Synergy of lithium salt and non-ionic surfactant for significantly improved tribological properties of water-based fluids

Yürüng Wang, Qiangles Yu, Meirong Cai, Lei Shi, Feng Zhou, 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

ARTICLE INFO

Keywords:
Ionic liquids
Non-ionic surfactant
Water-based lubricant
Additives

ABSTRACT

The paper reports the synergistic effect of lithium salt and non-ionic surfactant in improving the tribological and anticorrosion performance of water-based lubricant. The synergy comes from the in-situ formation of ionic liquids type of complex. The lubricating and anti-wear behaviour of 2% lithium salt +18% non-ionic surfactants additives in water for steel/steel contacts were evaluated with lithium salt and surfactant only as the control comparisons. The tribological results show that this additive has better lubricating performance than 2% lithium salt or 20% non-ionic surfactant. The lubricating mechanism was tentatively discussed according to electrical contact resistance measurement and X-ray photoelectron spectroscopy analysis.

1. Introduction

At present, the petroleum based lubricants are commonly used lubricating medium, which can significantly reduce the energy consumption caused by the friction, and greatly prolong the service life of machinery and equipment. But in some special fields (coal mining, metal processing, etc), the application of petroleum based products is restricted mainly because of its shortcomings, such as low flash point, flammable, low coefficient of thermal conductivity, etc and a threat to environment. Therefore, the low cost, non-combustible and high thermal conductivity coefficient and high specific heat capacity of water has become a good choice in these specific areas [1]. Water is not only a green and environmental-friendly resource, but abundant in content and can be seen everywhere. Water-based lubricants have a large number of advantages, such as incombustibility, excellent cooling ability, great cleaning effect, environmental compatibility and low cost [2]. At present, the cheap water-based lubricants have gradually become the leading products in the metalworking fluid market [3]. Especially, the water-based cutting fluids as lubricants can reduce the abrasion, the adhesion and the friction of the contact region between machined surface and flank face, chips and rake face [4]. So they are widely suitable for the industrial machining operations such as high speed cutting and grinding. However, compared with the mineral or synthetic oil, the existing water-based lubricants have lower viscosity, poor lubricating property, poor antitrust and anticorrosion performances. These characteristics profoundly limit its practical applications in industry [5]. To solve these problems, a number of water-based lubricant additives like corrosion-inhibitors, antitrust agents, antiwear additives, preservatives and thickeners, have been developed rapidly in recent years [6]. These additives play an important role in improving their functionality such as anti-corrosion, anti-rust, anti-wear, anti-pressure and excellent lubricating properties [7–11]. Most of them require tedious and costly synthesis. So it is urgent to develop a kind of low cost and without synthetic route water based additives.

Ionic liquids (ILs) as lubricants and lubricant lubricating oil additives have been widely studied in the last fifteen years [12–19]. It is well known that ILs have excellent tribological performances than traditional lubricants owing to the unique physicochemical properties and dipolar structure [20–24]. At present, there are few reports about ILs as water additives [25–29]. Unfortunately, a majority of reported ILs are typically made up of complicated structures including organic cations like the alkyl substituted nitrogen-containing cations and various anions such as fluorinated anions, which lead to their synthesis complicated, purification difficult and high cost drawbacks [30]. Therefore, these fundamental shortcomings compel us to find simple and low cost alternatives with excellent lubricating properties.

Recently, our group reported a new route of in situ forming IL lubricant additives in base oil without the synthesis [26–30]. These ILs not only are extremely easy to prepare, but also have excellent antifriction and anti-wear performances. “In situ” forming ILs can be used as additives in water? The key point is that in situ preparation of ILs have good solubility in the water. It is well known that the non-ionic surfactants, such as octyl phenoxy poly Ethoxy (OP) and Tween (TW), have been widely used in many fields because of its good dispersion, emulsifica-
tion, wetting and solubilization properties. Based on the advantages of nonionic surfactants, we prepared \([\text{Li}](\text{non-ionic surfactants})\) bis(trifluoromethane sulfonyl) imide salts, which have good solubility in the water. The tribological performances of \([\text{Li}](\text{non-ionic surfactants})\) salts as additives in water were studied by friction and wear test. The results showed that these additives have good friction reducing and antioxidation ability. This study provides a new strategy to improve the tribological performances of water by synergy of lithium salt and non-ionic surfactant by in-situ forming ionic liquids without the synthesis process.

2. Experimental section

2.1. Chemicals

The ionic liquid \([\text{Li}](\text{TW})\) bis(trifluoromethane sulfonyl) imide (LI-TW) was formed by stirring a suitable mass ratio of lithium bis(trifluoromethane sulfonyl) imide (LI) and Tween-20 (TW) at 40 °C ± 20 °C until transparent liquids were obtained. For example, 2% LI-TW was prepared by stirring 1:9 mass ratio of LI /TW at RT until transparent liquids were obtained. And using the same method, the IL \([\text{Li}](\text{OP})\) bis(trifluoromethane sulfonyl) imide (LI-OP) was obtained. Fig. 1 shows the chemical structures of LI, Octyl Phenoxo Poly Ethoxy (OP) and TW. The LI, OP and TW were purchased from J & K Scientific Ltd, Tianjin Feng Yue Chemical Co., Ltd. and Sinopharm chemical reagent Co., Ltd., respectively. The deionized water was used in all the experiment. All the percentage content mentioned in this paper refers to the mass concentration.

2.2. Spectroscopic characterizations

A Nicolet iS10 FTIR spectrometer between 4000 and 400 cm\(^{-1}\) with a resolution of 1 cm\(^{-1}\) was used to record the FTIR spectra of the ILs in suit. For the infrared (IR) spectroscopic measurements, a droplet of the liquid sample was spread on a dry KBr piece.

2.3. Viscosity and cast iron strip test

A SYP1003-III viscometer was used to examine the kinematic viscosity of different lubricants at 25 °C. The cast iron strip corrosion test was performed by using the GB6144-85 procedure. Four pieces of cast iron strips were immersed into 16 ml of water, 2% LI, 20% TW and 2% LI-TW, respectively. They were placed in a constant container of 55 °C ± 2 °C for 24 h. At the end, the samples of cast iron strips were taken out and then evaluate the corrosion level by comparing with the corrosion standards.

2.4. Friction and wear test

Two ILs, LI-TW and LI-OP consisting of different mass ratios of LI /TW and LI /OP (1:190, 1:30, 1:19, 1:9, 3:17, 1:4, 1:3) were added to the same quality of water to make the mass concentrations of 0.1%, 0.5%, 1%, 2%, 3%, 4% and 5%, respectively.

With an AISI 52100 bearing steel ball (hardness of 700–800 HV), diameter of 10 mm) sliding against a lower stationary disc (ø 24 mm ± 7.9 mm), the tribological properties were measured on an Optimal SRV-IV oscillating reciprocating friction and wear tester. The lower stationary disc was composed of AISI52100 bearing steel with hardness of 750–850 HV. The discs were polished to the mean roughness (Ra) of steel is about 0.02 µm by using CW400–CW2000 SiC abrasive paper in distilled water before the friction test. The mean roughness (Ra) of steel ball is about 0.02 µm. After the discs were cleaned completely with ethanol, put one drop of lubricant onto the ball-on-disc contact area. Each specimen was carried out for 3 times at a load of 100 N, frequency of 25 Hz, test duration of 30 min, amplitude of 1 mm and relative humidity of 20–50%. The best concentration of the ILs was selected and then carried on the frequency conversion and the variable load experiment. The corresponding friction curves and electrical contact resistance were recorded automatically on a computer using a data-acquiring system linked to the SRV-IV tester. The wear volumes of the low discs were measured via a MicroXAM-SD non-contact surface mapping profiler after washing the discs with ethanol.

A JEOL JSM-5600LV scanning electron microscope(SEM) (JEOL, Japan) was used to examine the worn surface morphologies of wear scars of the lower discs lubricated, respectively, by water, 2% LI, 20% TW and 2% LI-TW during a load ramp test from 100 to 400 N. The chemical composition of the wear scars after SRV-IV tests were performed on a PHI5702 multifunctional X-ray photoelectron spectroscopy (XPS) by using Al-K α radiation as the exciting source and the X-ray spot size of 650 µm. With using the binding energy of contaminated carbon (C1s:284.8 eV) as the reference, a passing energy of 29.35 eV of resolution with resolution of ± 0.3 eV was used to determine the binding energies of the target elements.

3. Results and discussion

3.1. Spectroscopic characterizations

The coordination between Li\(^+\) and O in CH\(_2\)–O groups could be legitimately affirmed by the assignments of IR bands [28,31]. The non-ionic surfactant OP as an example was used as base liquid to prove the main points of the coordination. Fig. 2 exhibits the IR spectra between 1520 and 3200 cm\(^{-1}\) of the C–H stretching mode of the LI-OP complex systems at different mass ratio, which put the corresponding adopted IR spectra of pure OP as comparison to demonstrate the Li\(^+\)–O coordination. The strong band at 2872 cm\(^{-1}\) of the lithium salt was added to OP, appearing at 2882 cm\(^{-1}\) and 2934 cm\(^{-1}\) corresponding band of LI-OP had a trend to split into two peaks after the lithium salt was added to OP, appearing at 2882 cm\(^{-1}\) and 2934 cm\(^{-1}\). This implies that some oxygen atoms from the –CH\(_2\)OC– group coordinate strongly with the Li\(^+\) to move the C–H coordination. The strong band at 2872 cm\(^{-1}\) legitimately a Lewis acidic complex cation [Li(OP)]\(^+\) that the donation of lone pairs on an oxygen atom of a OP molecule to a Li\(^+\) cation causing the weakening of the bond feature of CH\(_2\)–O group. Therefore, the C–H stretching band shifts to 2934 cm\(^{-1}\) for the LI-OP at 1:3:1 mass ratio. However, the C–H stretching band has a smaller shift when LI-OP content is 1:1 because of more free OP molecules that influence the
shift of C–H stretching band on the spectrum. And the existence of a large number of un-coordinated OP molecules at 1:9 may hide the minor movement of the C–H stretching band on the IR spectrum. In addition, other C–H bonds far from Li+–O coordination have a slight effect. These results definitely demonstrate that Li+ coordinate with CH₂–O in non-ionic surfactant. Furthermore, the observed phenomena of ILs preparation also further prove this hypothesis.

3.2. Viscosity and cast iron strip test

Table 1 exhibits the results of kinematic viscosity (25 °C) and cast iron strip test lubricated by different lubricants. It demonstrates that the kinematic viscosity of LI-TW and LI-OP in water was slightly increased than other lubricants at 25 °C. Compared with the corrosion grade of water and 2% LI, the corrosion level of 2% LI-TW has significantly reduced during the cast iron strip tests. It indicates that LI-TW has the potential to become the water-based additive.

3.3. Friction and wear test

The antifriction and antwear properties of LI-TW and LI-OP as lubricant additives in aqueous solution were investigated for the steel–steel contact at room temperature. It is explicitly found the LI-TW as water-based lubricant additive exhibited much better lubricating properties than other lubricant additives according these results. The variation of friction coefficient (COF) and wear volumes of lower sliding discs lubricated by these LI-based ILs additives in aqueous solution are presented in Figs. 3–5. Each value or curve in Figs. 3–5 represents the average values of three tests.

Table 1

<table>
<thead>
<tr>
<th>Lubricants</th>
<th>Kinematic viscosity at 25 °C (mm²/s)</th>
<th>Corrosion grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.773244</td>
<td>D</td>
</tr>
<tr>
<td>2% LI</td>
<td>0.813460</td>
<td>D</td>
</tr>
<tr>
<td>20% TW</td>
<td>2.851680</td>
<td>C</td>
</tr>
<tr>
<td>2% LI-TW</td>
<td>3.350724</td>
<td>B</td>
</tr>
<tr>
<td>20% OP</td>
<td>19.492384</td>
<td>C</td>
</tr>
<tr>
<td>2% LI-OP</td>
<td>29.242730</td>
<td>B</td>
</tr>
</tbody>
</table>

* : B, no rust but a slight loss of light; C, light rust and slight loss of light; D, heavy rust or severe loss of light.

Fig. 2. FTIR spectra of the C–H stretching mode of LI-OP at different mass ratio.

lubricant additives in aqueous solution. Fig. 4 reveals that 2% LI-TW and 2% LI-OP as water-based additive have best excellent lubrication and anti-wear properties than that of water, 2% LI, 20% TW and 20% OP by decreasing the friction and wear of steel discs. Although 2% LI-OP can significantly reduce the COF and wear volume, it obviously has higher COF and wear volumes than 2% LI-TW, indicating that the lubricating and anti-wear performances of LI-TW are much better than that of LI-OP. Why these Li(non-ionic surfactant) bis(trifluoromethane sulfonyl) imide can improve the lubrication and wear resistance of water? The above results show that we simply use the powder Li or non-ionic surfactant dissolved in water, they only slightly reduce friction and wear but accompanied by severe corrosion. When the addition of [Li(non-ionic surfactant)] bis(trifluoromethane sulfonyl) imide not only can significantly improve tribological performances of water, but also alleviate the corrosion (Table 1). This result indicated that the lithium salt and non-ionic surfactant do have a synergistic effect, which may be due to the in situ formed IL. The in-situ formed large size ion pairs have good affinity (boundary adsorption capability) to substrates so as to exhibit excellent lubricating and antiwear property. Compared with the OP molecule, the size of TW molecule is bigger so that LI-TW IL adsorbed layer is much thicker than that of LI-OP ILs and more difficult to be destroyed. So LI-TW ILs have better lubricating and anti-wear capacity.

To further investigate the friction reduction and extreme-pressure (EP) ability of [Li(non-ionic surfactants)] bis(trifluoromethane sulfonyl) imide salts as water-based lubricant additives, the experiments of changing the applied frequency and load were performed. Take LI-TW as an example, the evolution of COF with the frequency and load was shown in Fig. 5a and b. Fig. 5a shows a load ramp test from 100 to 400 N stepped by 100 N intervals at room temperature with 5-min test duration for each load. From this test, we can see that the load carrying ability of water containing 2% LI-TW is more than 400 N, and the value of COF is lowest and very stable in the whole friction process. In comparison, the average COF of 2% LI and 20% TW is very large, and reach 0.36 and 0.16, respectively. When the load reaches 300 N, 20% TW occurs lubrication failure. So the maximum load carrying capacity of 20% TW is only 200 N. This indicates that 2% LI-TW as the water-based lubricant additive has best lubricating and EP capacity compared with other two lubricant additives. Meanwhile, a frequency ramp test with three different additives from 10 to 40 Hz stepped by 5 Hz intervals with 5-min test duration for each frequency at 25 °C is shown in Fig. 5(b). As you can see, 2% LI-TW shows a very low and stable COF during the entire evolution of frequency. However, the COF of other two additives is very high and fluctuates all the testing process. This result further illustrates 2% LI-TW has excellent lubricating and reduce friction performance.

3.4. Analysis of worn surfaces

To further display the wear situations, SEM measurement of the lower sliding discs lubricated by 2% LI, 20% TW and 2% LI-TW were performed during a load ramp test from 100 to 400 N (SRV: stroke=1 mm, frequency=25 Hz, duration=30 min and temperature=25 °C). Fig. 6(a, a1) presents severe corrosion and scratches of the worn steel surface lubricated by 2% LI with a deeper and wider wear scar, and a great many deep grooves. Meanwhile, we can also see that the steel surface lubricated by 20% TW have a rather deep and long wear scar with severe scuffing and many deep grooves in Fig. 6(b, b1). However, Fig. 6(c, c1) shows a greatly shallow and narrow wear scar of the steel worn surface lubricated by 2% LI-TW with some slight grooves. Compared with the steel worn surfaces of 2% LI and 20% TW, the 2% LI-TW have a rather smooth worn surface with much alleviated scuffing and corrosion, which further suggests that 2% LI-TW in aqueous solution have excellent lubricating, extreme-pressure, antiwear and no-corrosive properties. These results are consistent with the data of friction and wear test above mentioned, and sufficiently
demonstrate that 2% LI-TW as the water-based additive has good anti-wear properties. This indicates that the LI-TW is expected to be an effective lubricating and wear resistance additive for water-based fluid.

3.5. Mechanism analysis

From the above results, it is definitely shown that the [Li(non-ionic surfactants)] bis(trifluoromethane sulfonyl) imide salts have the potential to be used as water-based lubricant additives. In order to get more information about the function mechanism of [Li(non-ionic surfactants)] bis(trifluoromethane sulfonyl) imide in aqueous solution through electrical contact resistance (ECR) measurement and X-ray photoelectron spectroscopy (XPS) were utilized.

According to previous reports, ECR measurement is a powerful evidence to prove the formation of an insulating tribo-film on the steel–steel contact surface [32]. To further illustrate the function mechanism of [Li(non-ionic surfactants)] additives in aqueous solution, the in situ ECR measurement was performed. Fig. 7 shows the ECR changes with the friction time lubricated by water, 2% LI, 20% TW, 20% OP, 2% LI-TW, 2% LI-OP at room temperature. From the result, we can see that...
the values of ECR of 2% LI-TW as additives in aqueous solution is much higher than that of water, 2% LI and 20% TW. This indicates that 2% LI-TW as water-based lubricant additives forms a relatively stable insulating tribofilm in the contact area during the friction process, which is consistent with the previous tribological results. Perhaps it’s because that the in-situ formed large size ion pairs have good affinity (boundary adsorption capability) to substrates so as to the forming the thicker protective film. So that [Li(non-ionic surfactants)] additives could effectively decrease the friction and wear on the metal surface.

The XPS analysis is able to verify the tribochemical products and the chemical states within a boundary film on the steel worn surfaces after friction. Fig. 8 presents the XPS spectra of Fe2p, O1s, S2p, Li1s, N1s and F1s of the worn surfaces lubricated by (a) neat LI-TW and (b) 2% LI-TW during a load ramp test from 100 to 400 N. From the picture, we can see the binding energies of O, S and Li on the steel worn surfaces lubricated by 2% LI-TW are all different from the binding energies of neat ILs. This result show that the specific tribochemical reaction take place during the friction process and produced new compounds. The XPS peak of Fe2p of worn surfaces lubricated by 2% LI-TW appear at 710.9 eV and 724.7 eV integrated with the peak of O1s at approximate between 529.8 and 532.6 eV, which is likely to be attributed to Fe2O3, Fe(OH)O, FeOOH, FeO, Fe2O4 [33]. And one peak of S2p at approximate 169.2 eV on the worn steel surface lubricated by 2% LI-TW is possibly ascribed to Fe2(SO4)3, FeSO4 or organic sulfo [33]. Moreover, the peak of Li1s of the worn surface lubricated by 2% LI-TW appears at about 55.6 eV, which may correspond to Li2O or Li2SO4 [33]. By the apparent peak of F1s at 688.8 eV (Fig. 8b), it illustrates that fluorinated carbons form on the worn steel surface [33]. What’s more, the binding energies of N and F of the worn surface lubricated by 2% LI-TW almost no move compared with that of neat ILs. These results suggest that 2% LI-TW may form a physical adsorption protective film on the steel worn surfaces. The above results indicate that LI-TW as the water-based additive not only experienced the formation of physical adsorption film by large size ion pairs, but also occurred a complicated chemical reactions on the steel surface during the friction with the formation of a protective film containing of Fe2O3, Fe(OH)O, FeOOH, Fe2(SO4)3, FeSO4 etc. This protective film can prevent the direct contact of the friction pair surface, and plays the role of lubrication and abrasion resistance.

According the spectroscopic characterizations of LI-OP, we speculate that the proposed ILs LI-TW with a weakly Lewis acidic complex cation [Li(TW)]+ can be obtained through the donation of lone pairs on an oxygen atom of a TW molecule to a Li+ cation [30]. The in-situ formed large size ion pairs have good affinity (boundary adsorption capability) to substrates so as to exhibit excellent lubricating and
antimwear property. Moreover, the lubricating mechanism of the water-based additives on the contact surface was tentatively discussed by ECR measurement and the surface composition analysis XPS. The analysis results indicated that complicated tribo-chemical reactions occurred on the contact surface, contributing to a relatively stable tribo-thin film, while the physical adsorption is likely to occur during the friction process. So this protective film formed by the physical adsorption and the tribo-chemical reaction is helpful to reduce friction and wear.

4. Conclusion

A new kind of [Li(non-ionic surfactant)] bis(trifluoromethane sulfonyl) imide IL was prepared by in-situ no-synthesis process, i.e. only blending. These ILs possess good solubility in water. The cast iron strip corrosion test shows that [Li(non-ionic surfactant)] bis(trifluoromethane sulfonyl) imide as additive can reduce corrosion of metal substrate. The addition of 2% LI-TW and LI-OP in water can significantly reduce friction and wear. The result of ECR measurement reveals that 2% LI-TW additive forms the effective boundary protective film during sliding process. XPS analysis demonstrates that the physical adsorption and tribo-chemical reactions occur on the steel contact surface, both contributing to the formation of a relatively stable protective film. So these lubricant additives have excellent friction reduction and abrasion resistance. These results show that [Li(non-ionic surfactant)] bis(trifluoromethane sulfonyl) imide have a potential as a highly efficient water-based lubricant additive applied in water-based metal cutting fluids to substitute of the traditional additives.

Fig. 8. XPS spectra of O1s, Cls, N1s and Fe2p of the worn steel surfaces lubricated by (a) Neat LI-TW (b) 2% LI-TW during a load ramp test from 100 to 400 N (SRV: stroke=1 mm, frequency=25 Hz, duration=30 min and temperature=25 °C).

Notes

The authors declare no competing financial interest.

Acknowledgments

The authors acknowledge the financial support from the National Natural Science Foundation of China (Grant Nos. 51675512, 51405477 and 51227804), Natural Science Foundation of Gansu Province (Grant No.1606RJZA051) and “973” program (2013CB632301).

References


[33] (http://srdata.nist.gov/xps/).