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The ecotoxicity and tribological properties of choline amino acid ionic liquid lubricants

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ABSTRACT

This research into environmentally-friendly ionic liquids (ILs) used a series of choline amino acid ILs ([Ch][AA] ILs) prepared from choline cations and several amino acid anions. Their physicochemical and tribological properties were tested, and the results showed that [Ch][AA] ILs had good lubricating properties for different friction pairs at room temperature (RT). Their toxicities were checked against three aquatic organisms: brine shrimp, zebrafish and green algae. The results showed that they have a remarkably low toxicity. Versus traditional IL 1-butyl-3-methyl imidazolium tetrafluoroborate (L-B104), the [Ch][AA] ILs had comparable or even better physicochemical and tribological properties. More importantly, they had the environmentally features of biodegradability and non-toxicity.

1. Introduction

Ionic liquids (ILs) are substances consisting of anions and cations that are liquid below 100 °C [1]. ILs have wide electrochemical windows, low volatility, good conductivity, no combustion, and other properties, and are widely used in electrochemistry, separation and purification and organic synthesis reactions [2,3]. ILs were first used as synthetic lubricants in 2001 [4]. Since then, various halogen-containing ILs have been prepared and investigated as fungible lubricants of fossil one. While they are beneficial only to reduce the air pollution, but it cannot reduce water pollution, especially water-soluble ILs.

Halogen-containing ILs are easily hydrolyzed in water to deliver highly toxic and corrosive hydrogen fluoride that restricts broad applications of these ILs [5–12]. Moreover, their impacts on aquatic organisms and ecosystems are unknown [13], and this has aroused people's concern about their toxicity to aquatic organisms [14–16] and corrosion to equipment. Thus, it is essential to determine the impacts of ILs on aquatic ecosystems. This will further reduce atmospheric pollution and avoid human diseases caused by pollution [17]. Recently, halogen-free ILs have attracted attention from chemists due to their biodegradability, non-toxicity, and environmentally benign features. Importantly, the physicochemical properties and tribological performance features of these ILs as lubricants are comparable to conventional ILs, and can be even better [5,18].

Choline is an essential nutrient for the synthesis of cell membranes and is a component of lecithin. It is widely found in animals and plants and is biodegradable [19–22]. Amino acids are raw materials for the synthesis of proteins. They not only have low toxicity and good biodegradability but are also good lubricants [23–26]. In this work, choline was used as a cationic donor, and eight amino acids (glycine, alanine, leucine, methionine, histidine, proline, phenylalanine and tryptophan) were used as anionic donors to synthesize IL lubricants ([Ch][AA] ILs). The tribology performance and aquatic ecological toxicity tests of these ILs show that [Ch][AA] ILs are high performance and environmentally friendly lubricants.

2. Experimental

2.1. Chemicals and materials

The IL 1-butyl-3-methyl imidazolium tetrafluoroborate (L-B104) was from Lanzhou Institute of Chemical Physics. The raw materials for the preparation of [Ch][AA] ILs were used without further purification: choline hydroxide (ChOH, 45% in water), glycine (Gly, 99%), alanine (Ala, 99%), histidine (His, 98%), proline (Pro, 99%), phenylalanine (Phe, 99%) and tryptophan (Trp, 99%). These were purchased from J&K

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Chemicals (Beijing, China); leucine (Leu, 99%) and methionine (Met, 99%) were from Aladdin Chemicals (Shanghai, China).

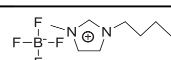
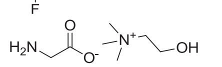
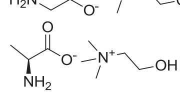
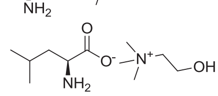
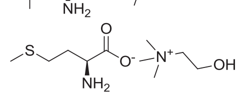
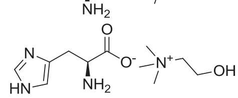
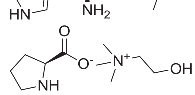
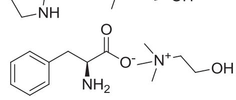
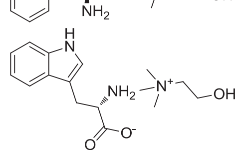
2.2. The preparation and characterization of [Ch][AA] ILs

The [Ch][AA] ILs were synthesized through an economical and feasible method. A typical process is shown in the Supplementary Information. The ^{1}H NMR and ^{13}C NMR spectra of the [Ch][AA] ILs were acquired on an Agilent 400 MHz nuclear magnetic resonance spectrometer (NMR), using D_2O as the solvent and the appropriate signal for residual solvent protons as the reference. The Fourier transform infrared (FT-IR) spectra of the [Ch][AA] ILs were recorded on a Nicolet-10 Fourier transform infrared (FT-IR) instrument. The high-resolution mass spectra (HRMS) used a Bruker Dalton micrOTOF-Q II instrument (Billerica, MA). The thermal stabilities of the samples were measured on a Netzsch synchronous thermal analyzer system (DSC/DTA-TG, STA 449F3) under nitrogen atmosphere with a flow rate of 50 mL/min. The temperature increased from RT to 600 °C, and the heating rate is 10 °C/min. The hydrolysis stability of the samples were tested according to our previous work [27–31]. Each sample was mixed with equal molar amounts of water, and then stirred at RT. The pH was measured to indicate hydrolysis stability after 30 min, 1 h, 2 h until 48 h. All the ILs were miscible with water, and the mixed solutions were used to measure the pH value changes. The viscosities of the [Ch][AA] ILs were studied at 40 °C and 100 °C, respectively, using a SYP1003-III kinematic viscosity tester. Viscosity indexes were calculated to evaluate the viscosity temperature characteristics of the samples. The molecular structures, names and codes of [Ch][AA] ILs and IL L-B104 are shown in Table 1.

2.3. Corrosion test

An electrochemical workstation (CHI660E B15086) was adopted to qualitative analysis of the corrosion of [Ch][AA] ILs. In this experiment, the three-electrode cell was made up of a saturated calomel electrode (as the reference electrode), a platinum foil of 1 cm^2 (as the counter electrode) and a steel rod with a geometric area of 0.5 cm^2 (as the working electrode). The surfaces were polished with emery paper (grade 400–800–1200–1500) and then rinsed with distilled water and acetone. For polarization measurements, the corresponding open-circuit potential is ±200 mV, the scan rate is 0.3 mV s^{-1} and the temperature is 25 °C. The electrochemical impedance spectroscopy (EIS) measurements were performed from 10^4 Hz to 10^{-2} Hz using a sinusoidal AC perturbation with an amplitude of 5 mV. Before the test, the electrode was immersed in ethanol at OCP (open circuit potential) until a steady state was obtained. Polarization curves and Nyquist plots were measured to obtain the electrochemical parameters and to evaluate the corrosion of the ILs. At the same time, a copper strip corrosion test was also used to judge the corrosion of [Ch][AA] ILs and the detailed process is presented in the Supplementary Information.

Table 1
The chemical structures and codes of the used samples.

Samples (code)	Chemical structure
1-Butyl-3-methylimidazolium tetrafluoroborate (L-B104)	
Choline Glycine ([Ch][Gly])	
Choline Alanine ([Ch][Ala])	
Choline Leucine ([Ch][Leu])	
Choline Methionine ([Ch][Met])	
Choline Histidine ([Ch][His])	
Choline Proline ([Ch][Pro])	
Choline Phenylalanine ([Ch][Phe])	
Choline Tryptophan ([Ch][Trp])	

2.4. Friction and wear test

The tribological properties of [Ch][AA] ILs and L-B104 were studied on an Optimol SRV-V oscillating reciprocating friction and wear tester. The tests were performed on three friction pairs at RT. The specification of the upper AISI 52100 bearing steel ball and the materials, specifications, and processing methods of the lower stationary disks are the same as the former [27,28,31]. In this test, the specific test conditions are 100 N, 25 Hz, 1 mm, and 30 min. The relative humidity of the test environment is about 35–45%. After the test, the wear volumes were measured by a non-contact surface mapping profiler (BRUKER-NPFLEX). Each set of data were repeated three times, and the averaged values were reported. The worn surfaces were analyzed with a PHI 5000 VersaProbe III X-ray photoelectron spectroscopy (XPS, PHI-CHINA Limited Company). During the test, monochromated Al Kα (1486.6 eV) was used as X-ray source; the X-ray beam surveyed 100 μm, (25 W, 15 kV). The photoelectron take-off angle is 45°, and the binding energy of C1s (C-C/C-H: 284.80 eV) was used to calibrate the peak position.

2.5. Toxicity test

In the research of environmentally-friendly ILs, toxicity is one of the most important evaluation criteria for green lubricants. Here, brine shrimp, zebrafish and green algae were used to evaluate the toxicity of [Ch][AA] ILs.

Brine shrimp purchased from Advanced Science and Technology Companies in the United States to evaluate the ecotoxicity of [Ch][AA] ILs. These shrimp are invertebrate organisms that inhabit estuarine ecosystems. They are widely employed in laboratory bioassays for toxicological applications through the estimation of the medium lethal concentration (LC_{50}). Artificial salty water (larvae medium) was obtained by dissolving 10 g marine salt in 1 L of distilled water and the pH of the solution was adjusted to 7.0–8.0 using $NaHCO_3$ to prevent pH changes during incubation (lethal to brine shrimp). Then it was divided into two parts. One part (A) was used for aquaculture shrimp: Shrimp eggs were added to the solution and incubated for 48 h at 28 °C under aerobic conditions. The other part (B) was prepared to configure different concentration gradients of the IL lubricants solution. Here, 100 μL of A containing 15–20 brine shrimp and 100 μL B were added to 96-well plates. Each concentration was done in three parallel runs. After 24 h of exposure, the live larvae were counted with microscope and, the LC_{50} value (Table 3) was calculated [32].

Zebrafish are one of the most widely model species used in the life sciences, because of their small size, low cost breeding and water quality tolerance. This study followed procedure 203 of the OECD (1992). Zebrafish were purchased from Eze-Rinka Biological Science and Technology Limited Company. Before the toxicity test, the fish were acclimated in the laboratory environment for at least 7 days with 12:12 h light/dark at 26 ± 1 °C to confirm normal growth condition and the mortality rate of zebrafish was zero. Prior to the formal experiment, preliminary experiments were performed to screen the death rate (10%–90%). The ILs were configured with different concentration gradients, and the solutions were added to glass beakers. Each beaker held 10 fish and 1.5 L solution. This confirmed that the solution has enough dissolved oxygen. The fish behavior was observed carefully, if there was no noticeable physical movement, then fish were considered dead and removed immediately. The number of dead fish was carefully recorded. The fish were not fed during the test to prevent fecal interference. After 96 h, the entire toxicity test was ended, and the median lethal concentration LC_{50} was calculated [33,34].

Green algae were purchased from Institute of Hydrobiology, Chinese Academy of Sciences. The toxicity test was conducted according to the GB/T 21805–2008 procedure. The green algae were propagated in an Erlenmeyer flask in GB11 medium with an initial concentration of approximately $5*10^4$/mL. The flask was kept in the laboratory and illuminated with white fluorescent light; the light intensity is $30 \pm 5\,\text{lE}\,m^{-2}\,s^{-1}$. This intensity kept the algal cells growing under normal conditions at 25 ± 5 °C and was used for testing in the logarithmic phase.

The samples were placed in different concentration gradients. Green algae was then added, and the algal concentration was measured using the OD_{650} values (the absorbance when wavelength is 650 nm). The half concentration effect (EC_{50}) was calculated to evaluate the toxicity. The most common toxicity test for algae is the growth inhibition test with a cultured species [35]. Each sample had 3 replications.

3. Results and discussions

3.1. Structure characterization and stability analysis

The structure and purity of [Ch][AA] ILs were confirmed with ^{1}H NMR, ^{13}C NMR, FT-IR and HRMS spectroscopic data. Detailed data are presented in the Supplementary Information.

ILs are often used as lubricants and should have good thermal stability and hydrolytic stability. The thermogravimetric (TG) and pH change curves of L-B104 and [Ch][AA] ILs are shown in Fig. 1. Fig. 1a shows that almost no weight change appeared before 150 °C for all tested samples. When the temperature increased to nearly 160 °C, the [Ch][AA] ILs started gradually decomposed; the [Ch][Gly], [Ch][Ala], [Ch][Leu], and [Ch][Pro] decomposed completely at about 290 °C. But [Ch][AA] ILs have a secondary decomposition stage because the structure reorganizes at higher temperature conditions [36,37]. Fig. 1b shows that the pH of L-B104 changed significantly over the first two hours. Versus L-B104, almost no pH change appeared in the solution of [Ch][AA] ILs during this test. Therefore, [Ch][AA] ILs are not easy to hydrolyze and can to be used as efficient green lubricants.

3.2. Viscosity

Table 2 shows the viscosities and viscosity indexes of the samples. The viscosity index was used to evaluate the viscosity-temperature properties of the samples. The viscosities of [Ch][AA] ILs, especially [Ch][His] and [Ch][Trp], are greater than L-B104 both at 40 °C and 100 °C. It is obvious

Table 2
Viscosities and viscosity indexes of the samples.

Samples	Kinematic viscosity (mm^2/s)		Viscosity index
	40 °C	100 °C	
L-B104	42.97	7.12	126.60
[Ch][Gly]	229.82	20.08	100.63
[Ch][Ala]	204.26	18.58	100.86
[Ch][Leu]	190.42	17.82	101.75
[Ch][Met]	420.10	28.75	95.56
[Ch][His]	1652.48	54.32	69.72
[Ch][Pro]	202.91	16.67	84.73
[Ch][Phe]	756.30	32.16	58.42
[Ch][Trp]	32539.51	288.24	72.85

that the introduction of N-containing heterocycles to [Ch][AA] ILs results in a significant increase in their viscosities [38]. Versus L-B104, the [Ch][AA] ILs have moderate viscosity indexes, and it can be summed up that their viscosities decrease and viscosity indexes increase with increasing alkyl chain length for the anionic part [39]. The viscosity-temperature property of [Ch][AA] ILs can be significantly improved upon the introduction of sulfur to the anionic part. In contrary, the viscosity is significantly reduced by the introduction of aromatic ring [40].

3.3. Corrosion test

Fig. 2 shows the polarization curves of [Ch][AA] ILs and L-B104. The potentials of [Ch][AA] ILs are more negative than L-B104 (Fig. 2) indicating that the [Ch][AA] ILs have a more predominant cathode inhibition activity [41]. Of these, the potential of [Ch][Trp] is larger than the others because indole caused the corrosion potential to move in a larger

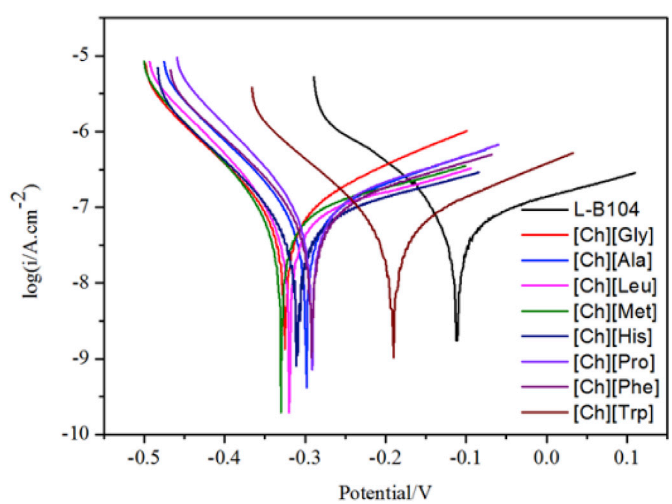


Fig. 2. Polarization curves of EIS for iron in the ILs solution.

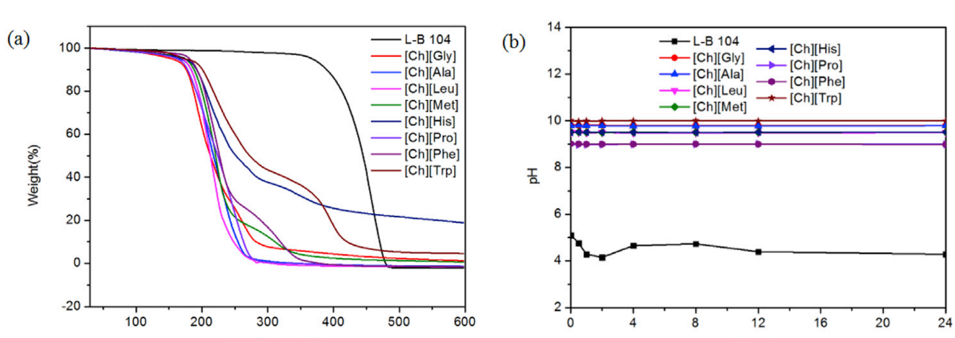


Fig. 1. TG (a) and the pH change curves (b) of L-B104 and [Ch][AA] ILs.

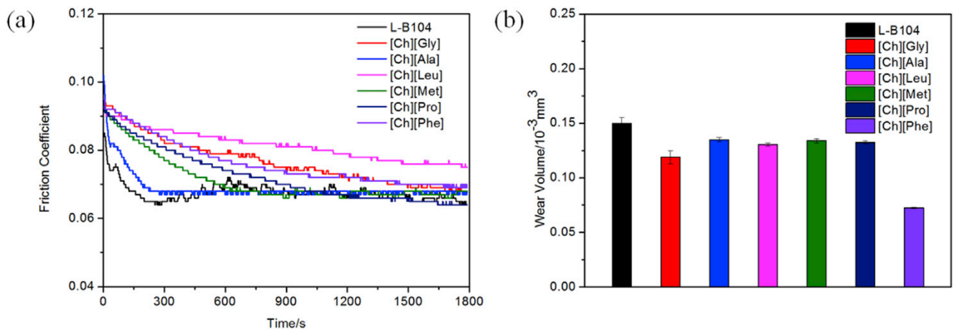


Fig. 3. The friction coefficient (a) evolves over time and wear volume losses (b) of sliding steel disks for samples.

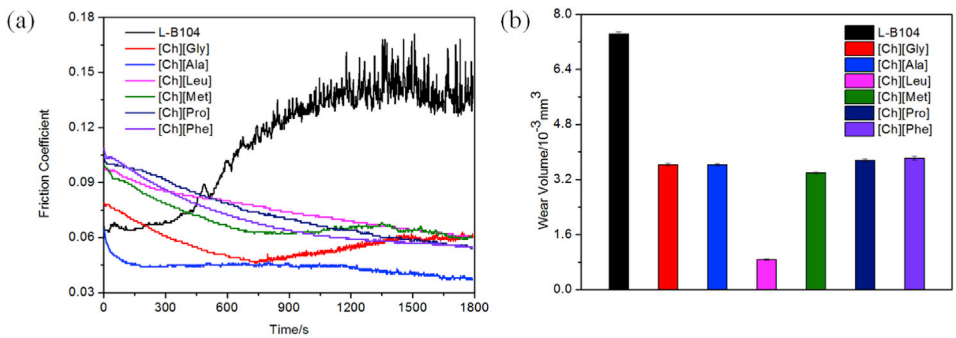


Fig. 4. The friction coefficient (a) evolves over time and wear volume losses (b) of sliding copper disks for samples.

direction. This means that the dissolution reaction of the anode is stronger than the cathodic oxidation/reduction reaction. This is consistent with previous research [42]. Other consistent electrochemical parameters, including corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic Tafel slope (β_a), and cathode Tafel slope (β_c) were obtained. These are seen in Supplementary Information (Table S1). All of these results indicate that the [Ch][AA] ILs are less corrosive than L-B104. This is consistent with the results of the copper strip corrosion shown in Supplementary Information (Fig. S1).

3.4. Friction and wear test and mechanism analysis

The tribological properties of [Ch][AA] ILs were studied on three types of friction pairs including steel/steel, steel/copper, and steel/aluminum; L-B104 was used as the reference sample. Figs. 3–5 show the friction coefficients and wear volume losses for the sliding discs. Fig. 3a shows that the friction coefficients of [Ch][AA] ILs are close to L-B104 on the steel/steel friction pairs at RT; only the friction coefficient curve of [Ch][Leu] is slightly higher than that of L-B104. The corresponding wear volume losses for the sliding discs are showed in Fig. 3b. The wear volume of L-B104 is larger than those of the [Ch][AA] ILs, especially compared with [Ch][Phe]. Indeed, the newly synthesized [Ch][AA] ILs have better anti-wear properties than L-B104.

Under the same conditions, [Ch][AA] ILs were applied on copper and aluminum friction pairs (Figs. 4 and 5). On copper friction pairs, the [Ch][AA] ILs were more prominent than L-B104 regardless of the friction coefficients or wear volumes (Fig. 4). On aluminum friction pairs (Fig. 5), the running-in times of [Ch][Ala] and [Ch][Phe] were similar to L-B104 but were longer than other [Ch][AA] ILs. All of the [Ch][AA] ILs have good friction reducing and anti-wear properties compared with L-B104. The wear volume is very small—especially for [Ch][Leu]. This is because a longer alkyl chain can prevent direct metal contact [24]. At the same time, the additional CH_3 group can enhance the anti-wear behavior [43]. Thus, we concluded that the IL L-B104 is not suitable to be used as a lubricant for lightweight materials such as copper and aluminum [24].

These results confirm that [Ch][AA] ILs are feasible as lubricants. XPS tests were conducted on the worn surfaces to further analyze the lubricating mechanism. Fig. 6 shows the XPS spectra of the worn copper surfaces lubricated by the [Ch][AA] ILs at RT and others are shown in the Supplementary Information. Fig. 6 shows the position and abundance of Cu2p, O1s and N1s peaks on the copper surfaces. These are almost the same before and after friction. Although the more obvious S2p were detected, the corresponding friction coefficient and wear volume of [Ch][Met] were not found in the smallest samples. Thus, the chemical reaction of the sulfur element has no effective lubrication effect during the sliding process.

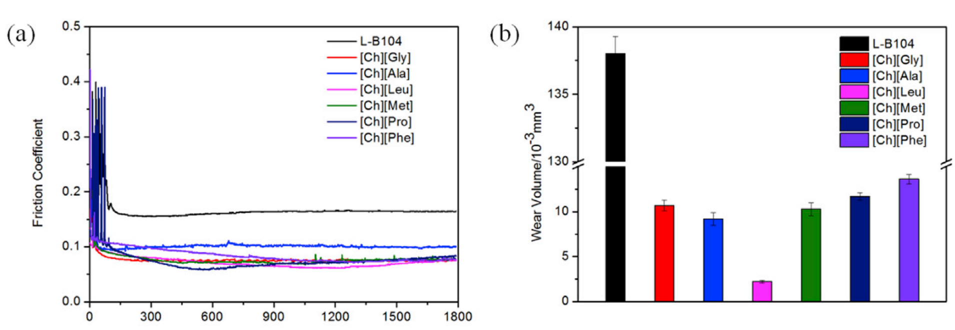


Fig. 5. The friction coefficient (a) evolves over time and wear volume losses (b) of sliding aluminum disks for samples.

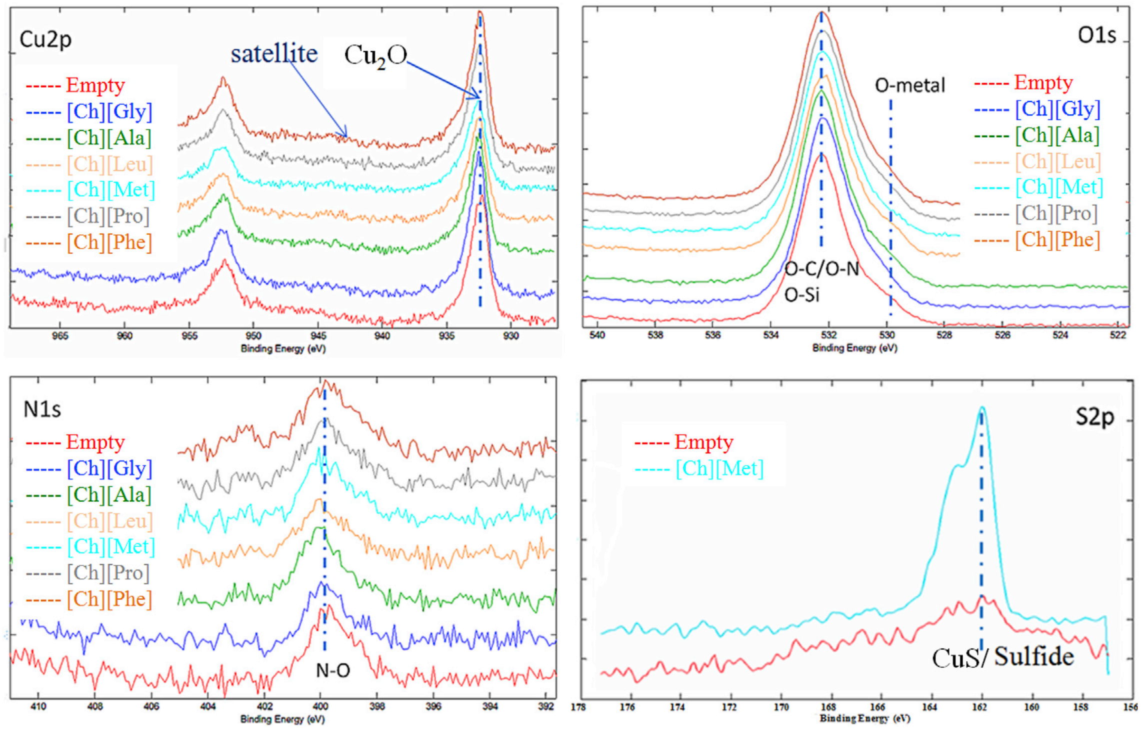


Fig. 6. XPS spectra of the worn copper surfaces lubricated by the [Ch][AA] ILs at RT.

It is well known that carboxylic acids can be easily adsorbed onto rubbed metallic surfaces to reduce friction and wear [44]. This means that the good tribological properties of [Ch][AA] ILs are mostly due to the physical adsorption films formed on the metal surfaces during the sliding process. These can be removed by ultrasonic rinsing before XPS testing [45,46]. During the rubbing process, low-energy electrons are emitted from the contact convex points on the rubbed metal surfaces. The carboxyl groups were firstly adsorbed onto the surfaces and then coated with cationic ions, preventing metal–metal contact and further reducing friction and wear [46,47]. The mechanism analysis of steel/steel and aluminum/steel friction pairs was similar, and the XPS spectrum were presented in the Supplementary Information (Figs. S2 and S3).

3.5. Toxicity test

Ecotoxicity study on ILs towards organisms is the most important environmentally benign features of a new developed product [48–55]. Brine shrimp [32,56] and zebrafish are widely used by the Organization for Economic Cooperation and Development (OECD) as biological indicators to test the toxic effects of chemicals [33,57–59]. Algae is sensitive to a wide range of contaminants and has been recommended in regulatory testing [35,60]. All three aquatic organisms were adopted here to show a detailed toxicity evaluation of [Ch][AA] ILs. The toxicities of [Ch][AA] ILs towards brine shrimp, zebrafish and green algae were assessed, and the test results are shown in Table 3.

The data presented in Table 3 show that the [Ch][AA] ILs were less toxic to brine shrimp than L-B104. In the eight kinds of [Ch][AA] ILs, the LC_{50} values decreased along with increasing alkyl chain length. The lipophilicity of the ILs enhanced with longer alkyl chains. This can increase membrane permeability and the cell damage, thereby causing the death of organism [55]. In those [Ch][AA] ILs, [Ch][Met] were more toxic than others, but its toxicity is still lower than L-B104. The LC_{50} of [Ch][Met] is 6515.87 mg/L, while that of L-B104 is 115.95 mg/L. Versus [Ch][Ala], the toxicities of [Ch][AA] ILs ([Ch][His], [Ch][Pro], [Ch][Phe] and [Ch][Trp]) were markedly lower than others; all of these contain nitrogen heterocycles or benzene rings. The [Ch][His] in particular has an imidazole ring. Here, the lipophilicity of the IL is decreased and its toxicity is significantly reduced.

Hazard ranking (HR) was used to evaluate the toxicity of the ILs: 0.1–1 mg/L, highly toxic (+++++); 1–10 mg/L, slightly toxic (++++); 10–100 mg/L, moderately toxic (+++); 100–1000 mg/L, practically harmless (++); greater than 1000 mg/L, relatively harmless (+).

Table 3 shows that the toxicity evaluation results obtained on zebrafish are consistent with the brine shrimp. The L-B104 has the highest toxicity due to the presence of imidazolium [61], and its LC_{50} was approximately twice as much as [Ch][AA] ILs. The toxicity in green algae was quantified using EC_{50} values. The L-B104 has much higher toxicity than the [Ch][AA] ILs. It is also noteworthy that longer alkyl chains obviously inhibit the growth of green algae. This result was consistent with previous findings [62–66].

In conclusion, no matter what kind of aquatic organisms were adopt, the effect of the studied ILs are similar: Toxicity increased with longer IL alkyl-chain length. The toxicity can be significantly reduced by introducing nitrogen heterocycles or benzene rings. The LC_{50} and EC_{50} of [Ch][AA] ILs are significantly higher than L-B104, which mean the toxicities of [Ch][AA] ILs are obviously lower than that of L-B104. Therefore, [Ch][AA] ILs are practically nontoxic and it is due to the eco-friendly nature of both the choline cation and the amino acid anion [53]. All the LC_{50} or

Table 3
The LC_{50} and EC_{50} values for three kinds of aquatic organisms after exposure to L-B104 and [Ch][AA] ILs.

Samples	brine shrimp		zebrafish		green algae	
	LC_{50} mg/L	HR	LC_{50} mg/L	HR	EC_{50} mg/L	HR
L-B104	115.95	++	85.44	+++	34.15	+++
[Ch][Gly]	15952.10	+	226.33	++	5766.63	+
[Ch][Ala]	9968.91	+	179.57	++	2474.40	+
[Ch][Leu]	9156.29	+	160.86	++	1011.56	+
[Ch][Met]	6515.87	+	155.16	++	1031.31	+
[Ch][His]	19213.91	+	274.46	++	9997.21	+
[Ch][Pro]	11186.72	+	184.76	++	4343.72	+
[Ch][Phe]	15720.64	+	203.52	++	3952.16	+
[Ch][Trp]	15383.49	+	194.27	++	3723.89	+

EC_{50} values of [Ch][AA] ILs are greater than 100 mg/L or greater than 1000 mg/L. This makes them “practically harmless” or “relatively harmless” according to the Acute Toxicity Rating Scale by Fish and Wildlife Service (FWS).

4. Conclusions

In this work, eight [Ch][AA] ILs were synthesized. The ILs have good tribological properties on steel/steel, copper/steel, and aluminum/steel friction pairs at RT. Concurrently, the toxicity of these compounds was evaluated against three aquatic organisms: brine shrimp, zebrafish and green algae. These are the most widely used organisms for ecotoxicity studies. The results show that the toxicities of [Ch][AA] ILs are significantly lower than that of L-B104. They can be used as high-performance and environmentally friendly room temperature IL lubricants.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.triboint.2018.01.063.

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