Tribol Lett (2010) 40:279–284
DOI 10.1007/s11249-010-9695-0

ORIGINAL PAPER

Transition in Wear Performance for Ionic Liquid Lubricants under Increasing Load

Anthony E. Somers · Patrick C. Howlett · J. Sun · Douglas R. MacFarlane · Maria Forsyth

Received: 21 June 2010 / Accepted: 8 September 2010 / Published online: 21 September 2010

Abstract The effect of ionic liquid (IL) lubrication for aluminium/steel systems is highly dependant on the applied load and the IL structure. This study illustrates that a change in anion of an IL lubricant results in different physicochemical properties that will alter its performance at a given load. As the load is increased there is a shift in lubricant performance and mechanism of the IL. Up to a load of 30 N the lowest wear coefficient was achieved by a phosphonium diphenylphosphate IL, whilst above 30 N a phosphonium bis(trifluoromethanesulfonyl)amide IL was able to form a more tenacious tribolayer that resulted in the lowest wear.

Keywords Boundary lubrication · Tribofilms · Ionic liquids · Friction · Wear · Surface interactions · Wear mechanisms

1 Introduction

The use of aluminium alloys in areas such as the automotive industry, aviation and space technology is increasing due to their high strength to weight ratio, corrosion resistance and high thermal conductivity [1–3]. Unfortunately, the tribological performance of aluminium and its alloys is considered to be poor [2, 4]. In particular, when steel and aluminium alloys come into contact high wear and seizing is likely to occur. This means that care must be taken to ensure the two alloys do not come into contact; for instance in diesel truck engines, aluminium blocks are being used to reduce weight, however, the cylinders must be lined to ensure the steel piston is not in contact with the aluminium alloy of the block [3]. These linings add considerable expense and complexity to the process. It would be advantageous for certain applications if suitable lubricants were developed such that steel could move in contact with aluminium without causing excessive wear.

The main requirement for a lubricant is to maintain a separation between moving parts to minimise wear and friction. At low loads, the lubricant forms a fluid film between the moving parts that reduces wear and friction. In this low load regime, the viscosity of the lubricant determines the amount of separation between the parts. At increased loads, the moving parts begin to come into contact with each other as the lubricant is squeezed out from between them [5]. When the moving parts begin to come into contact it has been shown that oil additives with long polar molecules, that bond to the surface of the moving parts, work well to reduce friction and wear [6, 7]. At higher contact pressures, where material contact increases, extreme pressure additives in oils, such as zinc-dialkyl-dithiophosphate (ZDDP) for steels, are thought to break down, as a result of the pressure. The breakdown products can then react with the metal surface to form low friction layers, called extreme pressure (EP) layers, which reduce wear and friction [8]. ZDDP has been shown to be incompatible with aluminium alloys and a viable alternative is yet to be found [8, 9].

Room Temperature Ionic Liquids (ILs) are salts that are liquid at or near room temperature. These materials have

A. E. Somers · P. C. Howlett · J. Sun · M. Forsyth (✉)
Department of Materials Engineering, Monash University, Wellington Rd, Clayton, Victoria 3800, Australia
e-mail: maria.forsyth@eng.monash.edu.au

P. C. Howlett · J. Sun · D. R. MacFarlane
School of Chemistry, Monash University, Wellington Rd, Clayton, Victoria 3800, Australia

been investigated for their use as environmentally benign solvents, electrolytes for devices (such as batteries, fuel cells and solar cells), lubricants and anti-corrosion coatings [10–12]. The specific properties of ILs that make them suitable as prospective lubricants are their low volatility, so that they can be used in reduced pressure applications and their non-flammability and thermal stability, meaning that they will be able to safely withstand increased temperatures involved when there is high friction. One of the main attractions of ILs is the variety of molecules that can be used; one estimate is that there is something in the order of a million combinations available, each with its own unique properties [13]. This means that ILs are highly tuneable for a particular application. For lubrication, current research is aimed at identifying those ILs that will improve the wear performance of various systems, including aluminium in contact with steel. For the steel–aluminium system, researchers have investigated RTILs with various cations, such as imidazoliums, pyridiniums, ammoniums and phosphoniums, and various anions, such as tetrafluoroborate, hexafluorophosphate, triflate, tosylate and bis(trifluoromethanesulfonyl)amide (NTf_2) [2, 12, 14–17].

In this study, the wear performance in a pin-on-disc test of ILs with a trihexyl(tetradecyl)phosphonium cation ($P_{66614}{}^+$) and two different anions will be investigated at loads of 1–40 N. The anions are the phosphorus-containing diphenyl-phosphate (DPP) and the fluorine-containing NTf_2. Whilst Minami et al. [18] have recently tested a number of tetraalkylphosphoniums with the NTf_2 anion as lubricants for steel on steel contact, their performance for lubricating steel on aluminium is yet to be investigated. The system studied here uses a 100Cr6 steel ball on an AA2024 aluminium disc in a rotating pin-on-disc test.

2 Experimental

The ionic liquids investigated in this study are shown below in Fig. 1. The synthesis and characterisation of the IL with the DPP anion are detailed elsewhere [19], whilst Cytec Canada Inc. supplied the NTf_2 anion-based IL. A fully formulated 15W-50 diesel engine oil was also tested for comparison. Table 1 shows the viscosity of the ILs and the oil at 40 °C, which were measured using an AMVn Automated Microviscometer. The wear tests were conducted at room temperature (22 °C) on a Nanovea pin-on-disc tester according to ASTM G99 using 6-mm 100Cr6 balls on 45-mm diameter AA2024 aluminium discs. Results were obtained from an average of three tests. The composition, Vickers hardness and average roughness, R_a, of the steel balls and aluminium discs are shown in Table 2. The supplier provided the composition, hardness and roughness of the steel balls. The supplier also provided the composition of the aluminium discs, whilst the hardness was determined using a Wolpert Wilson 452SVD Vickers Hardness tester with a 30 N load, and the roughness was measured using a Dektak 150 stylus profilometer. The discs were lubricated with 0.1 ml of lubricant. Experiments were conducted at loads of 1, 2, 5, 10, 20, 30 and 40 N for a distance of 2500 m, with a wear track diameter of 20 mm and a speed of 0.2 m/s. The coefficient-of-friction was recorded throughout the experiment. On completion of the wear tests, the wear depth was measured using the Dektak 150 stylus profilometer.

Optical micrographs of the wear scars were taken using a Leica MZ6 stereomicroscope. For more detailed analysis of the worn surface, SEM and EDS were undertaken using a JEOL JSM-840A scanning electron microscope.

Fig. 1 Molecular structures of Ionic liquids used in this study

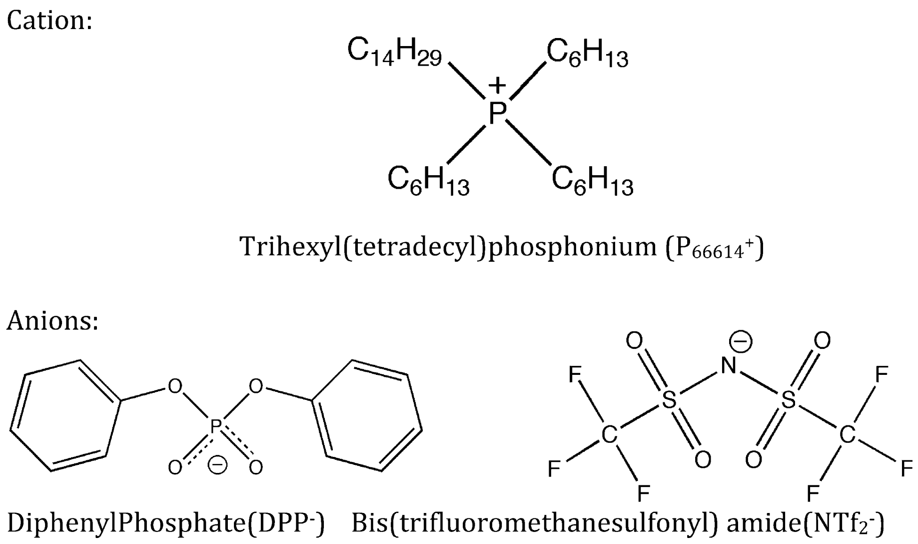


Table 1 Viscosities of lubricants tested at 40°C

Lubricant	Viscosity at 40 °C (mPa s)
P_{66614}NTf2	140
P_{66614}DPP	210
15W-50 oil	130

Table 2 Composition, hardness and roughness of alloys tested

Elemental composition (wt%)	Alloy	
	AA2024	100Cr6
C	–	0.98–1.10
Cu	3.8–4.9	–
Si	0.5 max	0.15–0.3
Mn	0.3–0.9	0.25–0.45
Mg	1.2–1.8	–
Cr	0.1 max	1.3–1.6
Zn	0.25 max	
Ti	0.15 max	
S	–	0.025 max
P	–	0.025 max
Others	0.15 max	–
Fe	0.5 max	Balance
Al	Balance	–
Hardness (Vickers)	145	850
R_a (μm)	0.09	0.05 max

3 Results and Discussion

3.1 Wear Tests

The average coefficient-of-friction for the pin-on-disc experiments is shown in Fig. 2a. For the lubricant with an NTf_2 anion, the friction traces used to calculate these averages were stable throughout the test from 1 to 20 N, with some short peaks occurring at the 30 and 40 N loads (For example see Fig. 3). For the DPP-based IL, the friction traces were stable from 1 to 30 N; however, at the 40 N load, the friction had a short peak, followed by a sharp increase in friction that did not recover (See Fig. 3) resulting in termination of this test. When the friction and wear becomes this extensive the lubricant is considered to have failed and the test is stopped. At each of the loads tested the $P_{66614}NTf_2$ had a slightly lower average coefficient-of-friction than the P_{66614}DPP lubricant. Both ILs had much lower coefficients-of-friction than the standard 15W-50 diesel engine oil. For all lubricants there is a shift from a low coefficient-of-friction at 1 N to a higher coefficient-of-friction at 10 N that remains relatively stable to the higher loads. This may be due to a change in lubrication regime from the hydrodynamic regime at low loads, where a lubricant film supports the load, through a elastohydrodynamic region, where metal asperities begin to come in contact, until, at high loads there is increased

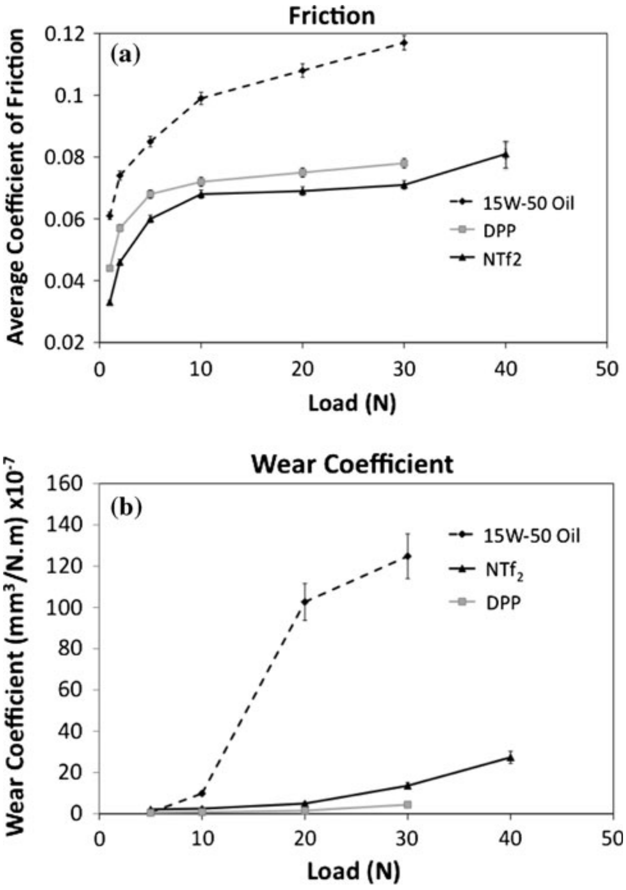


Fig. 2 **a** Average coefficient-of-friction and **b** wear coefficient as a function of load for 100Cr6 steel against AA2024 aluminium lubricated by ILs

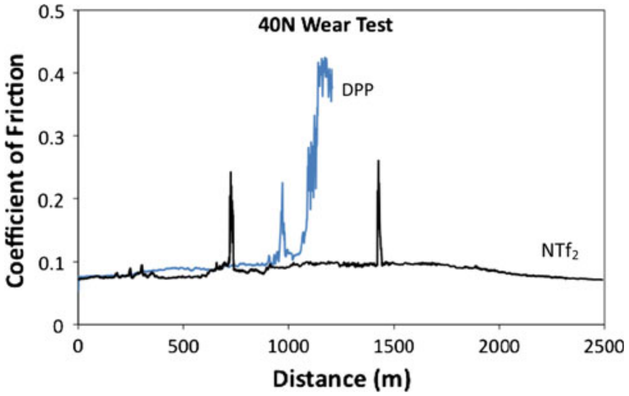


Fig. 3 Friction curves at a 40 N load for 100Cr6 steel against AA2024 aluminium lubricated by ILs

metal-on-metal contact, causing increased friction and resulting in the formation of boundary layers [6]. Since the lowest load available was 1 N, it is difficult to tell if the coefficient-of-friction could be further reduced, so even the initial wear condition undertaken here may be borderline in the elastohydrodynamic region. To assist in the determination of wear regime, minimum film thickness calculations were carried out for the test conditions as described above. These calculations used the equation from Hamrock and Dowson [5, 20] to calculate the film thickness:

$$H_{\min} = \frac{h_{\min}}{R_x} = 3.63U^{0.68}\, G^{0.49}\, W^{-0.073}\left(1 - e^{-0.068k}\right) \qquad (1)$$

One of the parameters required to calculate this property is the pressure viscosity coefficient, which is determined from pressure dependent viscosity measurements. As these measurements are not widely undertaken in the area of ILs, this calculation does not seem to be present in most reports of IL lubrication. However, in our study we have estimated this coefficient from data presented by Pensado et al. [21] and have estimated that the minimum film thickness, $h_{\min}$, ranges from 0.09 to 0.20 μm for the ILs tested at loads of 1–40 N. To take into account the effect of surface roughness the dimensionless film parameter, or Lambda ratio, a ratio of the film thickness, h, to the composite surface roughness of the contacting bodies, $\sum R_a$, was calculated [22]:

$$\Lambda = \frac{h}{\sum R_a} \qquad (2)$$

Values of Λ at or below unity are indicative of boundary lubrication. For the system tested the composite surface roughness was 0.12 μm, giving values of Λ of 0.75–1.67, indicating that initial wear regime at the loads of 1–40 N ranges from the mixed regime to the boundary regime [5].

The wear coefficients at each load, as shown in Fig. 2b for the two ILs and the engine oil, indicated a different trend than the average friction. The P_{66614}DPP lubricant showed considerably less wear than the $P_{66614}NTf_2$ lubricant at 5, 10, 20 and 30 N followed by a rapid increase in wear and friction at 40 N, as discussed above, such that the test was terminated. At loads of less than 5 N, wear depths were so low that they were not able to be distinguished from the surface roughness. The standard engine oil showed much higher wear than both ILs from 10–30 N, and was stopped after 1800 m at 40 N due to excessive wear. At 5 N, the engine oil's wear coefficient was similar to that of the IL's.

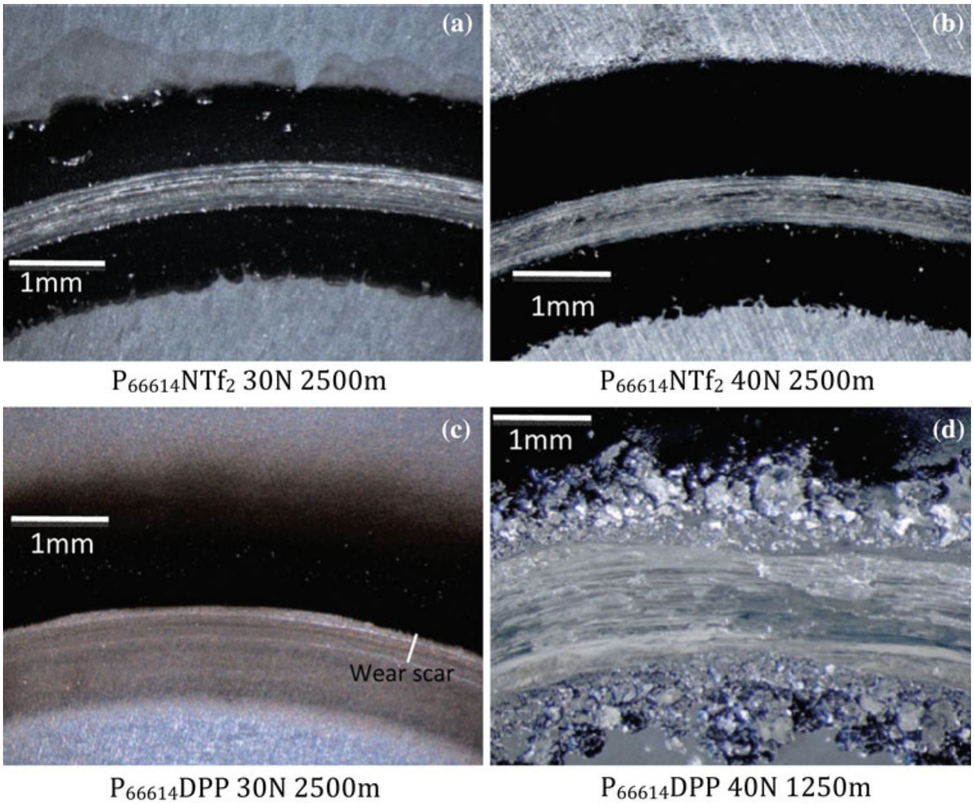
Figure 3 shows the complete friction trace at the 40 N load for the two ILs. As described above, the P_{66614}DPP lubricant showed a limited ability to recover once the coefficient-of-friction increased sharply. The $P_{66614}NTf_2$ lubricant, on the other hand, was able to recover from the spikes in friction, and in fact the coefficient-of-friction can be seen to be reducing towards the end of the test. It is proposed that these spikes in friction are due to large pieces of wear debris entering the wear scar and causing increased gouging of the aluminium alloy surface. For IL lubricants, it has been proposed that tribolayers form on the metal surfaces that lead to the reduced friction and wear exhibited [3, 16, 23]. For the $P_{66614}NTf_2$ lubricant it appears likely that the tribolayer formed is more able to withstand the large pieces of wear debris than the tribolayer formed by the P_{66614}DPP lubricant. This may be due to the tribolayer itself being more tenacious in the case of the $P_{66614}NTf_2$ lubricant, or it may be thicker than the tribolayer formed by the P_{66614}DPP lubricant.

The importance of the tribolayers may be accentuated in these experiments due to the use of large, 45-mm diameter 2024 aluminium discs with relatively small volumes of lubricant. As the test progressed the lubricant moved towards the outer surface of the disc, resulting in less lubricant in the wear path. Consequently, towards the end of the test, as the tribolayer is removed there is less lubricant available to reform this layer. This may explain the poorer performance of the IL lubricant with a DPP anion at 40 N as compared to that of the NTf_2-based lubricant.

4 Surface Analysis

The optical images in Fig. 4 show the change in performance of the DPP IL from 30 to 40 N. At 30 N, the wear scar for the system with the DPP IL lubricant is considerably smaller than that in the case of the NTf_2 IL and is marked on the figure with a white line to assist finding it. However, at 40 N the NTf_2 wear scar has hardly increased in size compared to that at 30 N, whilst the DPP wear scar has increased significantly, as has the amount of wear debris. The 40 N DPP sample was also stopped after 1250 m, whilst the NTf_2 samples went to 2500 m, so the amount of wear would almost certainly have been much higher if the tests were allowed to continue to 2500 m. This supports the idea that, as the load is increased from 30 to 40 N, the tribolayer formed by the DPP IL is not able to withstand the gouging by large wear particles, leading to metal-on-metal contact.

The EDX was used to further analyse the wear scar and to characterise the tribolayers formed by the $P_{66614}NTf_2$ and P_{66614}DPP lubricants. Figure 5 shows EDX spectra of the two wear scars at 30 N. It can be seen that the NTf_2 sample has fluorine and an increased amount of oxygen present, suggesting that a film-containing metal fluorides has formed. It has been proposed that this type of film can



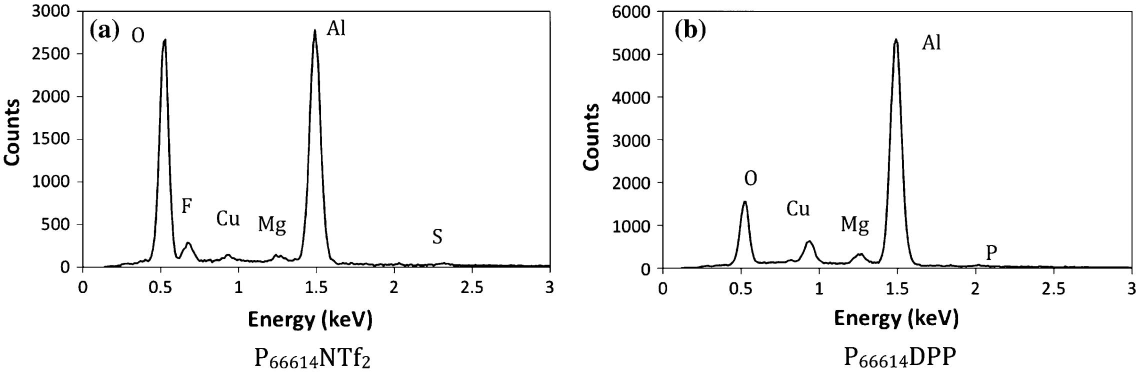
$P_{66614}NTf_2$ 30N 2500m

$P_{66614}NTf_2$ 40N 2500m

$P_{66614}DPP$ 30N 2500m

$P_{66614}DPP$ 40N 1250m

Fig. 4 Optical images of the wear scars at 30 and 40 N. **a** $P_{66614}NTf_2$ 30 N 2500 m, **b** $P_{66614}NTf_2$ 40 N 2500 m, **c** $P_{66614}DPP$ 30 N 2500 m and **d** $P_{66614}DPP$ 40 N 1250 m



$P_{66614}NTf_2$

$P_{66614}DPP$

Fig. 5 The EDX spectra for pin-on-disc wear scars on 2024 aluminium lubricated with IL lubricants tested at 30 N. **a** $P_{66614}NTf_2$ and **b** $P_{66614}DPP$

be a good EP film [23]. On the DPP wear scar, however, there is only a low intensity signal from phosphorous, and the oxygen peak is much smaller in this case. The increased amount of oxygen seen on the $P_{66614}NTf_2$ wear scar and the relatively large fluorine peak may indicate that a comparatively thick tribolayer comprising of aluminium oxides and aluminium fluorides has formed. Mu et al. [2] and Chen et al. [14] have found aluminium fluorides, aluminium oxides and aluminium hydroxides present in the wear scars formed by fluorine-containing IL lubricants that performed well. The much smaller oxygen and phosphorus peaks on the $P_{66614}DPP$ wear scar may indicate the presence of aluminium oxides and aluminium phosphates that have formed a thinner tribolayer. Due to the interaction volume of the EDX experiment, the sensitivity to very thin films can be low, even at the 5 kV used in the analysis. Thus, it appears that the film formed by the DPP IL is very thin, which contributes to its poor performance at 40 N. At loads of less than 40 N, the DPP IL showed lower wear coefficients than the NTf_2 IL. It has been proposed that phosphorus-containing ILs could form stable aluminium phosphates that reduce the wear rate of aluminium [2].

The thickness of the tribolayer may explain why the NTf_2 sample is able to withstand the 40 N load. At loads of

30 N or less, the tribolayer formed by the DPP lubricant leads to less wear at these loads; however it does not appear to be able to withstand the pressure applied by a load of 40 N. Further investigation into the nature of the tribofilms formed is being conducted.

5 Conclusion

The performance of two candidate IL lubricants was assessed for the steel/aluminium system at various loads using a pin-on-disc test. In reference to the friction results, as the applied load was increased the wear regime moved from the elastohydrodynamic region, where asperities begin to come into contact and into the EP region, where the increased pressure and temperature and the exposure of fresh metal surfaces causes the ILs to react and break down to form a low friction layer. It was shown that the performance of an IL lubricant is dependant on its structure and the load applied. At lower loads, the IL with a DPP anion appeared to form a more wear resistant tribolayer. At higher loads, however, the bis(trifluoromethanesulfonyl) amide anion resulted in lower wear and this may be due to the formation of a more tenacious or thicker tribolayer.

Acknowledgments The authors gratefully acknowledge the funding for this research from DP0986205 and Cytec Industries for their generous supply of ionic liquid.

References

1. Jiménez, A.-E., Bermúdez, M.-D.: Ionic liquids as lubricants for steel–aluminum contacts at low and elevated temperatures. Tribol. Lett. **26**(1), 53–60 (2007)
2. Mu, Z., Wang, X., Zhang, S., Liang, Y., Bao, M., Liu, W.: Investigation of tribological behavior of Al–Si alloy against steel lubricated with ionic liquids of 1-diethylphosphonyl-n-propyl-3-alkylimidazolium tetrafluoroborate. J. Tribol. **130**(3), art. no. 034501 (2008)
3. Qu, J., Blau, P.J., Dai, S., Luo, H., Meyer III, H.M., Truhan, J.J.: Tribological characteristics of aluminum alloys sliding against steel lubricated by ammonium and imidazolium ionic liquids. Wear. **267**(5–8), 1226–1231 (2009)
4. Iglesias, P., Bermúdez, M.D., Carrión, F.J., Martínez-Nicolás, G.: Friction and wear of aluminium–steel contacts lubricated with ordered fluids-neutral and ionic liquid crystals as oil additives. Wear. **256**(3–4), 386–392 (2004)
5. Hamrock, B.J.: Fundamentals of Fluid Film Lubrication. McGraw-Hill Series in Mechanical Engineering, 1st edn. McGraw-Hill, New York (1994)
6. Booser, E.R.: CRC Handbook of Lubrication (Theory and Practice of Tribology). Volume II. Theory and Design. CRC Press, Boca Raton (1984)
7. Kenbeek, D., Buenemann, T.F.: Organic friction modifiers. In: Rudnick, L.R. (ed.) Lubricant Additives: Chemistry and Applications, pp. 203–222. CRC Press, Boca Raton (2003)
8. Nicholls, M.A., Do, T., Norton, P.R., Kasrai, M., Bancroft, G.M.: Review of the lubrication of metallic surfaces by zinc dialkyl-dithiophosphates. Tribol. Int. **38**(1), 15–39 (2005)
9. Wan, Y., Cao, L., Xuet, Q.: Friction and wear characteristics of ZDDP in the sliding of steel against aluminum alloy. Tribol. Int. **30**(10), 767–772 (1997)
10. Howlett, P.C., Zhang, S., MacFarlane, D.R., Forsyth, M.: An investigation of a phosphinate-based ionic liquid for corrosion protection of magnesium alloy AZ31. Aust. J. Chem. **60**(1), 43–46 (2007)
11. MacFarlane, D.R., Pringle, J.M., Howlett, P.C., Forsyth, M.: Ionic liquids and reactions at the electrochemical interface. Phys. Chem. Chem. Phys. **12**(8), 1659–1669 (2010)
12. Ye, C., Liu, W., Chen, Y., Yu, L.: Room-temperature ionic liquids: a novel versatile lubricant. Chem. Commun. **21**, 2244–2245 (2001)
13. Yagi, T., Sasaki, S., Mano, H., Miyake, K., Nakano, M., Ishida, T.: Lubricity and chemical reactivity of ionic liquid used for sliding metals under high-vacuum conditions. Proc. Inst. Mech. Eng. J **223**(7), 1083–1090 (2009)
14. Chen, Y.X., Ye, C.F., Wang, H.Z., Liu, W.M.: Tribological performance of an ionic liquid as a lubricant for steel/aluminium contacts. J. Synth. Lubr. **20**(3), 217–225 (2003)
15. Jiménez, A.E., Bermúdez, M.D., Carrión, F.J., Martínez-Nicolás, G.: Room temperature ionic liquids as lubricant additives in steel-aluminium contacts: influence of sliding velocity, normal load and temperature. Wear. **261**(3–4), 347–359 (2006)
16. Liu, X., Zhou, F., Liang, Y., Liu, W.: Tribological performance of phosphonium based ionic liquids for an aluminum-on-steel system and opinions on lubrication mechanism. Wear. **261**(10), 1174–1179 (2006)
17. Qu, J., Truhan, J., Dai, S., Luo, H., Blau, P.: Ionic liquids with ammonium cations as lubricants or additives. Tribol. Lett. **22**(3), 207–214 (2006)
18. Minami, I., Inada, T., Sasaki, R., Nanao, H.: Tribo-chemistry of phosphonium-derived ionic liquids. Tribol. Lett. (2010). doi:10.1007/s11249-010-9626-0
19. Sun, J., Howlett, P.C., MacFarlane, D.R., Lin, J., Forsyth, M.: Synthesis and physical property characterisation of phosphonium ionic liquids based on $P(O)_2(OR)_2^-$ and $P(O)_2(R)_2^-$ anions with potential application for corrosion mitigation of magnesium alloys. Electrochim. Acta. **54**(2), 254–260 (2008)
20. Kabir, M.A., Higgs III, C.F., Lovell, M.R.: A pin-on-disk experimental study on a green particulate-fluid lubricant. J. Tribol. **130**(4), 041801-1–041801-6 (2008)
21. Pensado, A.S., Comuñas, M.J.P., Fernández, J.: The pressure-viscosity coefficient of several ionic liquids. Tribol. Lett. **31**(2), 107–118 (2008)
22. Nehme, G., Mourhatch, R., Aswath, P.B.: Effect of contact load and lubricant volume on the properties of tribofilms formed under boundary lubrication in a fully formulated oil under extreme load conditions. Wear. **268**(9–10), 1129–1147 (2010)
23. Bermúdez, M.D., Jiménez, A.E.: Surface interactions and tribochemical processes in Ionic Liquid lubrication of aluminium-steel contacts. Int. J. Surf. Sci. Eng. **1**(1), 100–110 (2007)