Bisimidazolium Ionic Liquids as the High-Performance Antiwear Additives in Poly(ethylene glycol) for Steel–Steel Contacts

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ABSTRACT Bisimidazolium ionic liquids [$C_{10}(m_2im)_2(NTf_2)_2$, $C_{10}(m_2im)_2(PF_6)_2$, and $C_{10}(m_2im)_2(BF_4)_2$] with different anions were evaluated as the antiwear additives in poly(ethylene glycol) at room temperature. Results showed that they could effectively reduce the friction and wear of sliding pairs compared with the cases without these additives. Especially, $C_{10}(m_2im)_2(NTf_2)_2$ showed better antiwear properties with an optimum concentration of 3 wt %, by which a significant improvement of its antiwear property by dozens of times with respect to the base oil was achieved. The excellent tribological properties are attributed to the formation of high-quality physical adsorption films and tribochemical product during friction and the good miscibility of ionic liquids with base oil.

KEYWORDS: friction • antiwear • additive • ionic liquid • tribology

1. INTRODUCTION

It is well-known that synthetic oils have many advantages as lubricating fluids over mineral oils and are more suitable for practical applications. Among various synthetic oils, poly(alkyl ether)s are one of the commonly used base oils in that they are ecofriendly and degradable. Unfortunately, their applications have largely been limited because the conventional lubricant additives for mineral oils are not always effective for polar base oils such as esters and ethers (1). Therefore, it is practically important to develop new additives suitable for polar base oils.

Lubricants usually contain a number of additives of different types to meet actual service requirements like anticorrosion, antioxidation, etc. Among them, the extreme pressure agents, antiwear (AW) additives, and friction modifier (FM) agents, etc., are particularly demanded. Recently, ionic liquids (ILs) have received considerable interest because of their favorable physical properties such as negligible volatility, nonflammability, high thermal stability, and low melting point (2, 3). The outstanding characteristics of ILs also make them good candidates as high-performance lubricants (4−19). ILs as additives in paraffinic−naftenic mineral base oil or water could improve the lubricating and AW behavior (20−23). Recently, Jiménez and Bermúdez studied the tribological properties of several ILs as additives in synthetic esters and found that highly polar ILs could reduce the wear of aluminum at room temperature and all

additives reduce both friction and wear at 100 °C (24). However, the improvement was very limited probably because of their poor solubility in synthetic esters, especially at low temperatures. Meanwhile, only monocationic ILs have been investigated so far. Dicationic ILs have been shown to have a number of advantageous physical properties over the monocationic counterparts (25, 26). It is found that dicationic ILs as high-temperature lubricants show excellent tribological properties (9, 16, 17). At the same time, they can also be used as ultrathin films (27). In this article, we report that dicationic 2-substituted imidazolium ILs have good solubility in polyether, which makes it possible for them to be used as effective additives. Three kinds of dicationic 2-substituted imidazolium ILs 1,1′-(1,10-decyl)bis(2,3-dimethyl-1*H*-imidazolium-1-yl) coordinated with different anions were synthesized, and the tribological properties of the ILs as additives in poly(ethylene glycol) (PEG) for steel−steel contacts were investigated on an Optimal SRV-IV oscillating friction and wear tester at room temperature. The influence of the anion and concentration of the ILs on the tribological properties of the base oil is discussed in detail, and the optimum formulation was obtained.

2. EXPERIMENTAL SECTION

The chemical structures of the ILs are given in Figure 1. 1,1′-(1,10-Decyl)bis(2,3-dimethyl-1*H*-imidazolium-1-yl) bis[(trifluoromethyl)sulfonyl]imide ($C_{10}(m_2im)_2(NTf_2)_2$), 1,1′-(1,10-decyl)bis(2,3-dimethyl-1*H*-imidazolium-1-yl) dihexafluorophosphate ($C_{10}(m_2im)_2(PF_6)_2$), and 1,1′-(1,10-decyl)bis(2,3-dimethyl-1*H*-imidazolium-1-yl) ditetrafluoroborate ($C_{10}(m_2im)_2(BF_4)_2$) were synthesized according to the literature (19, 28). PEG with hydroxyl termination at both ends was obtained from Lanzhou Petrochemical Co. The average molecular weight is 200 g/mol. The base oil and the additives were mixed thoroughly before tests, and the miscibility or solubility values are given in Table 1. Surprisingly, $C_{10}(m_2im)_2(NTf_2)_2$ has remarkable solubility in
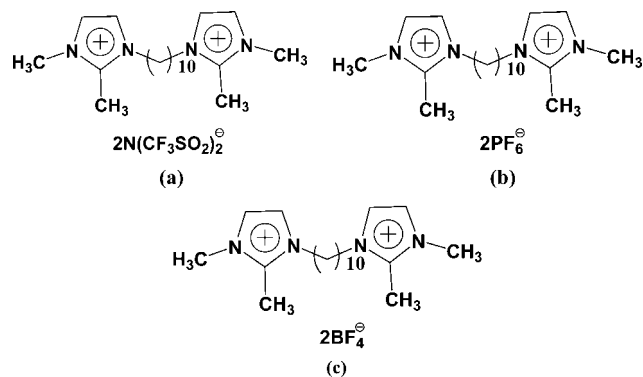
FIGURE 1. Molecular structures of the ILs: (a) $C_{10}(m_2im)_2(NTf_2)_2$, (b) $C_{10}(m_2im)_2(PF_6)_2$, and (c) $C_{10}(m_2im)_2(BF_4)_2$.

Table 1. Miscibility or Solubility of $C_{10}(m_2im)_2(NTf_2)_2$, $C_{10}(m_2im)_2(BF_4)_2$, and $C_{10}(m_2im)_2(PF_6)_2$ with the PEG Base Oil at Room Temperature

	$C_{10}(m_2im)_2(NTf_2)_2$	$C_{10}(m_2im)_2(PF_6)_2$	$C_{10}(m_2im)_2(BF_4)_2$
miscibility or solubility (weight fraction)	>40%	2−3%	3−5%

Table 2. Typical Properties of PEG, $C_{10}(m_2im)_2(NTf_2)_2$, and PEG with Different Additives

	kinematic viscosity (mm^2/s)		viscosity index	density (kg/m^3) at 15 °C
lubricant	40 °C	100 °C		
PEG	22.83	4.23	79.3	1136.4
$C_{10}(m_2im)_2(NTf_2)_2$	566.47	36.11	99.1	1461.9
1% $C_{10}(m_2im)_2(NTf_2)_2$	23.04	4.22	74.7	1138.9
2% $C_{10}(m_2im)_2(NTf_2)_2$	23.58	4.32	80.9	1141.6
3% $C_{10}(m_2im)_2(NTf_2)_2$	23.78	4.31	76.7	1144.2
4% $C_{10}(m_2im)_2(NTf_2)_2$	24.05	4.34	77.1	1146.5
5% $C_{10}(m_2im)_2(NTf_2)_2$	24.04	4.34	77.2	1148.4
2% $C_{10}(m_2im)_2(PF_6)_2$	24.24	4.39	81.3	1141.2
2% $C_{10}(m_2im)_2(BF_4)_2$	24.66	4.45	83.5	1141.3

PEG of over 40% weight fraction; the solubilities of the other two ILs are also considerably large to be used as additives. Their densities, viscosities, and viscosity−temperature indexes were measured by a SVM3000 Stabinger viscometer, and their corresponding results are shown in Table 2. It is seen that the addition of ILs into PEG does not significantly change the viscosity of the base oil.

The friction and wear tests were carried out on an Optimol SRV-IV oscillating friction and wear tester. The contact between the frictional pairs was achieved by pressing the upper running ball (diameter 10 mm, AISI 52100 steel) against the lower stationary disk (ø 24 mm × 7.9 mm, AISI 52100 steel). The upper ball was driven to reciprocate at a given frequency and displacement. The tribological tests were conducted at an amplitude of 1 mm and a relative humidity of 50−60%. Prior to the friction and wear test, 0.2 mL of lubricant was dropped onto the ball−disk contact area. The wear volume of the lower disk was measured by a MicroXAM 3D noncontact surface mapping profiler. Three repetitive measurements were performed for each wear of the disks, and the averaged values are reported in this paper. The wear rates of the worn surface were calculated using the equation $K = V/SF$, where V is the wear volume (in mm^3), S is the total sliding distance (in m), and F is the normal load (in N).

The morphologies of the worn surfaces were analyzed by a JSM-5600LV scanning electron microscope. The X-ray photo-
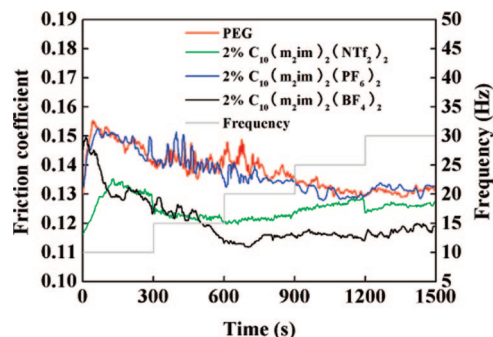

FIGURE 2. Evolution of the friction coefficient with time during a frequency ramp test from 10 to 30 Hz for PEG and different IL additives at room temperature (stroke, 1 mm; load, 100 N).
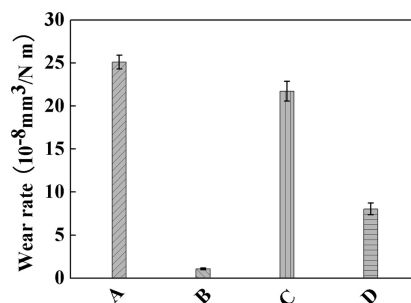

FIGURE 3. Wear rates of disks lubricated by PEG (A), 2% $C_{10}(m_2im)_2(NTf_2)_2$ (B), 2% $C_{10}(m_2im)_2(PF_6)_2$ (C), and 2% $C_{10}(m_2im)_2(BF_4)_2$ (D) after the frequency ramp test from 10 to 30 Hz at room temperature (stroke, 1 mm; load, 100 N; duration, 25 min).

electron spectrometry (XPS) analysis was carried out on a PHI-5702 multifunctional X-ray photoelectron spectrometer, using Al Kα radiation as the exciting source. The binding energies of the target elements were determined at a pass energy of 29.35 eV, with a resolution of about ±0.3 eV, using the binding energy of contaminated carbon (C 1s, 284.8 eV) as the reference.

3. RESULTS

3.1. Tribological Properties. *3.1.1. Friction at Variable Frequencies.* Figure 2 shows a frequency ramp test stepped from 10 Hz up to 30 Hz by 5 Hz at a load of 100 N for different IL additives and the base oil at room temperature. The test duration for each frequency was 5 min, and the corresponding wear rate after this experiment is given in Figure 3. As shown in Figure 2, a general order of friction coefficient values is observed as follows: $C_{10}(m_2im)_2(BF_4)_2$ < $C_{10}(m_2im)_2(NTf_2)_2$ < $C_{10}(m_2im)_2(PF_6)_2$|PEG. The friction coefficients of PEG and 2 wt% $C_{10}(m_2im)_2(PF_6)_2$ decreased with increments of the frequency, and the frictional behaviors as a function of the frequency for PEG and 2 wt% $C_{10}(m_2im)_2(PF_6)_2$ were quite similar. The friction coefficient of 2 wt% $C_{10}(m_2im)_2(NTf_2)_2$ quickly increased from about 0.118 to about 0.135 at the initial sliding stage, followed by a decrease to about 0.125 at a frequency of 15 Hz; this then changed little with increased frequency. As for $C_{10}(m_2im)_2(BF_4)_2$, the friction coefficient declined at first and remained relatively stable at low level when the frequency was higher than 15 Hz. The wear rates of steel disks lubricated by the IL additives and the base oil after the frequency ramp test are in the order of $C_{10}(m_2im)_2(NTf_2)_2$ < $C_{10}(m_2im)_2(BF_4)_2$ <
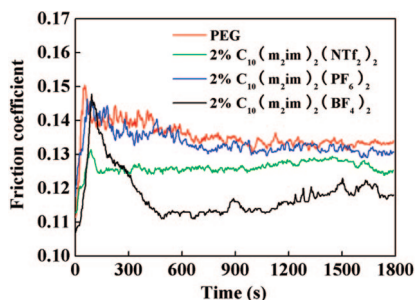
FIGURE 4. Evolution of the friction coefficient with time at 100 N for PEG and different IL additives at room temperature (stroke, 1 mm; frequency, 20 Hz).
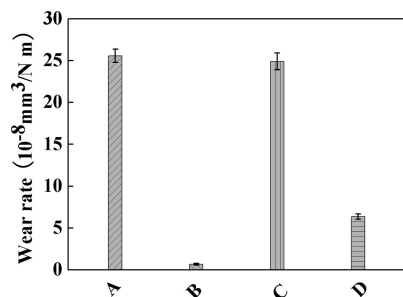

FIGURE 5. Wear rates of the disks lubricated by PEG (A), 2% $C_{10}(m_2im)_2(NTf_2)_2$ (B), 2% $C_{10}(m_2im)_2(PF_6)_2$ (C), and 2% $C_{10}(m_2im)_2(BF_4)_2$ (D) after the constant load test (stroke, 1 mm; frequency, 20 Hz; load, 100 N; duration, 30 min).
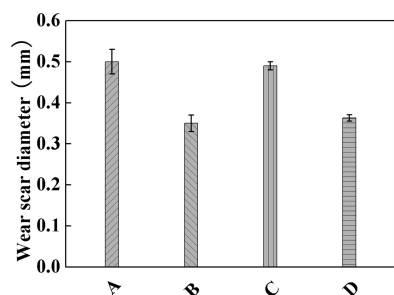

FIGURE 6. Wear scar diameters of the steel balls lubricated by PEG (A), 2% $C_{10}(m_2im)_2(NTf_2)_2$ (B), 2% $C_{10}(m_2im)_2(PF_6)_2$ (C), and 2% $C_{10}(m_2im)_2(BF_4)_2$ (D) after the constant load test (stroke, 1 mm; frequency, 20 Hz; load, 100 N; duration, 30 min).

$C_{10}(m_2im)_2(PF_6)_2$|PEG as shown in Figure 3. Two weight percent $C_{10}(m_2im)_2(BF_4)_2$ and 2 wt % $C_{10}(m_2im)_2(NTf_2)_2$ can improve the AW properties of the base oil by 3 and 23 times, respectively. This shows that 2 wt % $C_{10}(m_2im)_2(NTf_2)_2$ significantly improves the AW properties of PEG.

3.1.2. *Friction at Constant Frequency.* The influence of a constant load on the tribological behavior of different IL additives and PEG was investigated. The test duration in this experiment was 30 min, and the frequency was 20 Hz. The corresponding friction coefficient evolution at a constant load of 100 N, wear rates of the disks, and average wear scar diameters of the steel balls lubricated by additives and PEG after this experiment are shown in Figures 4−6, respectively. Results showed that the friction coefficients of the additives and PEG increased in the following sequence: $C_{10}(m_2im)_2(BF_4)_2$ < $C_{10}(m_2im)_2(NTf_2)_2$ < $C_{10}(m_2im)_2(PF_6)_2$|PEG, while the wear rates of the disks and wear scar diameters of the steels balls increased in the order of $C_{10}(m_2im)_2(NTf_2)_2$ < $C_{10}(m_2im)_2(BF_4)_2$ <
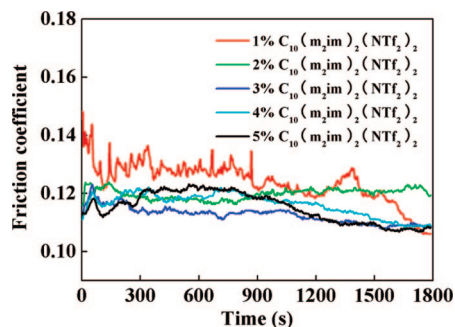

FIGURE 7. Evolution of the friction coefficient with time at 150 N for $C_{10}(m_2im)_2(NTf_2)_2$ additive with different concentrations at room temperature (stroke, 1 mm; frequency, 20 Hz).
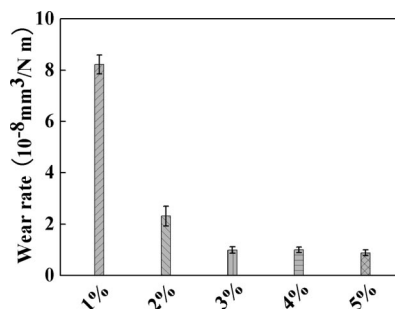

FIGURE 8. Wear rates of disks lubricated by $C_{10}(m_2im)_2(NTf_2)_2$ additive with different concentrations after the constant load tests (stroke, 1 mm; frequency, 20 Hz; load, 150 N; duration, 30 min).

$C_{10}(m_2im)_2(PF_6)_2$|PEG. This is similar to that observed in the frequency ramp test (Figures 2 and 3). What is different is that the AW properties of 2 wt % $C_{10}(m_2im)_2(BF_4)_2$ and 2 wt % $C_{10}(m_2im)_2(NTf_2)_2$ increased by 4 and 37 times as compared with the base oil. This indicates that $C_{10}(m_2im)_2(NTf_2)_2$ was an excellent additive of PEG, exhibiting outstanding AW properties, especially during the constant load test.

3.1.3. *Effect of the Concentration.* The friction coefficient evolution at a constant load of 150 N for 1−5 wt % $C_{10}(m_2im)_2(NTf_2)_2$ and wear rates after the tests are shown in Figures 7 and 8. As the concentration of $C_{10}(m_2im)_2(NTf_2)_2$ increased, friction coefficients of $C_{10}(m_2im)_2(NTf_2)_2$ changed little and wear rates of $C_{10}(m_2im)_2(NTf_2)_2$ reduced significantly at first. When the concentration of $C_{10}(m_2im)_2(NTf_2)_2$ reached 3 wt %, increasing the additive concentration had little effect on tribological properties of the base oil. Meanwhile, 3 wt % $C_{10}(m_2im)_2(NTf_2)_2$ can improve the AW properties of the base oil by 2.3 times as compared with 2 wt % $C_{10}(m_2im)_2(NTf_2)_2$. This indicates that 3 wt % $C_{10}(m_2im)_2(NTf_2)_2$ is the optimum concentration to provide significant friction and wear reduction.

3.2. Surface Analysis. Figure 9 gives the morphologies of worn steel surfaces lubricated by different IL additives and PEG after the constant load tests at 100 N. It can be seen that the worn surfaces of the steels lubricated by PEG (Figure 9a,b) and 2 wt % $C_{10}(m_2im)_2(PF_6)_2$ (Figure 9e,f) show much wider wear scar; severe scuffing occurred in this case. However, the width of the wear scar is smaller in size for the steel lubricated with 2 wt % $C_{10}(m_2im)_2(BF_4)_2$, as shown in Figure 9g,h. In marked contrast, when 2 wt %
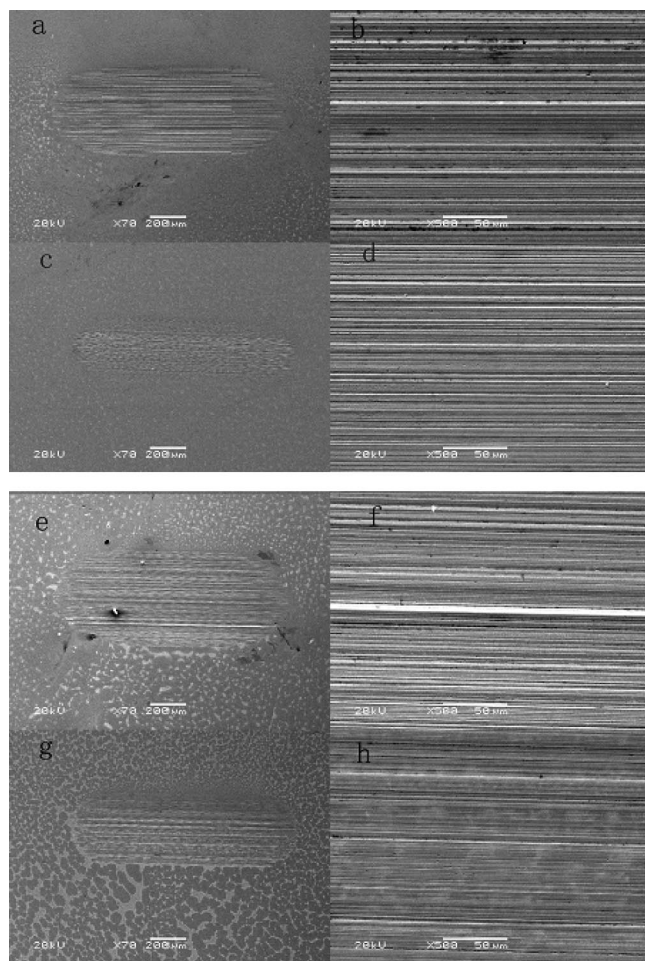
FIGURE 9. Scanning electron microscopy images of the worn surfaces lubricated by different ILs: (a and b) PEG, (c and d) 2% $C_{10}(m_2im)_2(NTf_2)_2$, (e and f) 2% $C_{10}(m_2im)_2(PF_6)_2$, and (g and h) 2% $C_{10}(m_2im)_2(BF_4)_2$ (the magnification of the left is 70×, and that of the right is 500×; load, 100 N; stroke, 1 mm; frequency, 20 Hz; duration, 30 min).

$C_{10}(m_2im)_2(NTf_2)_2$ is added into PEG, the wear scar obviously becomes narrow and the friction scratches also become thinner and more shallow (Figure 9c,d), which shows its excellent AW properties. This is consistent with the wear rate results, which again proved that having $C_{10}(m_2im)_2(NTf_2)_2$ as the additive can remarkably reduce the wear of sliding pairs.

In order to explore the lubricating mechanism of the IL additives, Figure 10 presents the XPS spectra and Table 3 gives the atomic percent on the worn steel surfaces lubricated by 2 wt % $C_{10}(m_2im)_2(NTf_2)_2$, 2 wt % $C_{10}(m_2im)_2(BF_4)_2$, and 2 wt % $C_{10}(m_2im)_2(PF_6)_2$, respectively. It can be seen that all peaks of N 1s appear at about 399.5 eV. Combined with the binding energy of O 1s at 533.08 eV, it is supposed that amine and/or their analogue or nitrogen oxide is generated on the worn surfaces (7, 17, 29). The P 2p peak of the worn surface lubricated with PEG plus 2 wt % $C_{10}(m_2im)_2(PF_6)_2$ appears at 133.7 eV, which corresponds to FePO$_4$ (7, 29). The peaks of O 1s and Fe 2p appearing at 529.7 and 706.6 eV may correspond to that in FePO$_4$ or ferric oxide (29). Other characteristics of absorption peaks such as F, S, and B could not be detected on the worn steel surfaces lubricated with all three kinds of IL additives. This
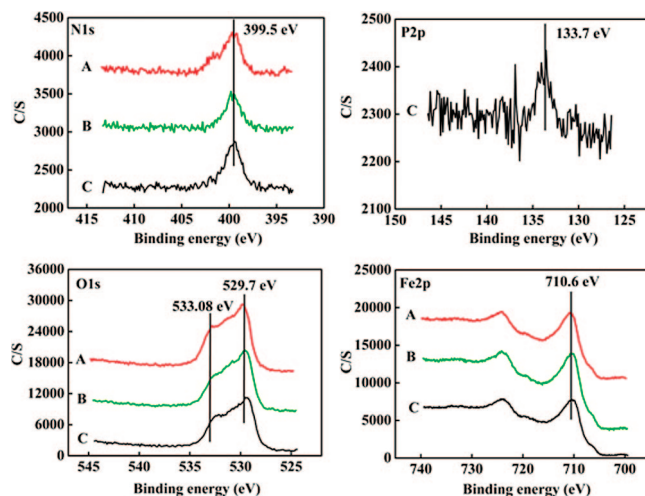

FIGURE 10. XPS spectra of N 1s, P 2p, O 1s, and Fe 2p of the worn surfaces lubricated by 2% $C_{10}(m_2im)_2(NTf_2)_2$ (A), 2% $C_{10}(m_2im)_2(BF_4)_2$ (B), and 2% $C_{10}(m_2im)_2(PF_6)_2$ (C).

Table 3. Atomic Percent of Elements of the Worn Surfaces Lubricated by 2% $C_{10}(m_2im)_2(NTf_2)_2$, 2% $C_{10}(m_2im)_2(BF_4)_2$, and 2% $C_{10}(m_2im)_2(PF_6)_2$

additive	C	N	O	Fe	Cr	P	F	S	B
2% $C_{10}(m_2im)_2(NTf_2)_2$	40.39	1.15	36.70	20.81	0.72				
2% $C_{10}(m_2im)_2(BF_4)_2$	39.92	1.30	36.17	21.45	0.97				
2% $C_{10}(m_2im)_2(PF_6)_2$	39.60	1.45	36.58	20.75		0.85			0.67

suggests that, besides FePO$_4$ formed on the worn surfaces lubricated by 2 wt % $C_{10}(m_2im)_2(PF_6)_2$, similar tribochemical reactions were involved during the friction process lubricated by all three kinds of IL additives. Therefore, although a tribochemical product containing nitrogen may contribute to the tribological properties, the tribochemical reaction was apparently not the determining mechanism for friction and wear reduction.

3.3. Discussion. From the tribological data and XPS analysis, it is seen that both the tribochemical reaction film of FePO$_4$ and nitrides were formed in the worn surfaces lubricated with PEG plus 2 wt % $C_{10}(m_2im)_2(PF_6)_2$, while only nitrides formed in the worn surfaces lubricated by 2 wt % $C_{10}(m_2im)_2(BF_4)_2$ and 2 wt % $C_{10}(m_2im)_2(NTf_2)_2$. However, 2 wt % $C_{10}(m_2im)_2(PF_6)_2$ exhibits the worst tribological properties among the three kinds of IL additives. On this basis, it can be deduced that physical adsorption films not chemical reaction films might play a determining role in the tribological properties of the IL additives. We know that, during the sliding process, low-energy electrons emitted from contact convex points on a metal surface and a positive charge formed at the surface of tiny convex volume (30). The anion of the ILs can be easily adsorbed onto the positively charged sites of the metal-worn surface by electrostatic attraction. Another layer of ILs may subsequently form via electrostatic attraction around these initial adsorbates. The thicknesses of the adsorbed molecular layers could be related to the polarity of the ILs and their miscibility with the base oil (24). The miscibility of the ILs in the base oil is in following sequence: $C_{10}(m_2im)_2(NTf_2)_2$ > $C_{10}(m_2im)_2(BF_4)_2$ > $C_{10}(m_2im)_2(PF_6)_2$ (Table 1). Besides, as

for NTf_2^-, the strong delocalization of the negative charge in the fluoroanion weakens its interaction with the ILs, while, on the other hand, having better affinity to the sliding metallic surfaces. Moreover, NTf_2^- assumes a spatially triangular conformation and so was more polar than the symmetric BF_4^- and PF_6^-, which also facilitate absorption of NTf_2^-. Furthermore, the film thicknesses of polar additives can be very high, thus giving rise to an effective viscosity higher than the mean viscosity of the fluid film (31), contributing to the friction and AW properties. NTf_2^- is highly flexible and adopts a number of conformations, as opposed to PF_6^- and BF_4^-, which are conformationally rigid. This can be reflected by the smaller viscosity of NTf_2^- ILs than the other two (18). The flexibility of the anions helps with its good solubility in PEG. All of these reasons make $C_{10}(m_2im)_2(NTf_2)_2$ a good additive in PEG.

4. CONCLUSIONS

Dicationic imidazolium ILs with different anions were synthesized and their tribological properties as additives investigated at room temperature. Results indicated that the anion of the ILs plays a very important role in determining the solubility in the base oil and improving its tribological properties. The friction coefficients of the additives and PEG increased in the following sequence: $C_{10}(m_2im)_2(BF_4)_2$ < $C_{10}(m_2im)_2(NTf_2)_2$ < $C_{10}(m_2im)_2(PF_6)_2|$PEG. The wear rates are in the order of $C_{10}(m_2im)_2(NTf_2)_2$ < $C_{10}(m_2im)_2(BF_4)_2$ < $C_{10}(m_2im)_2(PF_6)_2|$PEG. XPS analysis indicated that the good performance of the ILs as additives is attributed to the formation of effective physical adsorption films and tribo-chemical products. The flexibility and polarity of anion NTf_2 that permit good miscibility of $C_{10}(m_2im)_2(NTf_2)_2$ with the base oil and high-quality physical adsorption films are proposed to contribute to its excellent tribological properties.

Supporting Information Available: Details of the characterization of the IL $C_{10}(m_2im)_2(NTf_2)_2$, $C_{10}(m_2im)_2(PF_6)_2$, and $C_{10}(m_2im)_2(BF_4)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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