer (polymethyl methacrylate) [24]. Table 2 shows the abbreviation and types of

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the six multi-grade gear oils formulated using ILs or HITEC 343. The oils prepared with HITEC 343, as AW/EP package additive, were named HIW80 and HIW90, respectively. They were considered as standard (base) formulations and the performance of IL containing formulations was compared with them. All the components of IL containing oils (including additives and base oils) were the same as standard formulations, except that commercial AW/EP additive (HITEC 343) was replaced with ILs. The treat level of ILs in the new formulations was equal to the recommended dosage of commercial anti-wear and EP additive package, HITEC 343 (i.e. 4.4 %wt.). The oils containing IL3 as AW/EP additive were named IL3W80 and IL3W90, respectively. Also, oils containing IL4 were named IL4W80 and IL4W90, respectively.

Table 2. Abbreviations of multi-grade gear oils preparation with the prepared ILs and commercially available antiwear and EP additive HITEC 343.

Type of Additive	75w80 grade	75w90 grade
IL3	IL3W80	IL3W90
IL4	IL4W80	IL4W90
HITEC 343	HIW80	HIW90

For the preparation of oils, additive and base oils were charged into a 1.0 L beaker and blended for 1 h at 75 °C to form a homogeneous mixture. Viscoplex 0-223 additive (Evonik, Germany) was used as VI Improver to adjust the viscosity. Viscoplex 1-256 additive (Evonik, Germany) was used as a pour point depressant additive at the treat level of 0.5 weight percent (%wt.). The 1000 ppm stock emulsions of silicone defoamer prepared in the base oils was used. The defoamer stock emulsions were vigorously shaken each time before use.

3. RESULTS AND DISCUSSION

3.1. Identification of the Prepared ILs

The key identification data of ILs at different steps of synthesis are given in the experiential section. The FTIR spectra of the prepared ILs showed the presence of an imidazole ring in the region of 3442-3122 cm^{-1}. The peak at 1572 cm^{-1} is associated with C=C stretching vibration of the heterocyclic ring. Furthermore, an absorption band at 1310 cm^{-1} is related to C-N vibrational mode. Moreover, the peak appearing in 3145 cm^{-1} corresponded to the C-H bond. On the other hand, the absorption bands at 1194 and 1269 cm^{-1} were assigned to -FAP and -CF_3 anions. All the identification data and spectra (FT-IR and ^1H NMR) of the prepared ILs have been provided in the supplementary data included.

3.2. Wear and Load Carrying Capacity Study

To study the tribological properties of the prepared ILs, they were used at various treat rates in grade 4 base oil (Table 1) and tested by four-ball (ASTM D2596), TIMKEN (ASTM D2782), and FZG (ASTM D5182) tests to explore tribological properties of oils at different temperatures. A Four-ball test was used for the evaluation of tribological properties at room temperature (25 °C). TIMKEN test was used for evaluation of tribological properties at 37 °C, while the FZG test was used for evaluation of tribological properties at 90 °C. All these tests provided a thorough investigation of tribological properties of the prepared ILs over a wide temperature range and a comparison was made with the commercially available additive (HITEC 343). Table 3 shows the measured tribological parameters including weld points, wear scar diameter, Timken OK load, and FZG load stages for lubricants containing prepared ILs or HITEC 343.

The four-ball test rig was used for evaluating of the antiwear and EP (AW/EP) properties of the prepared ILs at room temperature (25 °C). The tester was operated with one steel ball under load rotating against three steel balls held stationary in the form of a cradle. The rotating speed was 1770 ± 60 rpm. Lubricants were brought to 27 ± 8 °C (80 ± 15 °F) and then subjected to a series of tests of 10 seconds duration at increasing loads until welding occurred. The higher load that welding occurs indicates the higher load-carrying capacity of the lubricant. According to data provided in Table 3, the weld point of the lubricated balls by virgin base oil was equal to 80 kg, while the 3.0 %wt. addition of ILs increased the weld point to 160 kg. Furthermore, 4.4 %wt. addition of HITEC 343 and IL3 increased the weld point to 200 kg. Interestingly, the 4.4 %wt. treat level of IL4 increased the weld point to 250 kg. This indicates better performance of IL4 compared to IL3 and HITEC

343. As can be seen in Table 3, increasing the treat level of IL4 to 5.0 %wt. did not result in higher weld points. This is probably because of the saturation of the ball surface, which provides a site for film-forming by additive molecules and consequently enhances the load-carrying capacity of the lubricant by boundary lubrication.

For measuring of wear scar diameter, the 40 kg load was applied for one h at 1770 ± 60 rpm, then the average wear diameter (mm) of three fixed balls were measured using a micrometer equipped with a microscope. All of the gear oils preparation using the prepared ILs or HITEC 343 showed a considerable reduction in wear compared to base oil with no additives. As can be observed in Table 3, 3.0 %wt. treat rate of IL3 and IL4 resulted in a two-fold decrease in the wear diameter. When the treat rate is 4.4 %wt., the wear diameter of balls lubricated by IL3 and HITEC 343 containing oil was approximately the same. However, the wear diameter of the balls lubricated by IL4 containing oil is smaller than the wear diameter of balls lubricated with IL3 and HITEC 343. This observation indicated that IL4 acts as better wear inhibiting oil additive. The higher treat rate (5.0 %wt.) of IL4 doesn't induce smaller wear diameter on the stationary balls, indicating that the optimum treat level is 4.4 %wt. This phenomenon can be related to saturation of the film-forming in the lubricated surface after a 4.4 %wt. treat level and the hence negligible effect of the extra IL on the tribological properties.

Timken test was used for the determination of load-carrying capacity at 37.5 °C. The tester was operated with a steel test cup rotating against a steel test block. The rotating speed was 123.71 ± 0.77 m/min which is equivalent to a spindle speed of 800 ± 65 rpm. Fluid samples were preheated to 37.8 ± 2.8 °C before starting the test. The maximum load at which the rotating cup will not rupture the lubricant film and cause scoring or seizure between the rotating cup and the stationary block is called OK value. The 3.0 %wt. of IL3 and IL4 increased the Timken OK value more than two-fold. The 4.4 %wt. use of IL3 and IL4 imparted better performance compared to the performance of the 4.4 %wt. treat rate of HITEC 343. The results of the Timken OK load followed the same trend as the four-ball test. As observed in the four-ball load-carrying capacity test, increasing the IL4 dosage to 5.0 %wt. did not add extra EP property to the gear oil. This observation can be related to the saturation of film-forming.

The enhanced load carrying capacity of IL4 in comparison to IL3 can be contributed to the anions used for these ILs, as the cations of these two ILs are the same and hence impart equal properties to the oil. The anion of IL4 has sulfur and nitrogen in its structure, which can bind to the surface and form a film, which leads to enhanced boundary lubrication [6]. Although the anion of IL3 has phosphorous that can bind to the lubricated surfaces and improve EP properties, it is associated with ethyl and fluorine that makes film-forming less probable because of the spatial interference. The anion in the IL3 has a friction modifying effect with weak EP/AW properties, but the anion of the IL4 acts as a friction modifier and EP/AW to the oil [6].

To study the effectiveness of the lubricants in high temperatures (90 °C), FZG (Forschungstelle für Záhnräder und Getriebebau) test method was used. The FZG visual method is used to measure the scuffing load capacity of oils used to lubricate hardened steel gears. Scoring, a form of abrasive wear is also included as failure criteria in this test method. An FZG gear test machine was operated at a constant speed (1450 rpm) for a fixed period (21700 revolutions, approximately 15 min) at successively increasing loads until the failure criteria was reached. The test gears were examined initially and after the prescribed duration at each load stage for cumulative damage (scuffing) to the gear tooth flanks. High EP type oils such as those oils meeting the requirements of API GL-4 and GL-5 generally exceed the capacity of the test rig. Therefore, they cannot be differentiated with this test method. However, FZG was used in this study as a complementary tool to evaluate the load-carrying capacity of understudy oils at high temperatures (90 °C). As can be observed from Table 3, all of the oils containing ILs or HITEC 343 pass the load stage 12, which demonstrates efficient load-carrying capacity at high temperatures.

From the results of the four-ball test, Timken as well as FZG, it was concluded that IL4 provides better tribological performance characteristics compared to HITEC 343 and IL3. It was also concluded that the prepared ILs are efficient at low and high temperatures.

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Table 3. The performance characteristics of the prepared ILs as antiwear and EP additive in gear oil formulations.

Materials	Four-ball weld load (kg)	Four-ball Wear diameter (mm)	Timken OK Value (lb)	FZG test
Base oil	80	4.5	12.8	7
3.0 %wt. IL3	160	0.24	26.1	>12
3.0 %wt. IL4	160	0.22	24.1	>12
4.4 %wt. IL3	200	0.11	31.1	>12
4.4 % wt. IL4	250	0.08	36.2	>12
4.4 %wt. HITEC 343	200	0.13	27.1	>12
5.0 %wt. IL4	250	0.10	36.4	>12

3.2.1. SEM Analysis

For further investigation, the surface of the damaged balls after four-ball wear tests was evaluated by the SEM imaging and EPS analysis. Fig. 1 shows the SEM images of the damaged surfaces of lubricated balls after four-ball wear tests. Fig. 1(a) shows the scar on the base oil-lubricated balls. The severe and deep grooves and wear on the ball surfaces show insufficient lubrication. On the other hand, Fig. 1(b) shows the surface of the balls lubricated with 3.0 %wt. of IL3. A considerable reduction in wear can be seen on the ball surfaces in comparison to the base oil. Moreover, Fig. 1(c) shows the wear of the balls lubricated with oil containing 3.0 %wt. of IL4. In comparison with Fig. 1(b), the depth of the groove is lower in Fig. 1(c), which demonstrates that IL4 imparts better tribological properties than IL3. Also, Fig. 4 (d) shows the wear on the balls lubricated with 4.4 %wt. of IL3. Furthermore, Fig. 4 (e) shows the wear behavior of lubricant containing 4.4 %wt. of IL4. At 4.4 %wt. treat level, the balls lubricated with IL3 have acquired relatively larger wear scars with more dense grooves than those lubricated with IL4. The wear scars generated by the IL4 additive exhibited smaller diameter scars with less dominant abrasion grooves. On the other hand, Fig. 1 (f) shows the wear scar on the balls lubricated with commercially available additive, HITEC 343. As can be seen, the density of grooves and their depth and pattern is approximately similar to IL3. These observations once again demonstrate that IL4 additive was the most effective in improving the tribological properties, providing the highest protection, while the performance of IL3 was equal to HITEC 343.

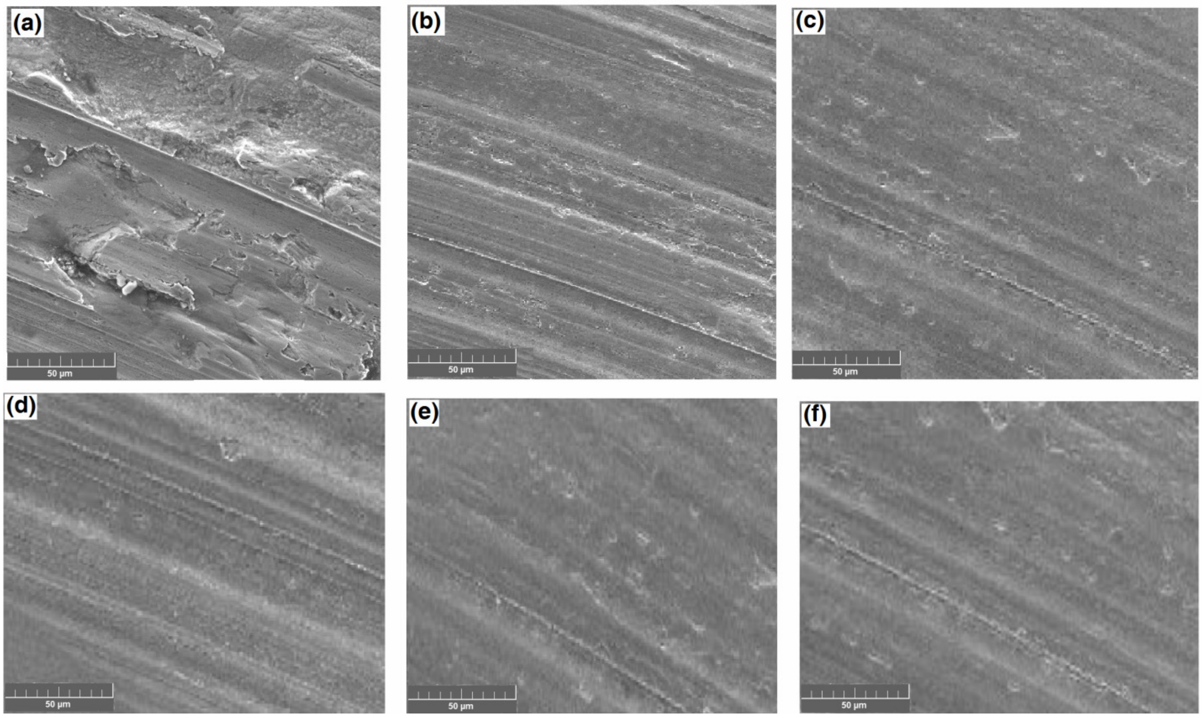

Fig. 2. The SEM images of the lubricated balls with different fabricated oils after the four-ball test: (a) Base oil, (b) 3.0 %wt. IL3, (c) 3.0 %wt. IL4, (d) 4.4 %wt. IL3, (e) 4.4 %wt. IL4, and (f) 4.4 %wt. HITEC 343.

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3.2.2. EDS Analysis

Energy-dispersive X-ray analysis (EDS or EDAX), is a well-known experiment which is used to identify the elemental composition of the surface of materials. After the four-ball wear test, the damaged balls impregnated with lubricant were studied by EDS. The balls were of the type AISI 5200 steel which is composed of the Fe (96.5-97.3%), Cr (1.3-1.6%), C (0.98-1.10%), Mn (0.25-0.45%), Si (0.15-0.30%), S ($\leq$ 0.025%) and P ($\leq$ 0.025%). The changes in concentration of these elements in the spectra can be a reliable indicator of the wear in damaged balls. Fig. 2 shows the EDS spectra of the balls after four-ball wear test when they were lubricated with ILs or HITEC 343 containing oils. The percentages of the Fe and Cr in the steel compositing were pretty high. Therefore, evaluating the wear by tracking the concentration changes of these elements in damaged balls is not a precise indicator of the amount of wear and role of different lubricants, as is shown in Fig. 2. Instead, the changes in the concentration of carbon can be a reliable indicator in this context. As can be seen in Fig 2 (a), the balls lubricated with virgin base oils show high content of carbon, while the balls lubricated with ILs or HITEC 343, showed considerable carbon (C) percentage reduction. It can be concluded from Fig. 2 that in the presence of prepared ILs, the amount of the abrasion on the ball surface reduces considerably. The same conclusion can be made about the HITEC 343 containing oil.

4. ELEMENTAL ANALYSIS

Table 4 shows the elemental composition of the oil formulations measured by ICP-OES according to ASTM D5185. Elemental analysis is of great importance for the condition monitoring of the machine. It can also provide insight on the presence of elements harmful to the environment, as are of high concern in the environmental regulations. Most of the AW/EP and friction modifying additives contain Mo, P, S, and Zn which are under environmental restrictions. Fortunately, the oils containing prepared ILs are free from any of the aforementioned toxic elements, except for IL4 which contains sulfur in its anion moiety. Indeed, some portion of the sulfur (approximately 100 ppm) existing in oils is related to its presence in the base oil. Other environmentally harmful elements such as Pb, Ba, and Mo are absolutely absent in lubricants containing ILs. Since the prepared ILs increase the desired lubrication properties of the base oil without using any toxic elements, therefore making them environmentally friendly compared to their commercial counterparts. This advantage combined with ILs' biodegradability allows considering them as green lubricants.

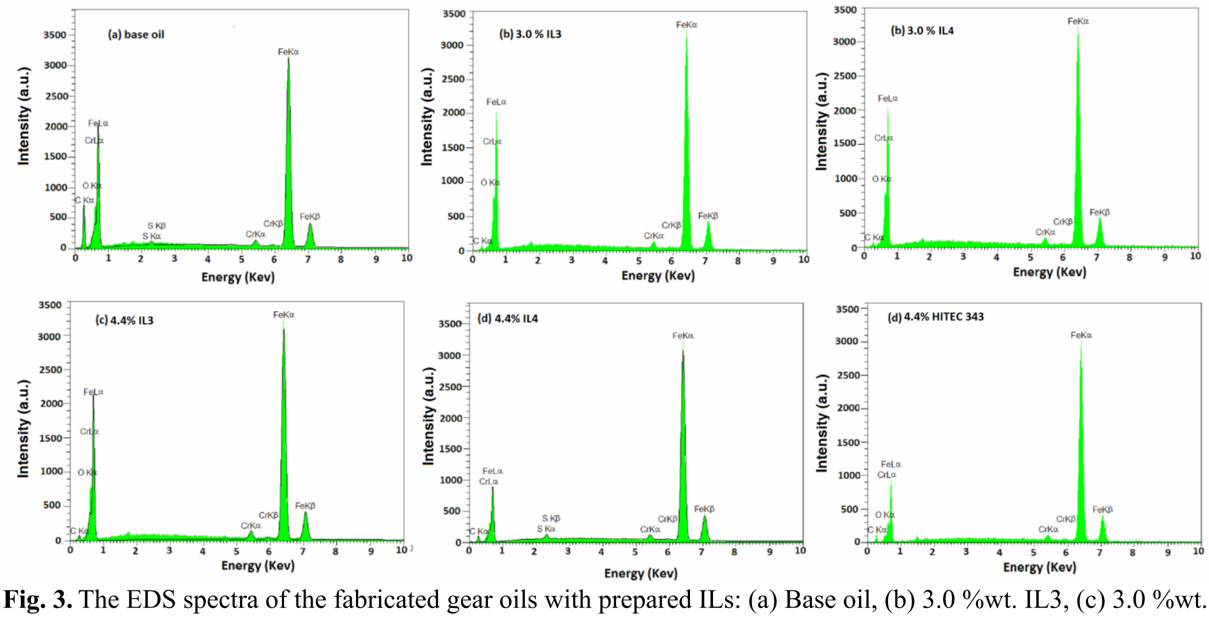

Fig. 3. The EDS spectra of the fabricated gear oils with prepared ILs: (a) Base oil, (b) 3.0 %wt. IL3, (c) 3.0 %wt. IL4, (d) 4.4 %wt. IL3, (e) 4.4 %wt. IL4, and (e) 4.4 %wt. HITEC 343.

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Table 4. Elemental composition of gear oils preparation according to ADSTM D5185

Element (ppm)	Base oil	4.4 %wt. IL3	4.4 %wt. IL4	4.4% HITEC 343
Fe	0	0	0	0
Cr	0	0	0	0
Al	0	0	0	0
Cu	0	0	0	0
Pb	0	0	0	0
Sn	0	0	0	0
Ni	0	0	0	0
Ti	0	0	0	0
Ag	0	0	0	0
Mo	0	0	0	0
Zn	0	0	0	316
P	0	246	0	251
Ca	0	0	0	0
Ba	0	0	0	0
Mn	0	0	0	0
Mg	0	0	0	0
Si	0	0	0	0
Na	0	0	0	0
B	0	0	0	0
V	0	0	0	0
K	0	21	0	0
Sulfur	96	102	289	416

4.1. Other Lubrication Properties

In previous sections, it was approved that the prepared ILs impart tribological properties more than or equal to HITEC 343 to the base oil. Also, it was demonstrated by ICP-OES elemental analysis that toxic and heavy metals are absent in the ILs, which marks them as potential green lubricants. In this section, to further explore the lubrication performance of the introduced ILs, the prepared IL containing oils were used in multi-grade GL-5 gear oils to see whether they can be used as an alternative to HITEC 343. Table 5 shows the physical and chemical characteristics of multi-grade gear oils described in section 2.3. The physical and chemical properties of the oils were evaluated according to internationally recognized gear oil standard specifications, i.e., MIL-L-2105 D, SAE J306, and DIN 51517-part 3 specifications.

The total acid number (TAN) was measured according to the ASTM D664 test procedure. This method is applicable for the determination of acids whose dissociation constants are larger than 10^{-9} $mole.L^{-1}$. This parameter must be minimum in oil, because the higher the TAN number, the formation of acidic products is more probable which may lead to machine failure. As can be seen, the addition of the introduced ILs to lubricant doesn't lead to a considerable acidity increase in acidity value of oil and hence the formation of acid products is less probable. On the other hand, the addition of HITEC 343 causes a much higher acidity increase in comparison to ILs.

On the other hand, the foam tests were measured according to ASTM D 892. This test method covers the determination of the foaming characteristics of lubricating oils at 24 and 93.5 $^{\circ}$C. The tendency of oils to form foam can be a serious problem in systems such as high-speed gearing, high-volume pumping, and splash lubrication. Indeed, inadequate lubrication, cavitation, and overflow loss of lubricant can lead to mechanical failure. Hence, this test method is used for the evaluation of oils for such operating conditions. Since ILs are surfactant like chemicals, and it is known that surfactants cause foaming in the lubricants [25], it was

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important to check the foaming of IL containing oils. As can be seen, the foaming tendency of IL containing oils was negligible and comparable to that of HITEC 343. This observation demonstrates that prepared ILs don't induce foaming.

Furthermore, the resistance against the corrosion of copper slabs in the oils was measured according to the ASTM D130 test procedure. In this procedure, a polished copper strip is immersed in a specific volume of the samples being tested and heated for 3 h at 100 °C. Finally, the color and tarnish levels of the strips is assessed against the ASTM Copper Strip Corrosion Standard. Table 5 shows the corrosion levels of copper slabs meanwhile Fig. 3(a) shows their appearance. As can be seen, the highest level of corrosion was observed for copper strips immersed into the base oil. Interestingly, the slabs were almost intact in the IL containing oils. On the other hand, the level of corrosion in HITEC 343 containing oils is less than virgin base oils, but more corrosion can be observed in comparison to IL containing oils. These observations demonstrate that ILs act as excellent corrosion inhibitors. In fact, the corrosion inhibition can be attributed to the presence of the heteroaromatic imidazole moiety in the structure of the ILs, which acts as a corrosion inhibitor [6].

Moreover, the rust preventive characteristics of the oils in the presence of distilled water were measured by the ASTM D665 test procedure. In many cases such as in gear systems, the water can be mixed with lubricant, and rusting of ferrous parts can occur. This test indicates how well inhibited mineral oils aid in preventing this type of rust. Fig. 3(b) shows the appearance of the test specimens in presence of oils containing ILs or HITEC 343. As can be seen, the test specimen immersed into the base oil has shown severe rusting. Interestingly, the immersion of the test specimens into IL containing oils has effectively prevented rusting as shown in Fig. 3(b). On the other hand, the immersion of test specimens into HITEC 343 containing oils has prevented rusting less than IL containing oils. These observations demonstrated that the prepared ILs impart excellent rust preventive properties to the base oil.

Also, the shear stability of oils was measured according to ASTM D7109 test procedure. This test method evaluates the percent viscosity loss of fluids resulting from the physical degradation of their consisting polymers in the high shear nozzle device. A polymer-containing fluid is passed through a diesel injector nozzle at a shear rate that may reduce its kinematic viscosity. The percent viscosity loss is a measure of the mechanical shear stability of the fluid. The shear stability of all oils is more or less than the base oil, demonstrating that ILs do not induce change shear stability of oils.

Furthermore, the water separability of the formulated lubricants was measured according to ASTM D1401 test procedure. This test method covers the measurements of the ability of petroleum or synthetic fluids to be separated from water and is specifically designed for lubricants that come into contact with water during operation. This method provides a guide for the determination of the demulsibility characteristic properties of lubricating oils that are prone to water contamination. Hence, such oils may encounter the turbulence of pumping and circulation capable of producing water in oil emulsions. In this procedure, a test specimen consisting of a 40 ml sample, 40 ml quantity of distilled water was stirred for 5 min in a graduated cylinder at 54 °C. The time required for separation or emulsion reduction to 3 mL or less was recorded. As can be seen from Table 1, complete separation of virgin base oil happens after five minutes, while this time for IL3, IL4, or HITEC 343 containing oils are 3, 3, and 14 minutes, respectively. The considerable decrease in water separability of oil in the presence of ILs demonstrates that they also act as efficient demulsifiers in the lubricant [26]. The time for water separability increases in the case of using HITEC 343 in the gear oils.

The measured tribological parameters including four ball welding points, FZG load stages, and Timken OK loads of the oils were in accordance to Table 3. As concluded before, the tribological tests demonstrated that IL4 shows better EP and anti-wear protection in comparison to IL3 and HITEC 343.

Other quality parameters including the kinematic viscosities, viscosity index (VI), low-temperature apparent viscosity, flash point, and pour point of all fabricated oils were in the range recommended by gear oil standard specifications.

Investigating the physical, chemical and

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tribological properties of oils showed significant improvement in the properties of the IL containing gearbox oils in comparison to the commercial additives.

Table 5. Physical and chemical properties of the fabricated gear oils.

Characteristics		IL3W80	IL4W80	IL3W90	IL4W90	HIW80	HIW90
Kin. vis. (100˚C)		7.69	7.82	14.52	14.60	8	14.58
Kin. vis. (40 ˚C)		37.88	38	67.67	68	40	68.6
Viscosity Index		178	178	170	171	175	170
Flash point (˚C)		200	202	210	212	190	204
Pour point (˚C)		-39	-39	-39	-39	-39	-39
TAN, mg KOH/g sample		0.15	0.18	0.12	0.21	1.15	1.23
Dynamic Vis -40 ˚C (Brookfield)		30000	35000	60000	62000	32000	65000
	Seq. I	10/0	10/0	10/0	10/0	30/0	20/0
Foam tendency	Seq. II	10/0	20/0	10/0	20/0	30/0	30/0
	Seq. III	10/0	10/0	10/0	20/0	50/0	30/0
Four ball weld point		200	250	200	250	200	200
TIMKEN OK load		31.1	36.2	31.1	36.2	27.1	27.1
FZG load stage		>12	>12	>12	>12	>12	>12
Water separability (min)		8	3	3	3	14	14
Rust test		Pass	Pass	Pass	Pass	Fail	Fail
Copper corrosion test		1a	1a	1a	1a	1b	1b
Shear stability (wt. %)		10	9	8.7	9	11	8.12

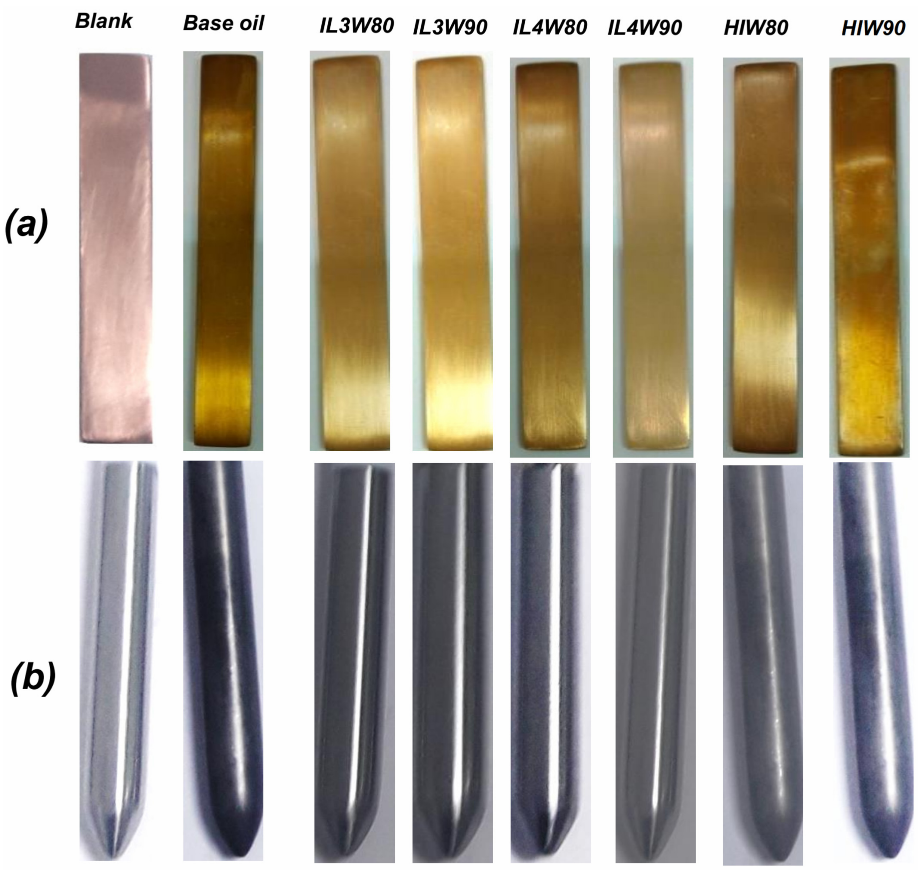

Fig. 4. The visual status of (a) copper strips before and after immersion into the fabricated oils (ASTM D130, 3h, 100 ˚C) and (b) rust test standard slabs (ASTM D 665, Method A) before and after rust testing.

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5. CONCLUSION

In this study, two novel ionic liquids (ILs) including [HMIM] TFSA and [HMIM] FAP were prepared from commercially available substrates and properly identified by spectroscopic methods. The prepared ILs were used in gear oil formulations and their tribological properties were examined thoroughly using four-ball as well as Timken tests in a wide range of temperatures. The SEM-EDS analysis demonstrated the effective lubrication role of the prepared ILs in comparison to the commercial additives. [HMIM] TFSA showed better tribological properties than [HMIM] FAP and HITEC 343, which had similar performance levels. In addition to favorable tribological characteristics, the ILs containing oils demonstrated corrosion resistance, rust resistance, water separability, and minimum foaming. All these properties led us to the conclusion, that the introduced ILs can be regarded as multifunctional and multipurpose single component package additives. A comparison of the lubrication mechanism between [HMIM] TFSA and [HMIM] FAP confirmed that [HMIM] TFSA (IL4) had slightly better tribological properties under boundary lubrication conditions. Also, due to avoiding the use of toxic and harmful elements in the preparation of ILs make the fabricated oils potential candidates for green lubricants.

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