ACS APPLIED MATERIALS & INTERFACES

Laxative Inspired Ionic Liquid Lubricants with Good Detergency and No Corrosion

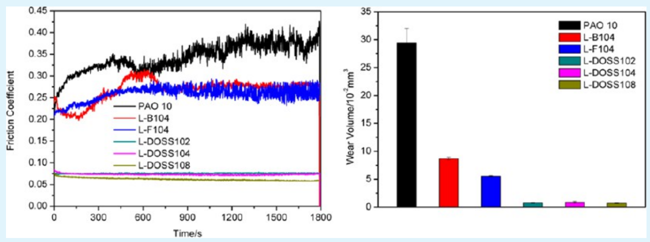
Mingjin Fan,[†] Zenghong Song,[†,‡] Yongmin Liang,[†] Feng Zhou,*[,†] and Weimin Liu*[,†]

[†]State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

[‡]University of Chinese Academy of Sciences, Beijing 100049, China

S Supporting Information

ABSTRACT: 1-Alkyl-3-methylimidazolium bis(2-ethylhexyl)-sulfosuccinate (L-DOSS10n, *n* = 2, 4, 8) ionic liquids (ILs) were synthesized from dioctyl sodium sulfosuccinate (NaDOSS), which is a cheap, bulk available laxative medicine used for the treatment of constipation. The ILs showed lower corrosion levels and higher hydrolysis stabilities than conventional ILs such as 1-butyl-3-methyl imidazolium tetrafluoroborate (L-B104) and 1-butyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)-imide (L-F104) due to their halogen-free characteristic. The tribological properties of the ILs were also better than those of L-B104 and L-F104 for various contacts. Thus, they can be used as replacements for conventional IL lubricants, which may solve the problems of corrosion and high cost to put conventional IL lubricants into industrial application. Coking test results indicated that the synthesized ILs have high deterging ability. Thus, these ILs may be used as lubricants that restrain carbonaceous deposition as well as oil sludge and varnish formation on the metal contacts during the sliding process. Moreover, the synthesized ILs can disperse, loosen, and remove the already formed harmful substances and keep the metal contacts clean.



KEYWORDS: *low cost, no corrosion, halogen-free, detergency, ionic liquids, lubricant*

INTRODUCTION

Dioctyl sodium sulfosuccinate (NaDOSS) is a safe, reliable, and effective laxative used for the treatment of constipation. After oral administration, it lowers the surface tension of the gastrointestinal tract and renders a hard fecal mass to be penetrated by water or mineral oil so that it becomes effectively softened. The drug is also an anionic surfactant used as a dispersant in topically applied preparations, as a penetrating and wetting agent in the textile industry, as an emulsifying agent, and a peticide.[1−7] NaDOSS is cheap and has been well-documented as nontoxic and biodegradable. These particular characteristics inspired us to explore the lubricating properties of ionic liquid (IL) lubricants made from NaDOSS.[8−13] The advantage of $DOSS^-$-based ILs is that they contain no halogen and can be synthesized from cheap, commercially available starting materials through an easier purification process than those for conventional halogen-containing ILs.[14−16]

The replacement of volatile organic compounds used as lubricants with stable alternatives is one of the most important areas in modern tribology. The discovery of ILs as high-performance synthetic lubricants was initiated in 2001.[17] Since then, a variety of ILs have been synthesized and tested for tribological use.[18−20] ILs have been found to be good candidates not only as high-performance lubricants but also as lubricant additives in base oil, grease or water because of their low volatility, nonflammability, and high thermal stability. However, when developing lubricant alternatives, shifting the environmental burden to another stage of the product life cycle must be avoided. Almost all conventional ILs described currently in the literature for lubricating applications contain halogen anions such as BF_4^-, PF_6^-, and $(CF_3SO_2)_2N^-(TFSI^-)$. Investigation on the using of halogen-free ILs as lubricants is relatively rare.[21] Halogen containing anions such as BF_4^- and PF_6^- do have "hidden" problems, including the hydrolytic instability, and may hydrolyze to produce HF under tribochemical reaction conditions, thereby causing corrosion and damage to the surface of the mechanical systems and generating halide waste to the surrounding environment.[22−24] Other relatively stable ILs based on anion $TFSI^-$ are all synthesized from expensive starting material lithium bis(trifluoromethylsulfonyl)imide (LiTFSI), which results in the high cost to use these ILs as neat lubricants.

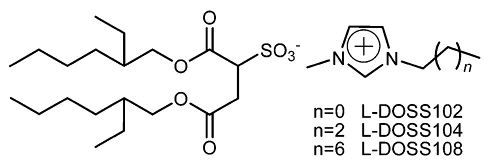


Figure 1. Chemical structures of L-DOSS102, L-DOSS104, and L-DOSS108.

Received: November 9, 2013
Accepted: February 18, 2014
Published: February 18, 2014

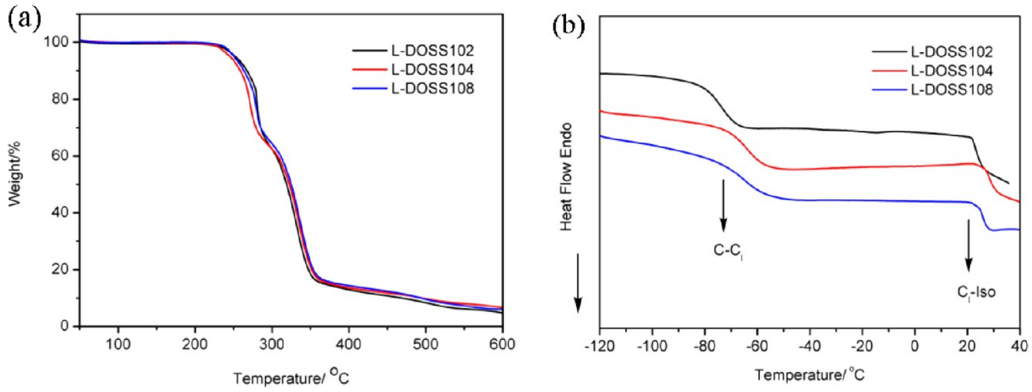


Figure 2. (a) TG curves and (b) DSC trace of the phase transitions of L-DOSS102, L-DOSS104, and L-DOSS108 (C = crystal, C_l = liquid crystal and Iso = isotropic liquid).

Table 1. Some Performance Parameters of L-DOSS102, L-DOSS104, and L-DOSS108

	kinematic viscosity (mm²/s)				TG temperature (°C) per weight loss		
ILs	40 °C	100 °C	viscosity index	corrosion grade	10%	20%	50%
L-DOSS102	2450.84	81.75	90.07	1a	260.4	279.0	316.0
L-DOSS104	1345.60	62.43	98.32	1a	257.8	270.1	322.0
L-DOSS108	4605.13	124.97	94.45	1b	267.3	278.8	327.0

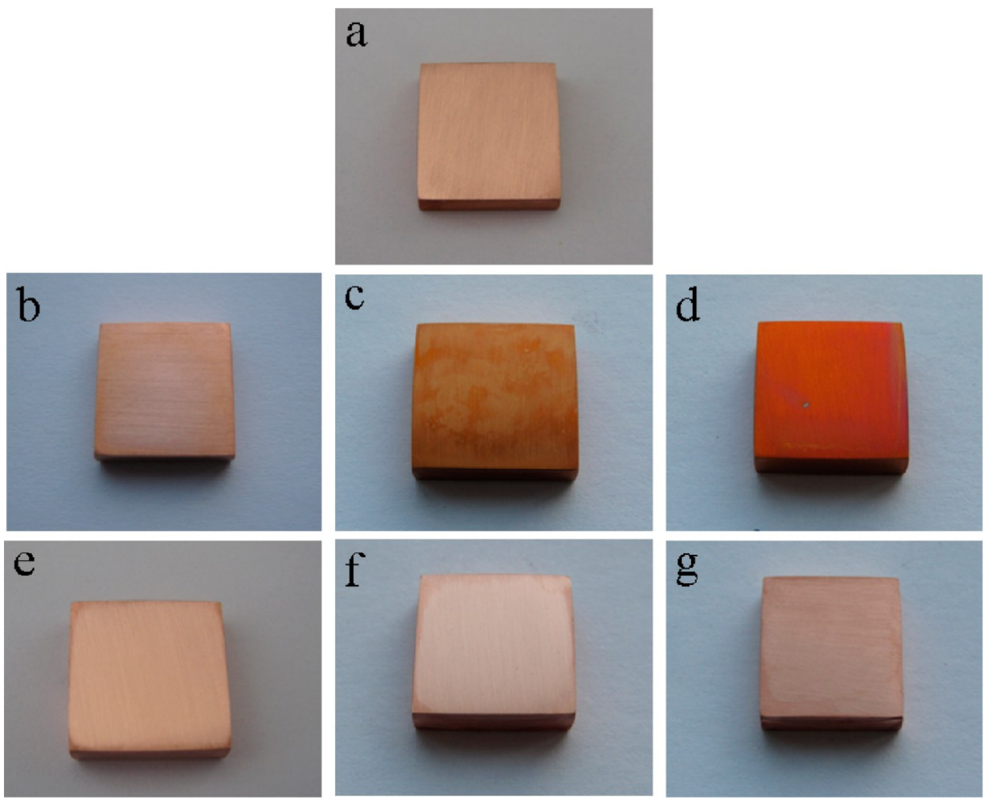


Figure 3. Copper strip corrosion test photographs: (a) copper before corrosion; (b–g) coppers immersed in (b) PAO 10, (c) L-B104, (d) L-F104, (e) L-DOSS102, (f) L-DOSS104, and (g) L-DOSS108 after corrosion, respectively.

These disadvantages are key problems to put ILs into industrial application even after ten years of extensive development in this area. Therefore, development of new low cost and halogen-free anion containing ILs for lubrication is highly desired. DOSS⁻ based ILs were selected for this purpose because of their high technical availability at relatively low cost and well documented nontoxicity, biodegradability, and high adsorption ability of anion DOSS⁻ on metal surfaces.[25,26] In this paper, we present the synthesis and physicochemical and tribological properties of the sulfonate-based ILs, 1-ethyl-3-methylimidazolium

Table 2. Deterging Performance of the Synthesized ILs

sample oil	carbonaceous deposit (mg)
base oil	21.50
base oil + 3% L-DOSS104	9.56

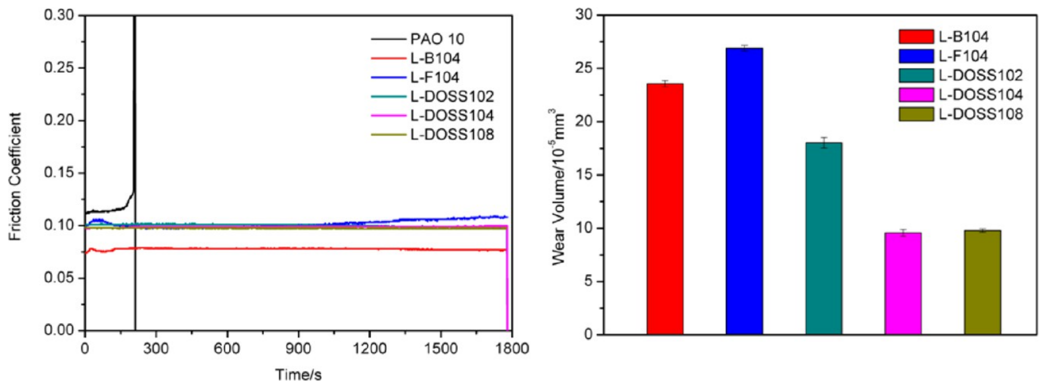


Figure 4. Evolution of friction coefficient/time and wear volume of the lower disks lubricated by PAO 10, L-B104, L-F104, L-DOSS102, L-DOSS104, and L-DOSS108 at RT (with load of 300 N and frequency of 25 Hz).

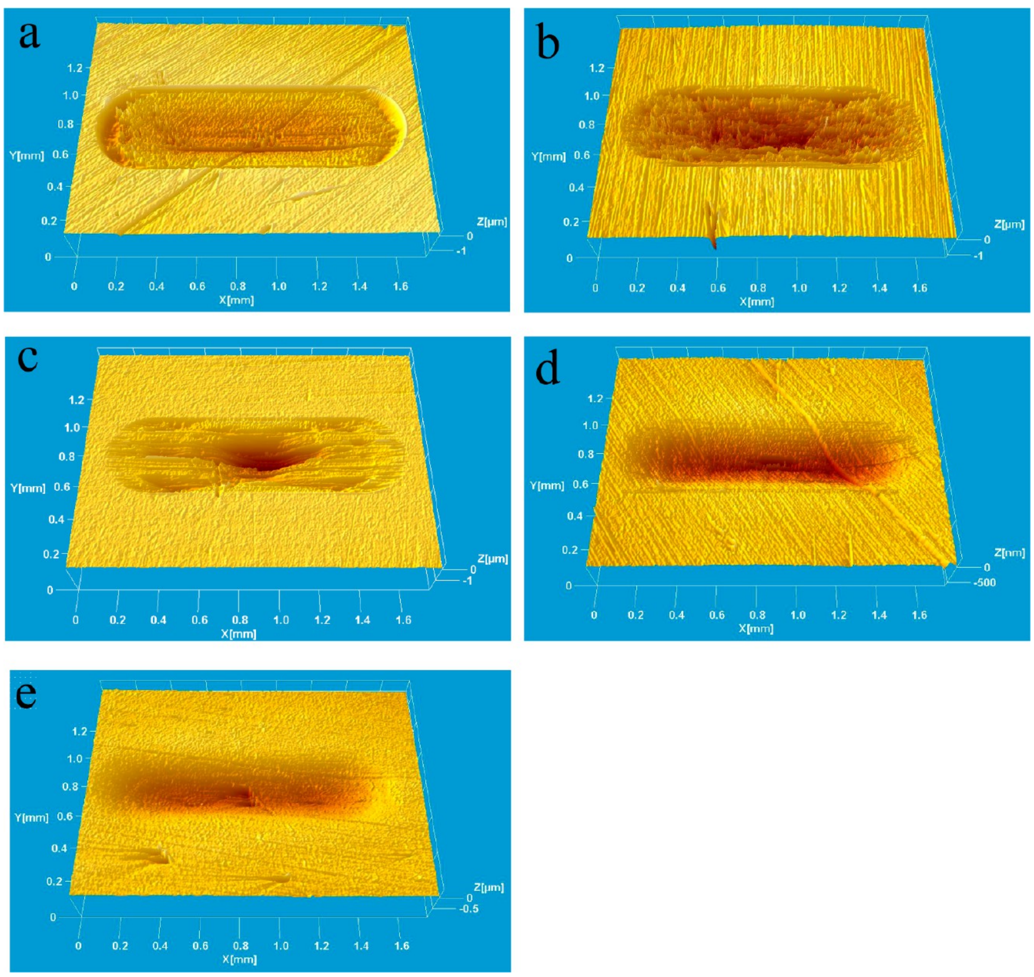


Figure 5. The 3D optical microscopic images of wear tracks corresponding to L-B104 (a), L-F104 (b), L-DOSS102 (c), L-DOSS104 (d) and L-DOSS108 (e).

bis(2-ethylhexyl)sulfosuccinate (L-DOSS102), 1-butyl-3-methylimidazolium bis(2-ethylhexyl)sulfosuccinate (L-DOSS104) and 1-octyl-3-methylimidazolium bis(2-ethylhexyl)sulfosuccinate (L-DOSS108), as lubricants (Figure 1).

■ EXPERIMENTAL SECTION

Chemicals. The following reagents and materials were used as received: Esterex adipate ester A51 and PAO 10 (Poly Alpha Olefin, Exxon Mobil Companies), NaDOSS (J&K, ≥94%). All the used 1-alkyl-3-methylimidazolium bromides were kindly provided by Professor Deng's group in our institute (99%). Other chemicals used in the synthesis were of AR grade. 1-Butyl-3-methyl imidazolium tetrafluoroborate (L-B104) and 1-butyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide (L-F104) were synthesized according to the literature.[27] L-DOSS102, L-DOSS104 and L-DOSS108 were synthesized according to a modified literature reported procedure.[28] They were synthesized by mixing 1-alkyl-3-methylimidazolium bromide (0.05 mol) and NaDOSS (0.05 mol) in 100 mL of acetone. The mixture was stirred at room temperature (RT) for 48 h. The solid precipitate was separated, and the solvent was removed under vacuum. The resulting viscous compound was dissolved in 100 mL of diethyl

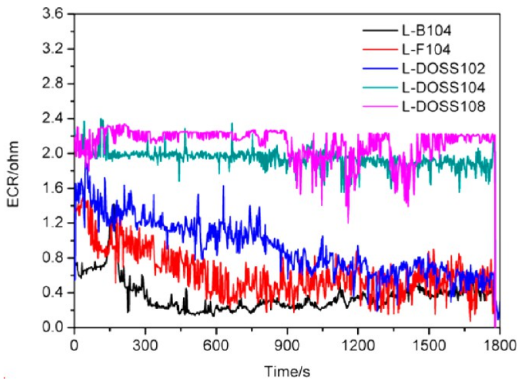


Figure 6. Contact resistance during lubrication with L-B104, L-F104, L-DOSS102 L-DOSS104, and L-DOSS108 at RT (with load of 300 N and frequency of 25 Hz).

ether or acetonitrile. The solid precipitate was separated, and the solvent was removed under vacuum. The resulting viscous compound was again dissolved in 50 mL of diethyl ether or acetonitrile and the solid precipitate was separated. The solvent was removed and the products were dried under a vacuum at 60 °C for several hours to give the final products.

Spectroscopic Characterization. The structures of the ILs were characterized by proton nuclear magnetic resonance (^{1}H NMR, 400 MHz), carbon nuclear magnetic resonance (^{13}C NMR, 100 MHz), FTIR and elemental analysis. The FTIR spectra of the samples were recorded on a Nicolet iS10 FT-IR spectrometer between 4000 and 400 cm^{-1} with a resolution of 2 cm^{-1}. A droplet of the liquid sample was spread on a dry KBr piece for the infrared (IR) spectroscopic measurements. Elemental analysis was carried on a Vario EL elemental analyzer.

Thermal Analysis. The phase transition temperature of the ILs was measured on a DSC 200F3 differential scanning calorimeter (DSC, NET ZSCH). The samples were first cooled to −130 °C with liquid nitrogen and then heated to 40 °C at a rate of 10.0 K/min. The thermal behavior of the samples was carried out on an STA 449 C Jupiter simultaneous TG-DSC instrument. The temperature was programmed to increase from the initial temperature of 20 °C to approximately 600 °C, at a rate of 10 °C/min in air. The weight loss and heat flow values were monitored in the TG-DSC analysis.

Viscosity and Copper Strip Test. The kinematic viscosity of the lubricants was carried out on a SYP1003-III viscometer at 40 and 100 °C, respectively. The copper strip test was performed using the GB-T5096−1985 (91) procedure. A piece of bright finish copper was immersed in a certain amount of ILs followed by heating at 100 °C for 24 h. At the end of the test, the copper was taken out and washed for comparison with the corrosion standard tint board to determine the corrosion levels of the ILs.

Hydrolysis Stability Analysis. Mixtures of 1 g IL and 1 g (the IL/water proportion is w/w = 1/1) water were heated to 80 °C. Samples were taken at 30 min intervals and the pH of the solution was qualitatively checked to determine the hydrolysis stability of the ILs.

Coking Test. Coking test was used to study the high temperature detergency of the synthesized ILs. A panel coker (L-1) from Lanzhou Petroleum Processing & Chemical Complex was used. Esterex adipate ester A51 was used as a base oil. 3% of L-DOSS104 was dissolved in Esterex adipate ester A51 to get a representative coking test sample. The test was performed using the FTM 791−3462 procedure. The plate temperature was 320 °C and the oil temperature was 150 °C. The test was maintained for 6 h. Each sample was tested three times and the average carbonaceous deposit content was adopted.

Friction and Wear Test. The friction and wear tests were carried out on an Optimol SRV-IV oscillating reciprocating friction and wear tester. The contact between the frictional pair was achieved by pressing the upper running ball against the lower stationary disk, which was driven to reciprocate at a given frequency and displacement. For steel/steel contacts, the upper ball is AISI 52100 steel with 10 mm diameter and approximately 61−64 HRC hardness. The lower stationary disk is AISI52100 steel with Φ 24 mm × 7.9 mm and hardness of approximately 61−64 HRC. For steel/copper contacts, the upper ball is AISI 52100 steel with 10 mm diameter and approximately 61−64 HRC hardness. The lower stationary disk is Cu alloy with Φ24 mm ×7.9 mm and hardness of approximately 130−160 HV. For steel/aluminum contacts, the upper ball is AISI 52100 steel with 10 mm diameter and approximately 61−64 HRC hardness. The lower stationary disk is Al alloy with Φ24 mm × 7.9 mm and hardness of approximately 140−170 HV. The friction and wear tests in this work were conducted at amplitude of 1 mm and frequency of 25 Hz. The relative humidity was 15−45%. The wear volume of the lower disk was measured by a MicroXAM 3D noncontact surface mapping profiler. The morphology of the worn surfaces was analyzed by a JSM-5600LV scanning electron microscope (SEM).

The XPS analysis was carried out on a K-Alpha X-ray photoelectron spectrometer (XPS) using Al Ka radiation as the exciting source. The samples were rinsed three times with ultrasonic in ethanol before scanning. The binding energy of the target elements was determined at a pass energy of 29.35 eV with a resolution of about ±0.3 eV. The binding energy of contaminated carbon (C1s: 284.8 eV) was used as the reference.

RESULTS AND DISCUSSION

Spectroscopic Characterization. The structures and purities of the synthesized ILs were finely confirmed by ^{1}H NMR, ^{13}C NMR, FTIR, and elemental analysis. The detail data are presented in the Supporting Information.

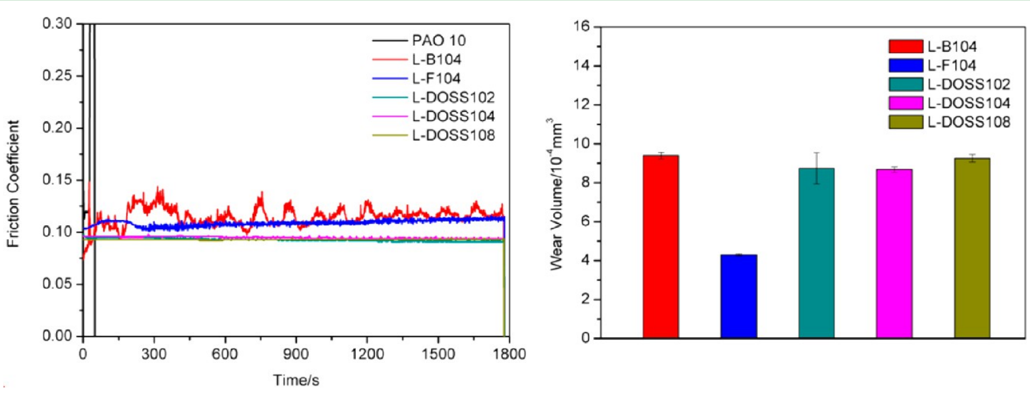


Figure 7. Evolution of friction coefficient/time and wear volume of the lower disks lubricated by PAO 10, L-B104, L-F104, L-DOSS102, L-DOSS104, and L-DOSS108 at 100 °C (with load of 300 N and frequency of 25 Hz).

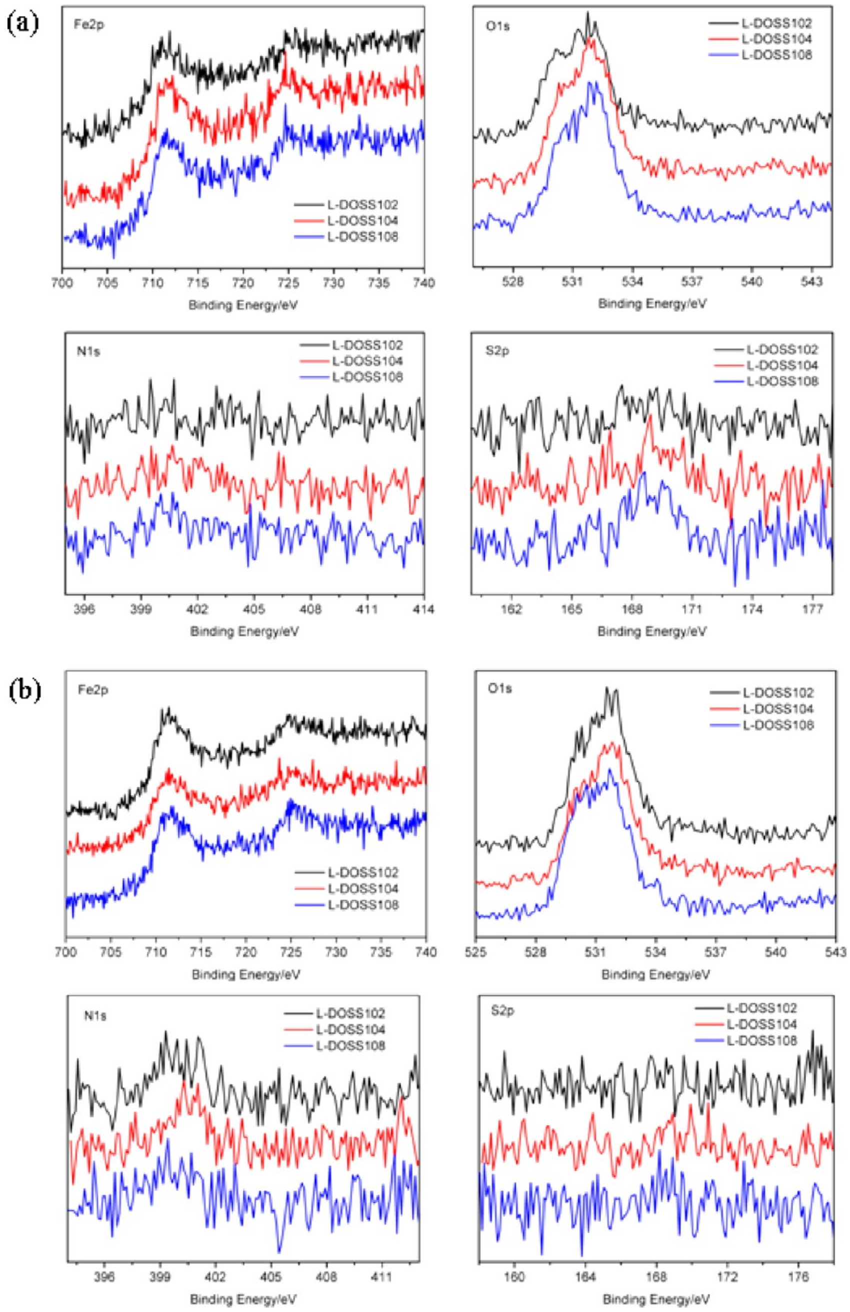


Figure 8. XPS spectra of elements Fe, O, N, and S on the worn surfaces after lubricated by L-DOSS102, L-DOSS104, and L-DOSS108 at (a) RT and (b) 100 °C.

Physical Properties of the Synthesized ILs. *Thermal Analysis.* Figure 2a shows the thermogravimetry (TG) curves of the sulfonate-based ILs. It is obviously seen that the ILs show good thermal decomposition temperatures above 250 °C. For example, the temperature for 10% weight losses of L-DOSS102, L-DOSS104 and L-DOSS108 are 260.4, 257.8, and 267.3 °C, respectively (Table 1), and 50% weight losses at 316.0, 322.0, and 327.0 °C, respectively. Figure 2b shows the typical differential scanning calorimetry (DSC) traces of the phase transitions of the sulfonate-based ILs. An endothermic peak related to a crystal to liquid crystalline phase transition ($C-C_l$) is observed in each DSC trace and appears at about −70 °C. This transition temperature increases slightly as the carbon chain length on the imidazole ring increases, which is attributed the increasing in the ion size and thereby increasing of van der Waals interactions.[29] After that, a liquid crystalline phase is seen up to about 20 °C, as the reference reported.[11] This phase melts to yield an isotropic liquid at temperature higher than 25 °C (C_l-Iso).[30,31]

Viscosity. The kinematic viscosities of the sulfonate-based ILs were measured at 40 and 100 °C, respectively. The viscosity index was calculated to reveal the viscosity-temperature characteristic of the ILs (Table 1). It is seen that the viscosities of L-DOSS10n (n = 2, 4, 8) at 40 °C and at 100 °C both decrease first as the carbon chain length on the imidazole ring increases (n = 2 to n = 4). Then the viscosities increase obviously as the carbon chain length increases (n = 4 to n = 8). The same tendency was found in the viscosity index. Normally, the viscosities of ILs should increase when aliphatic chain increases, which is attributed the increasing van der Waals interactions.[32]

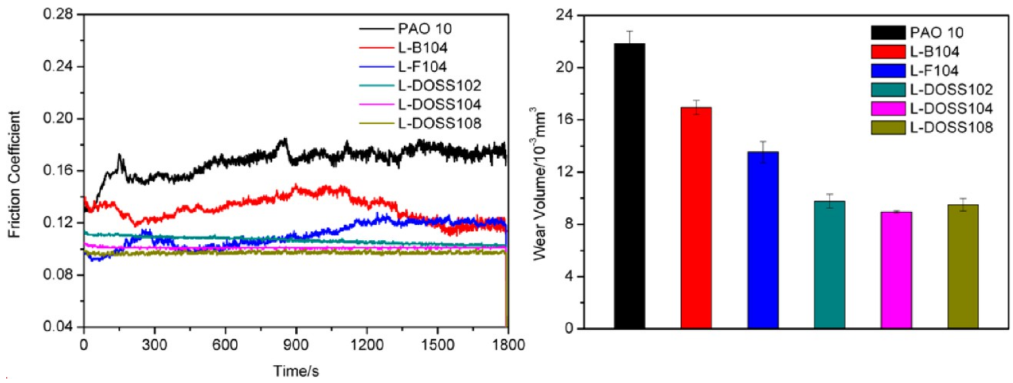


Figure 9. Evolution of friction coefficient/time and wear volume of the lower copper disks lubricated by PAO 10, L-B104, L-F104, L-DOSS102, L-DOSS104, and L-DOSS108 at RT (with load of 100 N and frequency of 25 Hz).

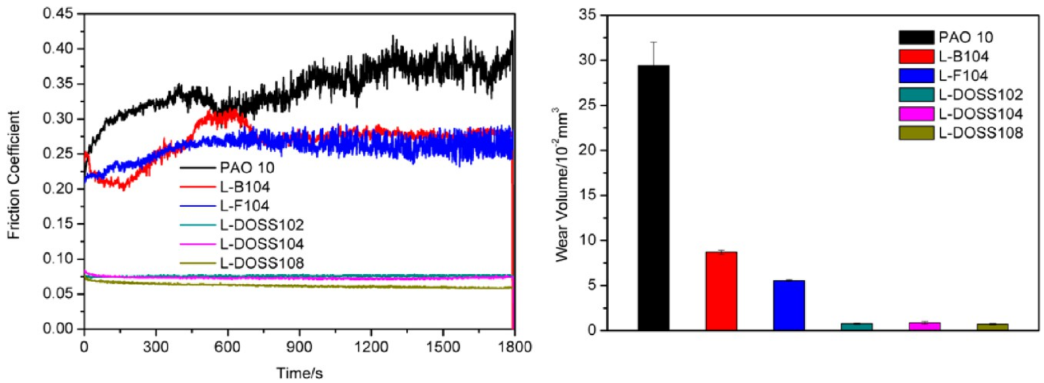


Figure 10. Evolution of friction coefficient/time and wear volume of the lower copper disks lubricated by PAO 10, L-B104, L-F104, L-DOSS102, L-DOSS104, and L-DOSS108 at 100 °C (with load of 100 N and frequency of 25 Hz).

But the reason for the higher viscosity of L-DOSS102 than that of L-DOSS104 is not very clear. Nevertheless, L-DOSS104 may be concluded to have the best viscosity-temperature characteristic among the sulfonate-based ILs.

Copper Strip Test. Sulfonate-based ILs are expected to have far lower corrosion levels and higher hydrolysis stabilities than conventional ILs due to their halogen-free characteristic. The copper strip test was used to confirm this assumption. Commercially available synthetic oil (PAO 10) and conventional ILs (L-B104 and L-F104) were used for comparison. The comparing photographs of the copper sheets are shown in Figure 3. Almost no corrosion was observed on the copper strips immersed in sulfonate-based ILs as well as PAO 10 and their corrosion grades were 1a or 1b. By contrast, severe corrosion occurred on the copper sheets soaked in L-B104 and L-F104 and the corrosion grades of these sheets were 3a and 3b, respectively (Table 1). These findings indicate that the synthesized sulfonate-based ILs, similar to synthetic oil PAO 10, have far lower corrosion property than conventional ILs L-B104 and L-F104.

Hydrolysis Stability. To confirm the expected hydrolysis stability of the sulfonate-based ILs, we stirred ILs with the same mass as water (w/w = 1/1) at 80 °C for several hours. Samples were then taken in regular intervals.[33] The pH of the aqueous samples was qualitatively recorded to monitor the extent of IL hydrolysis. L-B104 showed quick hydrolysis under the conditions of this experiment (within the first 30 min). No decrease in pH was seen in PAO 10, L-F104, L-DOSS102, L-DOSS104, and L-DOSS108 during the next 10 h. This finding indicates that the synthesized ILs are hydrolysis stable as PAO 10 in neutral aqueous solution up to 80 °C.

Detergency. sulfonate-based ILs are expected to have high deterging ability because of the high deterging ability of anion DOSS$^-$. Coking test was used to study the high temperature detergency of the synthesized ILs. Esterex adipate ester A51 was used as a base oil for comparing because synthetic ester oils have good deterging ability. From Table 2, it can be seen that the carbonaceous deposit of the base oil decreased significantly (over 50%) after adding 3% L-DOSS104. Thus, using the developed ILs as lubricants may be advantageous in machining operations because such ILs can restrain carbonaceous deposition, oil sludge and varnish formation on the metal contacts during the sliding process. Moreover, these ILs can loosen and remove the already formed harmful substances and keep the metal contacts clean.

Tribological Properties. The tribological properties of the sulfonate-based ILs were tested. Commercially available synthetic oil (PAO 10) and conventional ILs (L-B104 and L-F104) were used for comparison. The evolution of friction coefficient and wear volume of sliding discs under the lubrication of these lubricants at RT is shown in Figure 4. It is seen that L-DOSS102, L-DOSS104, and L-DOSS108 have similar friction-reducing properties at RT and the carbon chain length on the imidazole ring does not significantly influence this property, but it has influence on the antiwear properties of the sulfonate-based ILs because L-DOSS104 and L-DOSS108 have better antiwear properties than that of L-DOSS102. Although the friction coefficient of L-F104 is similar to those of the sulfonate-based ILs at the beginning of the test, it increases as

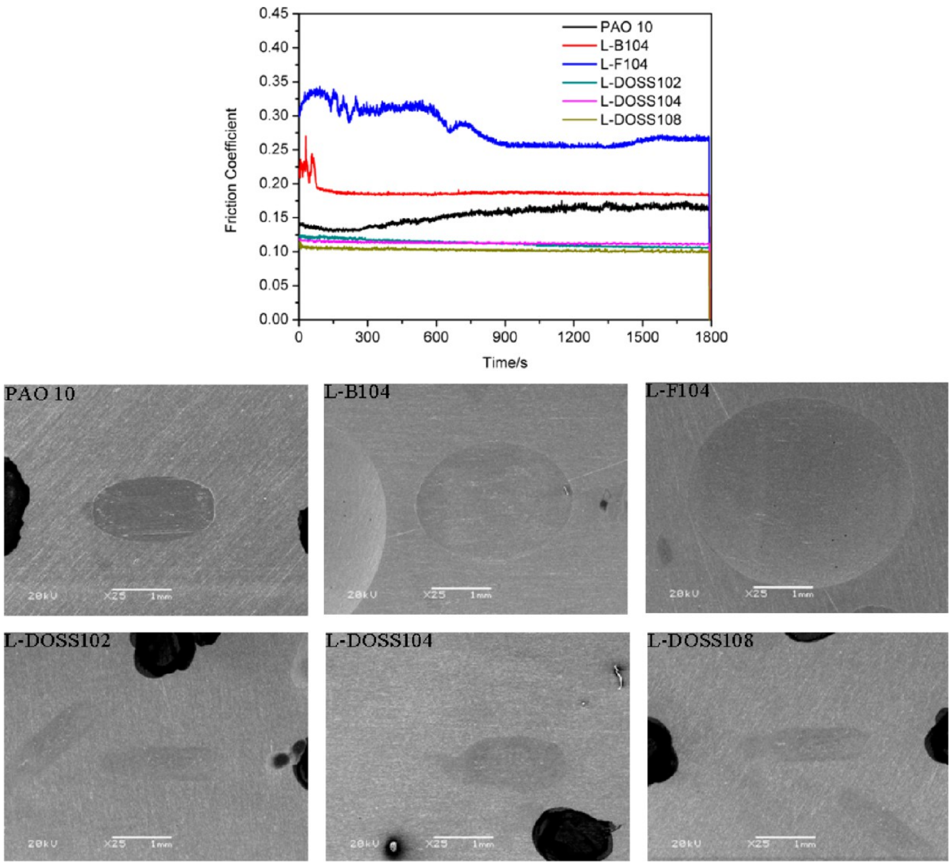


Figure 11. Evolution of friction coefficient/time and SEM micrographs of the lower aluminum disks lubricated by PAO 10, L-B104, L-F104, L-DOSS102, L-DOSS104, and L-DOSS108 at RT (with load of 100 N and frequency of 25 Hz, the black spots on the micrographs were marked to easily find the position of the wear scar).

the sliding process proceeds. The friction coefficient of L-B104 is lower than those of the sulfonate-based ILs, but the wear volume of the lower disc lubricated by L-B104 is larger than those of L-DOSS102, L-DOSS104 and L-DOSS108. It is worthy of note that, under the same test condition, PAO 10 has the worst tribology property among these lubricants. However, it exhibited much high friction coefficient (>0.4), so the test had to be stopped after 3 min. Figure 5 shows the three-dimensional morphology of the corresponding wear scars obtained during the sliding process. The wear scars after lubrication by L-B104 and L-F104 are obviously larger than those lubricated by the sulfonate-based ILs. These results further confirm the excellent antiwear properties of the newly synthesized ILs. The ILs appear to have comparable or even better tribological properties than PAO 10, L-B104, and L-F104 at RT. Undoubtedly, they can be used as alternatives to these lubricants.

The good lubricating behavior of the sulfonate-based ILs can be attributed to the polarity of their molecules as well as their ability to form ordered adsorbed layers, which results in the formation of effective physical adsorption protective films on the sliding metallic surfaces. Because of the relatively large size and strong adsorption ability of $DOSS^-$, the adsorption layer formed by sulfonate-based ILs is supposed to be much thicker than the adsorption layer formed by ILs such as L-B104 and L-F104, so it is more difficult to be destroyed. To confirm the rationality of this speculating, we detected the contact resistances of the lubricants under the friction of sliding pairs and show the results in Figure 6. It is obviously seen that the contact resistances of L-DOSS104 and L-DOSS108 are much higher than those of L-B104 and L-F104. Such a finding indicates abundant molecules absorption and much effective protection film are formed between the sliding pairs so that much effective antiwear property was achieved. The results further confirm our speculating and verify the high feasibility of applying L-DOSS10n as lubricants. Among the detected resistances, the contact resistance of L-DOSS102 is not much higher than those of L-B104 and L-F104. The reason why the behavior of L-DOSS102 is so different from the results of L-DOSS104 and L-DOSS108 is not very clear.

The tribological properties of the sulfonate-based ILs were also tested at high temperature (100 °C) and results are shown in Figure 7. From Figure 7, it can be seen that all the sulfonate-based ILs show very stable friction behavior, which is superior to L-F104 and even more so to L-B104. L-B104 exhibits a high and unstable friction coefficient which indicates that L-B104 is unsuitable to be used as lubricant at high temperature. But at 100 °C, L-F104 has better antiwear property than sulfonate-based ILs, which is probably due to the tribochemical reaction of $TFSI^-$ with the sliding metallic surface and the formation of a tribochemical reaction protective film on the surface to alleviate wear. Under the same test condition, PAO 10 also showed the worst tribology property among these lubricants. It exhibited a much higher friction coefficient (>0.5) and the test had to be stopped at the beginning of the test.

X-ray photoelectron spectrometry (XPS) analysis of the worn surfaces was performed to verify their surface composition after friction. XPS spectra results are shown in Figure 8.

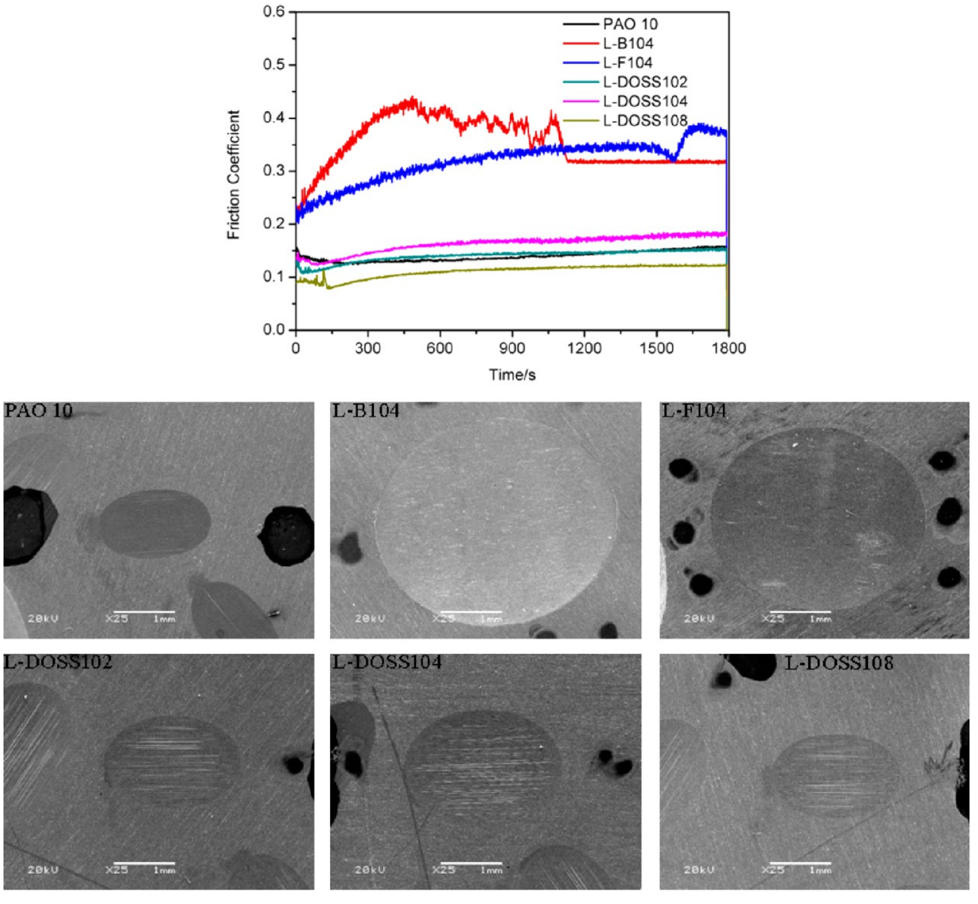


Figure 12. Evolution of friction coefficient/time and SEM micrographs of the lower aluminum disks lubricated by PAO 10, L-B104, L-F104, L-DOSS102, L-DOSS104, and L-DOSS108 at 100 °C (with load of 100 N and frequency of 25 Hz).

It is seen that no obvious difference is observed on the XPS spectra of Fe2p and O1s for worn steel surfaces lubricated by L-DOSS102, L-DOSS104 and L-DOSS108. On the XPS spectra of Fe2p, peaks appear at approximately 711.5 and 725.0 eV, which may correspond to FeO, Fe_2O_3, Fe_3O_4, Fe(OH)O, FeOOH, or FeF_2.[34] On the O1s spectra, wide peaks appear at the range of 529.0−533.0 eV, which may be assigned to Fe_2O_3, Fe(OH)O, or FeOOH. No obvious peak was observed on all the spectra of N1s and S2p even at high temperature as 100 °C. Thus, under the existing conditions, determination of the exact tribological protective film species on the worn steel surfaces is difficult. But on the basis of the data presented above, it can be speculated minimally here that the excellent tribological properties of the sulfonate-based ILs are more attributed to the formation of physical adsorption films than tribochemical reaction films on the sliding metallic surface, which may be removed by ultrasonic rinsing before the XPS tests. Because of the relatively large size of anion $DOSS^-$, the adsorption layer of sulfonate-based ILs is much thicker than the adsorption of L-B104 and L-F104 and more difficult to be destroyed. This feature contributes to the excellent antiwear properties of the sulfonate-based ILs. Our results were also confirmed by above measured contact resistance results and indicate undoubtedly the high feasibility of applying sulfonate-based ILs as lubricants.

Sulfonate-based ILs are effective lubricants not only for steel/steel contacts, but also for steel/aluminum and steel/copper contacts. Such contacts have been extensively used as engineering and bearing material in industry, but they are usually difficult to lubricate because of their low Young's modulus.[35−38] It is known that conventional ILs are poor lubricants for these contacts because such ILs promote oxidative and corrosive wear.[39,40] The sulfonate-based ILs were found to be excellent lubricants for steel/aluminum and steel/copper contacts due to their halogen-free and non-corrosion characteristics. The evolution of friction coefficient and wear volume of the copper and aluminum discs under the lubrication of the sulfonate-based ILs is shown in Figure 9−12. The tribological properties of the sulfonate-based ILs are far better than PAO 10 and traditional ILs such as L-B104 and L-F104 at RT. These properties are even more prominent at high temperature for steel/copper contacts. For steel/aluminum contacts, the wear volumes of the lower discs lubricated by L-B104 and L-F104 are much larger than those of the sulfonate-based ILs. They were too large to be measured by a MicroXAM 3D noncontact surface mapping profiler, so the SEM micrographs of these worn surfaces were given (Figures 11 and 12).

■ CONCLUSION

This paper reports on how a laxative inspires us to explore its lubricating property in conventional mechanical lubrication. A series of sulfonate-based ILs were synthesized and evaluated as lubricants for steel/steel, steel/aluminum, and steel/copper contacts. The synthesized ILs have far lower corrosion levels, higher hydrolysis stability, and better tribological properties than conventional ILs with fluorine-containing anions. The results of this study may be of particular interest for future, industrial applications of ILs in lubrication engineering.

ASSOCIATED CONTENT

Supporting Information

Additional details of the sulfonate-based IL characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Email: zhouf@licp.cas.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of this work by the "973" Program (2013CB632300), NSFC (51105353, 21173243), and Outstanding Youth Scholarship (21125316).

REFERENCES

(1) Aveyard, R. B.; Binks, P.; Fletcher, P. D. I.; Kirk, A. J.; Swansbury, P. *Langmuir* **1993**, *9*, 523−530.
(2) Khougaz, K.; Gao, Z.; Eisenberg, A. *Langmuir* **1997**, *13*, 623−631.
(3) Sager, W. F. C. *Langmuir* **1998**, *14*, 6385−6395.
(4) Luan, Y.; Xu, G.; Yuan, S.; Xiao, L.; Zhang, Z. *Langmuir* **2002**, *18*, 8700−8705.
(5) Zheng, P.; An, X.; Peng, X.; Shen, W. *J. Phys. Chem. B* **2009**, *113*, 13566−13575.
(6) Rosal, R.; Rodea-Palomares, I.; Boltes, K.; Fernández-Piñas, F.; Leganés, F.; Petre, A. *Chemosphere* **2010**, *81*, 288−293.
(7) Tsukahara, S.; Shishino, Y.; Fujiwara, T. *Langmuir* **2011**, *27*, 7392−7399.
(8) Cardinaels, T.; Lava, K.; Goossens, K.; Eliseeva, S. V.; Binnemans, K. *Langmuir* **2011**, *27*, 2036−2043.
(9) Ziyada, A. K.; Azmi Bustam, M.; Wilfred, C. D.; Murugesan, T. *J. Chem. Eng. Data* **2011**, *56*, 2343−2348.
(10) Brown, P.; Butts, C.; Dyer, R.; Eastoe, J.; Grillo, I.; Guittard, F.; Rogers, S.; Heenan, R. *Langmuir* **2011**, *27*, 4563−4571.
(11) Brown, P.; Butts, C. P.; Eastoe, J.; Fermin, D.; Grillo, I.; Lee, H. -C.; Parker, D.; Plana, D.; Richardson, R. M. *Langmuir* **2012**, *28*, 2502−2509.
(12) Lava, K.; Evrard, Y.; Van Hecke, K.; Van Meervelta, L.; Binnemans, K. *RSC Adv.* **2012**, *2*, 8061−8070.
(13) Hamada, S.; Mochida, T. *J. Organomet. Chem.* **2013**, *725*, 34−36.
(14) Fukaya, Y.; Iizuka, Y.; Sekikawa, K.; Ohno, H. *Green Chem.* **2007**, *9*, 1155−1157.
(15) Ferraz, R.; Branco, L. C.; Marrucho, I. M.; Araújo, J. M. M.; Rebelo, L. P. N.; Nunes da Ponte, M.; Prudêncio, C.; Noronha, J. P.; Petrovski, Ž. *Med. Chem. Commun.* **2012**, *3*, 494−497.
(16) Florindo, C.; Araújo, J. M. M.; Alves, F.; Matos, C.; Ferraz, R.; Prudêncio, C.; Noronha, J. P.; Petrovski, Ž.; Branco, L.; Rebelo, L. P. N.; Marrucho, I. M. *Int. J. Pharm.* **2013**, *456*, 553−559.
(17) Ye, C. -F.; Liu, W. -M.; Chen, Y. -X.; Yu, L. G. *Chem. Commun.* **2001**, *21*, 2244−2245.
(18) Minami, I. *Molecules* **2009**, *14*, 2286−2305.
(19) Bermúdez, M. D.; Jiménez, A. E.; Sanes, J.; Carrión, F. J. *Molecules* **2009**, *14*, 2888−2908.
(20) Zhou, F.; Liang, Y.; Liu, W. *Chem. Soc. Rev.* **2009**, *38*, 2590−2599.
(21) Qiao, D.; Wang, H.; Feng, D. *J. Eng. Tribol.* **2013**, *227*, 1261−1271.
(22) Cao, Y.; Chen, Y.; Sun, X.; Zhang, Z.; Mu, T. *Phys. Chem. Chem. Phys.* **2012**, *14*, 12252−12262.
(23) Shah, F. U.; Glavatskih, S.; MacFarlane, D. R.; Somers, A.; Forsyth, M.; Antzutkin, O. N. *Phys. Chem. Chem. Phys.* **2011**, *13*, 12865−12873.
(24) Uerdingen, M.; Treber, C.; Balser, M.; Schmittc, G.; Werner, C. *Green Chem.* **2005**, *7*, 321−325.
(25) PAN Pesticides Database: Dioctyl sodium sulfosuccinate. http://www.pesticideinfo.org.
(26) Hazardous Substances Data Bank (HSDB): Bis(2-Ethylhexyl) Sodium Sulfosuccinate. http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB.
(27) Bonhôte, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 1168−1178.
(28) Ziyada, A. K.; Azmi Bustam, M.; Wilfred, C. D.; Murugesan, T. *J. Chem. Eng. Data* **2011**, *56*, 2343−2348.
(29) Xu, W.; Cooper, E. I.; Austen Angell, C. *J. Phys. Chem. B* **2003**, *107*, 6170−6178.
(30) Blesic, M.; Swadźba-Kwaśny, M.; Holbrey, J. D.; Canongia Lopes, J. N.; Seddon, K. R.; Rebelo, L. P. N. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4260−4268.
(31) Brown, P.; Butts, C. P.; Eastoe, J.; Fermin, D.; Grillo, I.; Lee, H. -C.; Parker, D.; Plana, D.; Richardson, R. M. *Langmuir* **2012**, *28*, 2502−2509.
(32) Tokuda, H.; Hayamizu, K.; Ishii, K.; Md. Susan, A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2005**, *109*, 6103−6110.
(33) Wasserscheid, P.; van Hal, R.; Bösmann, A. *Green Chem.* **2002**, *4*, 400−404.
(34) NIST X-ray Photoelectron Spectroscopy Database, Version 4.1; National Institute of Standards and Technology: Gaithersburg, MD, 2012). Accessed on March 26, 2013. http://srdata.nist.gov/xps/.
(35) Wan, Y.; Liu, W.; Xue, Q. *Wear* **1996**, *193*, 99−104.
(36) Wan, Y.; Liu, W.; Xue, Q. *Wear* **1996**, *196*, 87−91.
(37) Mu, Z.; Zhou, F.; Zhang, S.; Liang, Y.; Liu, W. *Tribol. Int.* **2005**, *38*, 725−731.
(38) Wan, Y.; Cao, L.; Xue, Q. *Tribol. Int.* **1997**, *30*, 767−772.
(39) Espinosa, T.; Sanes, J.; Jiménez, A. -E.; Bermúdez, M. -D. *Wear* **2013**, *303*, 495−509.
(40) Liu, X.; Zhou, F.; Liang, Y.; Liu, W. *Tribol. Lett.* **2006**, *23*, 191−196.