Functional Room-temperature Ionic Liquids as Lubricants for an Aluminum-on-Steel System

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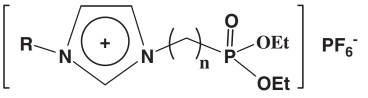
A new series of imidazolium cation based room-temperature ionic liquids (RTILs), with *O*,*O*-diethylphosphonyl groups on the alkyl side-chain has been prepared; the tribological properties of the ionic liquids were evaluated and possible mechanisms were discussed.

It is well known that, even in the presence of a lubricant, the sliding contact between aluminum and steel will still result in the transfer of the aluminum to the steel surface as well as the seizure failure of the aluminum. Therefore, the aluminum-on-steel pair is an extremely difficult system to lubricate. In boundary lubrication, the chemical reaction of the lubricant with the rubbing surfaces is especially important. The interactions between aluminum and alcohols, esters and ethers, chlorine-containing and phosphorus-containing oil additives have been extensively investigated for the lubrication of the aluminum-on-steel system. However, up to now, none of the lubricants used in the aluminum-on-steel system has been found to be as effective as those used in the lubrication of the steel-on-steel system.[1] New synthetic lubricants for this system are required.

Recently, room-temperature ionic liquids have attracted significant and growing interest, especially those based upon the 1-alkyl-3-methylimidazolium cation.[2] This is because they have intrinsically useful properties. They have also been referred as "designer solvents."[3] The design and synthesis of some task-specific RTILs has been extensively focused on.[4] For example, some new dense fluoroalkyl-substituted imidazolium ionic liquids[5] and a new series of imidazolium cation-based RTILs[6] with ether and alcohol functional groups on the alkyl side-chain have been successfully prepared. We found in our previous work that RTILs could be used as novel versatile lubricants.[7] More importantly, they might be superior to conventional lubricants in some harsh conditions involving extremely high or low temperature and extremely high or low pressure where the excellent thermal stability and very much small vapour pressure of the liquid lubricants are first of all stressed. Further, it could be feasible to develop novel RTILs lubricants by incorporating one of the most commonly used antiwear and extreme-pressure element phosphorous into imidazolium cations. Thus we synthesized a new series of imidazolium cation-based RTILs, according to the reported procedures,[6] whose *O*,*O*-diethylphosphonyl groups sit on the alkyl side-chain. For example, one of the synthetic RTILs, 1-(3′-*O*,*O*-diethylphosphonyl-*n*-propyl)-3-octylimidazolium hexafluorophosphate[8] is abridged as [DPPOIM][PF_6] (Figure 1).



1a: R = C_4H_9, *n* = 2, [DPEBIM][PF_6] 1b: R = C_4H_9, *n* = 3, [DPPBIM][PF_6]
2a: R = C_6H_{13}, *n* = 2, [DPEHIM][PF_6] 2b: R = C_6H_{13}, *n* = 3, [DPPHIM][PF_6]
3a: R = C_8H_{17}, *n* = 2, [DPEOIM][PF_6] 3b: R = C_8H_{17}, *n* = 3, [DPPOIM][PF_6]

Figure 1. Molecular structure of the new functional ionic liquids.

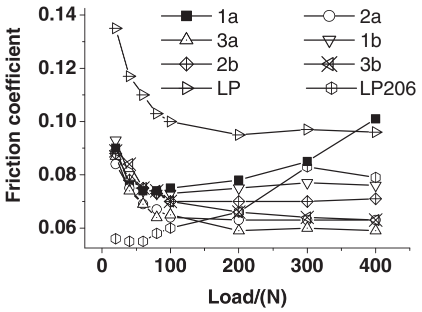


Figure 2. Variation of friction coefficient as the function of testing load when lubricanting with ionic liquids and LP.

Table 1. Tribological properties of ionic liquids and liquid paraffin (LP) for Al2024/steel contact (SRV tester, frequency 25 Hz, amplitude 1 mm, duration 30 min, temperature, 20 °C)

Load	Wear Volume/$\times 10^{-3}$ mm^3							
/N	1a	2a	3a	1b	2b	3b	LP	LP206
20	0.60	0.06	0.12	0.38	0.12	0.08	1.22	1.16
40	1.80	0.24	0.16	0.80	0.22	0.19	1.92	1.40
60	2.50	0.61	0.29	1.88	0.50	0.24	2.76	1.48
80	4.00	0.69	0.34	2.80	0.56	0.26	3.44	3.64
100	4.48	3.00	0.64	3.48	2.92	0.62	3.60	4.80
200	14.04	7.00	2.40	13.12	6.56	1.65	6.96	8.72
300	21.84	15.20	4.32	15.20	10.08	4.04	11.60	14.48
400	26.28	22.48	6.40	22.48	14.24	6.24	12.16	15.20

The tribological behaviors of the RTILs under relatively high loads were evaluated on an SRV oscillating friction and wear tester in a ball-on-disc configuration. The friction and wear test results are shown in Figure 2 and Table 1. It is seen that the synthetic ionic liquids have good lubricity for the aluminum-on-steel system (Figure 2). Except for **1a**, all the synthetic ionic liquids show better friction-reducing ability than a conventional ionic liquid 1-ethyl-3-hexylimidazolium hexafluorophosphate (coded as LP206). This is especially prominent at a relatively higher load, which indicates that the presently synthesized ionic liquids could be promising candidates as novel high-temperature liquid lubricants. At a lower load, the coefficients of the new ionic liquids are relatively higher than that of LP206, which can be attributed to their high viscosity. Moreover, they show better antiwear abilities than LP206 for the Al-on-steel pair as well

(Table 1). Interestingly, the friction-reducing and antiwear abilities of the synthetic ionic liquids for the Al-on-steel contact is related to the length of the alkyl chain[9] attached to the imidazolium cation. Namely, of the six functional ionic liquids, **3b** possesses the best antiwear ability, while **2a**, **3a**, and **3b** record the friction coefficients of little difference at a relatively higher load, which could be because 3b has a larger alkyl chain attached to the imidazolium cation than **3a**. The different tribological behaviors of various different liquid lubricants can be well ascribed to the corresponding boundary lubricating films of different formation mechanisms and properties. Take the ionic liquids **2a** and LP206 as the examples, the formation of the boundary lubricating films involves three stages, i.e., the physical adsorption dominating the friction and wear at a lower load, the chemical adsorption governing the friction and wear at a moderate load, and the tribochemical and corrosive stage dominating the friction and wear at a high enough load. It must be noted that the ionic liquids of different alkyl chain attached to the imidazolium cation would function to reduce the friction and wear of the Al-steel pair at different activated loads, owing to the different chemical stability of the ionic liquids and the different chemical activities between the phosphonylethyl groups and the phosphonylpropyl groups. The chemical stability of the ionic liquids is ranked as 3a > 2a > 1a or 3b > 2b > 1b, which agrees well with their ranking of the friction-reducing and antiwear behaviors except that **2a** registers a smaller wear volume loss than **3a** at a small load of 20 N.

At the chemical adsorption stage, the functional groups of the ionic liquids undergo hydrolysis in the presence of atmospheric moisture and react with Al to form five-membereds ring, which conforms to the five- or six-membereds ring bidentate bonding hypothesis supposed by Hotton and Wan.[10] The ionic liquids of longer alkyl chain have stronger adsorption on the sliding metallic surface and are easier to form chemisorbed film thereon, and hence show better antiwear ability than the one of shorter alkyl chain. This supposition is supported by the observation of the residue lubricants after the tests with naked eyes. Namely, the residue ionic liquids remain transparent, while that of LP206 appears as mushy black liquid and contain a large number of wear debris. Moreover, the *O*,*O*-diethylphosphonyl groups in the alkyl side-chain attached to the imidazolium cation play an important role in governing the tribochemistry as compared with the non-functional ionic liquid LP206, because those functional groups have strong reaction activity with the freshly exposed Al or Fe element during the sliding process. The distribution of Al determined by energy dispersive spectrometry (EDS) on the wear scar of the counterpart steel ball indicates that the transfer of the Al onto the steel surface is almost completely prevented under the lubrication of the ionic liquids synthesized in the present work, as compared with LP206.

However, the decomposition of the functional ionic liquids at too high normal load should be taken into account carefully. This is because some of the decomposed products of the ionic liquids or even themselves can be harmful to the Al and steel owing to the chemical corrosiveness.[10] In this sense, it still remains a challenge to develop novel ionic liquids of excellent tribological behaviors and least corrosive damages to the metallic pairs.

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8 The functional ionic liquids, for example, 1 - (3′-*O*,*O*-diethyl phosphonyl-*n*-propyl)-3-octylimidazolium hexafluorophosphate ([DPPOIM][PF$_6$]), were prepared as follows:

In a nitrogen atmosphere, 3-bromo-*n*-propyl-phosphonate (25.90 g, 0.10 mol) and octylimidazole (18.0 g, 0.10 mol) were added to around-bottomed flask fitted with condenser and stirred for 24 h at 80 °C. The mixture was then cooled to room temperature and washed for three times with 90 mL (30 mL × 3) of anhydrous diethyl ester, followed by removing the solvent in vacuo. The residue was then dried overnight at reduced pressure. The resulting phosphonyl-appended imidazolium bromide was (41.95 g, 95.56%) was transferred to a flask. In the flask acetone (150 mL) and NH$_4$PF$_6$ (21.19 g, 0.13 mol) was sequentially added. The resultant mixture was stirred at room temperature for 2 h to allow the formation of waxy solid precipitates. The waxy precipitates were collected by filtration and washed with acetone (50 mL × 3). The organic layer was collected by washing the waxy precipitates with acetone, dried (MgSO$_4$), filtered, and the solvent removed in vacuum to give the colourless liquid product [DPPOIM][PF$_6$] (47.31 g, 98.24%). IR (KBr film): 3161, 3116, 2930, 2859, 1567, 1467, 1393, 1238, 1166, 1099, 1028, 966, 839, 643, 558 cm^{-1}; ^{1}HNMR (CDCl$_3$, δ/ppm relative to TMS): 8.72 (s, 1H), 7.47 (s, 1H), 7.37 (s, 1H), 4.33 (t, 2H, $J =$ 13.5 Hz), 4.17 (t, 2H, $J = 14.7$ Hz), 4.09 (m, 4H, $J = 16.8$ Hz), 2.18 (m, 2H, $J = 29.4$ Hz), 1.84 (m, 2H, $J = 22.2$ Hz), 1.74 (m, 2H, $J = 15.3$ Hz), 1.35 (m, 16H), 0.87 (t, 3H, $J = 12.3$ Hz); Elem. Anal.: Calcd. for $C_{18}H_{36}F_6N_2O_3P_2$: C, 42.86; H, 7.14; N, 5.56. Found: C, 42.59; H, 7.23; N, 5.53%.

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